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# Controllable synthesis of high loading LiFePO<sub>4</sub>/C nanocomposites using bimodal mesoporous carbon as support for high power Li-ion battery cathodes

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#### Abstract

Mesoporous LiFePO<sub>4</sub>/C composites containing 80 wt% of highly dispersed LiFePO<sub>4</sub> nanoparticles (4–6 nm) were fabricated using bimodal mesoporous carbon (BMC) as continuous conductive networks. The unique pore structure of BMC not only promises good particle connectivity for LiFePO<sub>4</sub>, but also acts as a rigid nano-confinement support that controls the particle size. Furthermore, the capacities were investigated respectively based on the weight of LiFePO<sub>4</sub> and the whole composite. When calculated based on the weight of the whole composite, it is 120 mAh·g<sup>-1</sup> at 0.1 C of the high loading electrode and 42 mAh·g<sup>-1</sup> at 10 C of the low loading electrode. The electrochemical performance shows that high LiFePO<sub>4</sub> loading benefits large tap density and contributes to the energy storage at low rates, while the electrode with low content of LiFePO<sub>4</sub> displays superior high rate performance, which can mainly be due to the small particle size, good dispersion and high utilization of the active material, thus leading to a fast ion and electron diffusion.

#### Key words

LiFePO<sub>4</sub>; high loading; fast ion diffusion; high rate performance; lithium-ion batteries

# 1. Introduction

In recent years, olivine lithium iron phosphate (LiFePO<sub>4</sub>) has been extensively and intensively studied as a cathode material for power batteries in electric vehicles (EVs) because of its excellent electrochemical properties with a capacity of 170 mAh·g<sup>-1</sup>, low cost and low toxicity [1]. The storage of electrical energy at high charge and discharge rate is an important technology in today's society; unfortunately, the rate performance of the original LiFePO<sub>4</sub> was significantly restricted by sluggish kinetics of electron and lithium-ion transport [2,3]. To solve the problem, strategies have mainly focused on reducing the particle size to shorten the diffusion path for Li ions [4–6] or coating with carbon to improve the electronic conductivity [7–11].

Using porous carbon to synthesize LiFePO<sub>4</sub> cathodes is an attractive approach to obtain high rate materials because of the unique porosity and continuous carbon network. Doherty et al. reported LiFePO<sub>4</sub> inside hierarchically porous carbon with a high capacity [12]. Yang et al. synthesized LiFePO<sub>4</sub>/C composites using microporous and mesoporous carbon as support [13]. Wang et al. prepared LiFePO<sub>4</sub>/C nanocomposites with excellent performance based on the mesoporous carbon CMK-3 [14]. Our group developed an effective approach using colloidal silica as the hard template and poly(benzoxazine-co-resol) as carbon source for the fabrication of the 3D nitrogen-doped carbon framework with large pore volume and thin walls, which allows a high LiFePO<sub>4</sub> loading of 85.4 wt%, exhibiting a stable reversible capacity and superior rate performance [15].

Inspired from these previous studies, herein, novel mesoporous LiFePO<sub>4</sub>/C composites with high ion diffusion rate and conductive connectivity have been achieved using bimodal mesoporous carbon (BMC) which possesses a unique bimodal pore system. The synthesized LiFePO<sub>4</sub> nanoparticles are homogeneous and highly dispersed due to the confinement effect of the small mesopores and the carbon walls are thin and uniform, thus allowing faster ions and electrons diffusion. Moreover, the synthesized electrode can achieve up to 80 wt%

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of LiFePO<sub>4</sub> impregnation benefited from the large pore volume of BMC carbon framework (1.99 cm<sup>3</sup>·g<sup>-1</sup>), resulting in much enhanced energy density. By tuning the amount of LiFePO<sub>4</sub> impregnation, LiFePO<sub>4</sub>/C composites can be controllably synthesized to meet the different rate requirement.

# 2. Experimental

# 2.1. Synthesis of bimodal mesoporous carbon (BMC) and LiFePO<sub>4</sub>/BMC composite

All chemicals used in this study are of analytical grade and without further purification. BMC was prepared using SBA-15 as a template according to our previous work [16-19]. Using BMC as support, LiFePO<sub>4</sub>/C composites were successfully prepared. The lithium iron phosphate precursor solution was prepared using  $Fe(NO_3)_3 \cdot 9H_2O_3$ ,  $C_2H_3O_2Li \cdot 2H_2O$  and  $H_3PO_4$  (molar ratio of 1:1:1) dissolved in a minimal amount of water with stirring to ensure the total solution of 5 mL and the concentration of 2 mol· $L^{-1}$ . Then, the transparent solution was added dropwise to 0.1 g of carbon with quick stirring, followed by drying at 90 °C. The amount of the impregnating solution was based on the pore volume of BMC. Finally, the powder was heated under a flowing atmosphere of H<sub>2</sub> (5 vol%)/N<sub>2</sub> (95 vol%) at  $3 \,^{\circ}\text{C} \cdot \text{min}^{-1}$  to  $750 \,^{\circ}\text{C}$  and maintained at this temperature for 6 h to yield a black powder which was denoted as LFP-1/C. The sample which was denoted as LFP-2/C was synthesized by the same precursor solution concentration, and only the impregnation times were changed to 2. To bring about full utilization of the pores, we increased the precursor concentration to 2.3 mol· $L^{-1}$  and impregnated them 3 times. The obtained product was denoted as LFP-3/C. In contrast, the pure LiFePO<sub>4</sub> which was denoted as Pure-LFP was synthesized by the same precursor solution and experimental conditions, only the carbon framework BMC excluded.

#### 2.2. Structural and morphological characterization

The X-ray diffraction (XRD) measurements were taken on a Rigaku D/Max 2400 diffractometer using Cu- $K_{\alpha}$  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 ( $S_{\text{BET}}$ ). 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  $10 \,^{\circ}\text{C}\cdot\text{min}^{-1}$  using a STA449 F3 Jupiter thermogravimetric analyzer (NET-ZSCH).

### 2.3. Electrochemical analysis

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 Nmethyl-2-pyrrolidone (NMP) to form a slurry. The slurry was spread onto A1 foil and dried in a vacuum oven at 100 °C overnight. The electrode area is  $1.13 \text{ cm}^2$  and the loading of the active material is  $2.0\pm0.5$  mg·cm<sup>-2</sup>. 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 mol/L LiPF<sub>6</sub> 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. The electrochemical impedance spectroscopy (EIS) was performed using EG&G model 273 Galvanostat/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

To determine the pore structure and the Brunauer-Emmett-Teller (BET) surface areas of both the carbon framework and the LiFePO<sub>4</sub>/C composites, the nitrogen sorption isotherms were measured. As shown in Figure 1(a) and (c), all isotherms feature hysteresis loop between the desorption and adsorption branches, indicating the presence of mesopores. BMC has a high surface area (1419 m<sup>2</sup>·g<sup>-1</sup>) and large total pore volume (1.99 cm<sup>3</sup>·g<sup>-1</sup>). After infiltration, the surface area and pore volume reduce largely which indicates that LiFePO<sub>4</sub> filled in the mesoporous channels of the carbon framework. Furthermore, with an increase in the LiFePO<sub>4</sub> loading, the specific surface area and pore volume of the composites will continually decrease.

The pore size distributions in Figure 1(b) and (d) further confirm that BMC has a bimodal pore system concentrated at 3.7 and 5.4 nm which disappeared in the LiFePO<sub>4</sub>/BMC composites as expected. The parameters of these samples are summarized in Table 1. It is noted that all the samples have certain surface area after infiltration, which can be attributed to the unique mesostructure by recruiting BMC framework and the dispersion of small LiFePO<sub>4</sub> nanoparticles throughout the carbon network.



Figure 1. Nitrogen sorption isotherms of the carbon structure of BMC (a) and LiFePO<sub>4</sub>/BMC composites (c); The corresponding pore size distributions using the BJH formula from the adsorption branch of BMC (b) and LiFePO<sub>4</sub>/BMC composites (d)

Samples	Loading times	$V_{\text{total}}$ (cm <sup>3</sup> ·g <sup>-1</sup> )	$S_{\text{BET}}$ (m <sup>2</sup> ·g <sup>-1</sup> )	D <sub>peak</sub> (nm)	LFP loading (wt%)
BMC	_	1.99	1419	3.7, 5.4	_
LFP-1/C	1	0.43	624	_	47
LFP-2/C	2	0.23	337	_	66
LFP-3/C	3	0.20	213	_	80

 
 Table 1. Parameters of mesoporous carbon (BMC) and LiFePO<sub>4</sub>/BMC composites

For better understanding the structure, we used XRD to characterize crystal phase of the LiFePO<sub>4</sub>/C composites. As shown in Figure 2, all the samples showed the characteristic peaks, which could be indexed to the orthorhombic LiFePO<sub>4</sub> (JCPDS No. 81–1173), indicating that LiFePO<sub>4</sub> nanoparticles distributed both inside and outside mesopore channels. The observed unconspicuous broad wave band with  $2\theta$  between 15° and 35° in sample LFP-1/C may be due to the presence of large amounts of amorphous carbon. Unlike the other two samples, LFP-1/C shows relatively wide peaks, suggesting smaller particles with better dispersion. Moreover, the loading content of LiFePO<sub>4</sub> was determined to be approximately 80 wt% via TG analysis (listed in Table 1), which was consistent with the narrow patterns in XRD analysis.

The SEM and TEM images of the sample LFP-2/C are shown in Figure 3. The LiFePO<sub>4</sub>/BMC composite inherits the

morphology of the carbon framework with an ordered tubular structure (Figure 3a), which further confirms that LiFePO<sub>4</sub> crystallites mostly nucleated and grew within the mesopores without affecting the external morphology of BMC. The SEM observation is well in agreement with the findings by  $N_2$  sorption measurements.



Figure 2. Powder X-ray diffraction patterns of the LiFePO<sub>4</sub>/BMC composites



Figure 3. (a) SEM and (b) TEM images of the LFP-2/C composite

To obtain further insight into the morphology of LiFePO<sub>4</sub> nanoparticles and surrounding carbon walls, the synthesized LiFePO<sub>4</sub>/BMC powders are examined by TEM. As shown in Figure 3(b), ultrafine LiFePO<sub>4</sub> particles are highly dispersed and homogeneously embedded in the mesoporous channels of the carbon framework. Unlike pure LiFePO<sub>4</sub>, the synthesized LiFePO<sub>4</sub> particles are several to tens of nanometers, owing to a restrictive effect of the mesopores in BMC, which connect each other to form a highly conductive network through which electrons could be effectively supplied. Also, the welldeveloped porosity of BMC allows for good electrolyte access to the LiFePO<sub>4</sub> surfaces, thus increasing the electrodeelectrolyte interface and decreasing the diffusion distance for Li ions.

The electrochemical performance of the LiFePO<sub>4</sub>/BMC composites is presented in Figure 4. Based on the whole composite, LFP-1/C delivers a capacity of 60 mAh $\cdot$ g<sup>-1</sup> at 0.1 C, while a capacity of 120 mAh $\cdot$ g<sup>-1</sup> is obtained for LFP-3/C; the higher capacity of LFP-3/C at low rate may be due to the moderately high loading of the active material up to 80%. The cycling stabilities are almost the same good for all of the LiFePO<sub>4</sub>/C composites at 0.1 C, however, the rate performance varies. When the current rate is raised to 1 C, LFP-1/C, LFP-2/C and LFP-3/C respectively retain 99.6%, 86.4% and 73.5% of their corresponding capacity at 0.1 C. The difference becomes more obvious when the rate up to 10 C, indicating that LFP-1/C can endure high rate charge and discharge. Such significant difference can be attributed to the high specific surface area of LFP-1/C, which increases the interface between the active material and the electrolyte, promising the fast Li-ion transfer and better utilization of the active material. Furthermore, low active material loading contributes to better contact with the conductive BMC network, thus improving the electronic conductivity of the composite.

Figure 4(e) shows the AC impedance spectroscopy results for the LiFePO<sub>4</sub>/BMC composite samples and the inset is the equivalent circuit fitted for the impedance spectra. Sample LFP-1/C shows a smaller diameter semicircle, reflecting lower charge transfer impedance within the electrode material [20]. By tuning the impregnation of active materials, the electrode reaction kinetics may be improved. The inclined lines in the low frequency range in Figure 4(e) are attributed to warburg impedance, which is associated with lithium-ion diffusion within the LiFePO<sub>4</sub> electrode. As can be seen in Figure 4(f), lithium-ion diffusion coefficients of samples LFP-1/C, LFP-2/C and LFP-3/C were calculated to be  $1.61 \times 10^{-13}$ ,  $2.82 \times 10^{-14}$  and  $2.05 \times 10^{-13}$  cm<sup>2</sup>·s<sup>-1</sup> according to Zre, which are drastically promoted compared with  $1.56 \times 10^{-15}$  cm<sup>2</sup>·s<sup>-1</sup> in the pure LiFePO<sub>4</sub> electrode [15]. This can be attributed to that the nanosized LiFePO<sub>4</sub> crystallites confined in the mesoporous carbon significantly shorten the diffusion path for electrons and ions.

For clarity, the specific capacities of LiFePO<sub>4</sub>/BMC composites calculated based only on the weight of LiFePO<sub>4</sub> are shown in Figure 5. At low rate of 0.1 C, the discharge capacities of three samples are similar. When the charge-discharge rate increased to 1, 5, 10 and 20 C, LFP-1/C demonstrates a remarkable reversible capacity of 129, 117.9, 101.7 and 75.4  $mAh \cdot g^{-1}$ , respectively. Compared with the pure LiFePO<sub>4</sub> (see supporting information Figure S3), the whole capacity and the rate performance of the LiFePO<sub>4</sub>/BMC composites were obviously improved because of the small particles with good dispersity from the confinement effect of BMC. As rate increases, there are significant differences in the decay rate of the discharge capacity, as shown in Figure 5(b). LFP-1/C, LFP-2/C and LFP-3/C at 10 C can retain 74.5%, 59.5% and 24.3% of the capacity that at 0.1 C, respectively, which further confirms the superior rate performance of LFP-1 and better utilization of the active material. To give further insight, the correlation between the electrochemical performances and their textural parameter has also been discussed. It can be seen from Figure 5(c) that the capacity difference between the low rate (0.1 C) and high rate (10 C) becomes smaller as the specific surface area increases. LFP-1/C with a high surface area of  $624 \text{ cm}^2 \cdot \text{g}^{-1}$  achieves the highest capacity even at the high rate of 10 C, which associates with the effective interface and facile ion transfer, and this result is in good agreement with above analysis.



**Figure 4.** (a) Charge-discharge curves at 0.1 C (0.1 C corresponds to  $17 \text{ mA} \cdot \text{g}^{-1}$ ); (b) Cycling performance at 0.1 C; (c) Rate performance at current rates from 0.1 C to 10 C and back to 0.1 C for 5 cycles; (d) Average capacity versus discharge rates from 0.1 C to 10 C; (e) AC impedance spectroscopy of the batteries placed 12 h after assembled and the inset is equivalent circuit fitted for the impedance spectra; (f) Variations and fittings between Zre and reciprocal square root of the angular frequency at low frequency region. All the current densities and specific capacities calculated based on the weight of LiFePO<sub>4</sub>/BMC composite



Figure 5. The rate and cycling performance: (a) Rate performance at current rates from 0.1 C to 20 C, and back to 0.1 C for 5 cycles and cycling performance at 1 C for cycles 52-151; (b) Average capacity versus discharge rates from 0.1 C to 20 C; (c) Average capacity versus surface area for three samples (filled markers discharged at 0.1 C and open markers at 10 C). All the current densities and specific capacities calculated based on the weight of LiFePO<sub>4</sub> only

## 4. Conclusions

A mesoporous carbon BMC with bimodal pore system and large pore volume was employed as supporting skeleton and conductive framework for the fabrication of high loading LiFePO<sub>4</sub>/BMC composites. The impact of LiFePO<sub>4</sub> loading on the electrochemical performance of the composites was also discussed in detail. The key parameter for LIB regarding rate performance greatly benefits from the high specific surface area, small dimensions and good dispersity, which promise high utilization of the active material and offer a rapid ion and electrons transport. This unique structure model may be valid for better understanding the rate performance and might be extended for fabrication of other high power cathode and anode electrode materials.

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## References

- Hu Y S, Guo Y G, Dominko R, Gaberscek M, Jamnik J, Maier J. Adv Mater, 2007, 19(15): 1963
- [2] Chung S Y, Bloking J T, Chiang Y M. Nat Mater, 2002, 1(2): 123
- [3] Padhi A K, Nanjundaswamy K S, Goodenough J B. J Electrochem Soc, 1997, 144(4): 1188
- [4] Wang Y G, Wang Y R, Hosono E J, Wang K X, Zhou H S. Angew Chem Int Ed, 2008, 47(39): 7461
- [5] Gibot P, Casas-Cabanas M, Laffont L, Levasseur S, Carlach P, Hamelet S, Tarascon J M, Masquelier C. *Nat Mater*, 2008, 7(9): 741
- [6] Liu X F, Huang J Q, Zhang Q, Liu X Y, Peng H J, Zhu W C, Wei F. J Mater Chem, 2012, 22(36): 18908
- [7] Yun N J, Ha H W, Jeong K H, Park H Y, Kim K. J Power Sources, 2006, 160(2): 1361
- [8] Wu Y M, Wen Z H, Li J H. Adv Mater, 2011, 23(9): 1126
- [9] Zhang X D, He W, Yue Y Z, Wang R M, Shen J X, Liu S J, Ma J Y, Li M, Xu F X. J Mater Chem, 2012, 22(37): 19948
- [10] Sinha N N, Shivakumara C, Munichandraiah N. ACS Appl Mater Interfaces, 2010, 2(7): 2031
- [11] Su D S, Centi G. J Energy Chem, 2013, 22(2): 151

- [12] Doherty C M, Caruso R A, Smarsly B M, Adelhelm P, Drummond C J. Chem Mater, 2009, 21(21): 5300
- [13] Yang M, Gao Q M. J Alloys Compd, 2011, 509(8): 3690
- [14] Wang G X, Liu H, Liu J, Qiao S Z, Lu G Q M, Munroe P, Ahn H. Adv Mater, 2010, 22(44): 4944
- [15] Cheng F, Wang S, Lu A H, Li W C. *J Power Sources*, 2013, 229: 249
- [16] Lu A H, Schmidt W, Spliethoff B, Schüth F. Adv Mater, 2003, 15(19): 1602
- [17] Lu A H, Schmidt W, Spliethoff B, Schüth F. *Chem-Eur J*, 2004, 10(23): 6085
- [18] Lu A H, Li W C, Schmidt W, Kiefer W, Schüth F. Carbon, 2004, 42(14): 2939
- [19] Han F, Li W C, Li M R, Lu A H. J Mater Chem, 2012, 22(19): 9645
- [20] Shin H C, Cho W I, Jang H. Electrochim Acta, 2006, 52(4): 1472