

A porous LiFePO₄ and carbon nanotube composite†

Yingke Zhou,^a Jie Wang,^a Yuanyuan Hu,^a Ryan O'Hayre^b and Zongping Shao^{*a}

Received 3rd June 2010, Accepted 9th July 2010

DOI: 10.1039/c0cc01721c

A novel composite electrode structure with highly-conductive 3D nanotube networks superimposed into interlaced porous LiFePO₄ media was designed and realized via an *in situ* sol-gel process, yielding a high-performance multidimensional composite cathode for high-energy and high-power lithium-ion batteries.

Lithium-ion batteries (LIBs) have been widely investigated in recent years due to the increasing demand in the portable electronics market and emerging applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs). Numerous efforts have been undertaken to increase the capacity and rate capability (and hence improve the energy and power density) of LIBs by using advanced device configurations or electrode materials.^{1–11} However, significant challenges must still be overcome, especially regarding kinetic limitations of the electrodes,^{4,12,13} to expand the use of LIBs as power supplies for EVs and HEVs. Since the pioneering work by Padhi *et al.*,¹⁴ the olivine structure lithium iron phosphate (LiFePO₄) with its numerous appealing features such as high theoretical capacity (170 mAh g⁻¹), acceptable operating voltage (3.4 V vs. Li⁺/Li), high safety, environmental benignity and low cost, has attracted extensive interest as a potential candidate to replace the commercial layered LiCoO₂ material which shows relatively lower capacity and lower safety.^{15–23} The major issue with LiFePO₄ is its sluggish mass and charge transport, as corroborated by recent work on single crystals.²⁴

Considerable efforts have been made^{15–23} to overcome the electronic and ionic transport limitations by cationic doping with foreign atoms, decreasing the particle size, or coating with electronically conductive agents (carbon, Ag, conducting polymers, *etc.*). In particular, the widely applied carbon-coating technique has enabled high absolute capacities, while decreasing the LiFePO₄ particle size to the nanometre level is now widely recognized to enhance the lithium ion diffusion. In this communication, we report an alternative optimized nano/micro electrode structure design by combining the advantages of porous active particles and carbon nanotubes (CNTs). This design makes use of the manifold benefits of CNTs (including high electronic conductivity, special tubular nanoscale morphology, corrosion resistance and high specific surface area) to create a highly-conductive 3D network which is superimposed

into the porous LiFePO₄ media, yielding a high-performance multidimensional composite cathode for high-energy and high-power lithium batteries (Fig. 1). In porous materials, the distance between the pores determines the materials kinetics and the pores serve as channels for fast lithium supply; in contrast, for nanosize electrode materials, the solid-state diffusion of lithium is determined by the diameter of nanoparticles. The highly dispersed conductive networks could then greatly facilitate the kinetics by ensuring sufficient electron supply, especially at high rates. The other benefit of such porous composites is the reduction of potential health and environmental hazards associated with the nanoparticulate nature of some functional materials.²⁵

As illustrated in Fig. 1, achieving a uniform dispersion of CNT networks into the porous LiFePO₄ is crucial for performance, so that the nanotubes not only decorate the surface, but also incorporate and intrude into the pores and bulk of the LiFePO₄ particles, thus forming a hierarchical architecture. This structure yields promising electrode performance, as the interlaced LiFePO₄ mesopores can serve as channels for fast Li supply, while the interlaced carbon nanotube networks facilitate fast electron transfer.

The porous LiFePO₄-CNT composites were synthesized via a facile *in situ* sol-gel method (see details in the experimental section of ESI), where the carbon nanotubes were functionalized using a mixed acid method to ensure uniform dispersion into the aqueous sol. The nanotubes retained their dispersion and were incorporated directly into the porous LiFePO₄ particulates during the subsequent gelatinization and calcination steps resulting in an intimately interlaced 3D composite network. The formation of such a hierarchical composite was supported by the SEM and TEM investigations shown in Fig. 2. As shown in Fig. 2a, the “pristine” (non-CNT modified) LiFePO₄ particles are several microns in size and highly porous. This porous LiFePO₄ material was observed to be covered with a thin layer of carbon (around 1–2 nm) on the wall surface, attributed to decomposition residues from the citrate-containing starting gel. Overall weight loading of carbon in this porous LiFePO₄ was determined to be around 3 wt%.

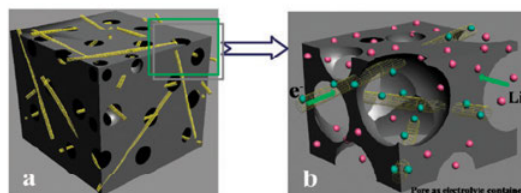


Fig. 1 Schematic illustrations of the porous LiFePO₄-CNT composite. (b) is an enlarged zone from (a), showing the corresponding electron transport and ion diffusion mechanisms.

^a State Key Laboratory of Materials Oriented Chemical Engineering, College of Chemistry & Chemical Engineering, Nanjing University of Technology, No. 5 Xin Moan Road, Nanjing 210009, China. E-mail: zhouyk@njut.edu.cn; shaozp@njut.edu.cn; Fax: 86-25 8317 2256; Tel: 86-25 8317 2256

^b Department of Metallurgical & Materials Engineering, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401, USA

† Electronic supplementary information (ESI) available: Details of experimental procedures, XRD patterns, impedance spectra. See DOI: 10.1039/c0cc01721c

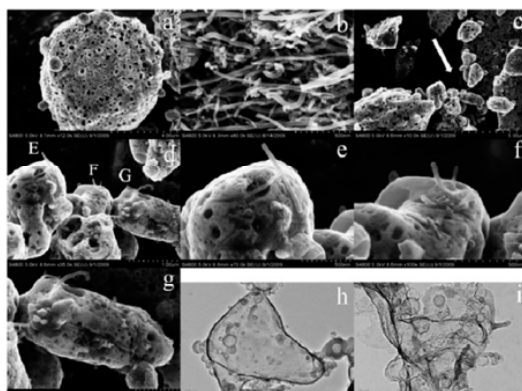


Fig. 2 Typical SEM images: (a) porous LiFePO₄; (b) CNT; (c) LiFePO₄-CNT composite; (d) zoom-in image of the zone indicated by the arrow in (c); (e) further zoom-in image of zone (E) in (d); (f) further zoom-in image of zone (F) in (d); (g) further zoom-in image of zone (G) in (d); Typical TEM images: (h) porous LiFePO₄; (i) LiFePO₄-CNT composite.

however this carbon coating was not uniformly distributed, leading to insufficient electronic conduction and therefore limited enhancement of rate performance.

As shown in Fig. 2b, the pristine carbon nanotubes show a typical tubular morphology and average length of hundreds of nm to several microns. Typical SEM images of the LiFePO₄-CNT composites are shown in Fig. 2c-g; Fig. 2d provides a higher magnification detail from a portion of Fig. 2c (location indicated by the arrow) and Fig. 2e-g provide magnified details from different locations on Fig. 2d (as marked). The composites show clear incorporation of the carbon nanotube networks into and around the porous LiFePO₄ particles. To further examine the extent of the LiFePO₄-CNT network interpenetration, TEM investigations were conducted and the results are shown in Fig. 2h and i. Comparison of the unmodified LiFePO₄ particle TEM image (Fig. 2h) with the LiFePO₄-CNT network composite (Fig. 2i) clearly shows how the cross-linked, interlaced carbon nanotube networks are intimately embedded and incorporated into the porous LiFePO₄ particle structure. Furthermore, the SEM and TEM investigations indicate that three-dimensional carbon nanotube networks have been incorporated into the LiFePO₄ without affecting the overall porous characteristics of the LiFePO₄ particles. As further confirmation, Fig. S1 (see ESI) compares the X-ray diffraction (XRD) patterns of pristine LiFePO₄ versus the composite material. Both patterns could be indexed to the orthorhombic olivine structure (space group: *Pnma*), indicating that the addition of carbon nanotubes had no effect on the main structure, due to the low content of CNT.

In order to test the potential applicability in Li batteries, we investigated the electrochemical performance of the LiFePO₄-CNT composites with respect to Li insertion/extraction using the coin-type cell configuration. Typical charge-discharge profiles at a current rate of 10 mA g⁻¹ for both the unmodified porous LiFePO₄ and the LiFePO₄-CNT composite are shown in Fig. 3a. As it usually takes several initial

cycles for the capacity to stabilize, the electrochemical results discussed herein refer to the stable performance obtained after several initial cycles. A flat discharge potential plateau was observed for both the unmodified LiFePO₄ and the LiFePO₄-CNT systems at around 3.4 V, indicating that the two-phase redox reaction proceeds via a first-order transition between FePO₄ and LiFePO₄.¹⁴ Shown in Fig. 3b is the comparison of the rate performance of pristine porous LiFePO₄ and LiFePO₄-CNT composites with charge/discharge rates of 10 to 1000 mA g⁻¹. At low rates, for example 10 mA g⁻¹, the pristine material displays a discharge capacity of 142 mAh g⁻¹, while the composite material displays a discharge capacity of 159 mAh g⁻¹, indicating the specific capacity was improved by incorporation of the CNTs. At higher rates, the superior capacity characteristics of the composite are even clearer, with the composite material retaining a capacity of 110 mAh g⁻¹ in contrast to only 66 mAh g⁻¹ for the pristine material. To further understand the superior electrode performance of the composite material, we carried out electrochemical cyclic voltammetry and complex impedance measurements, as reported in Fig. 3c and Fig. S2 (ESI). As shown in Fig. 3c, oxidation and reduction peaks appear at around 3.55 and 3.35 V, respectively for the pristine LiFePO₄, and the potential interval between two peaks is 0.20 V. In contrast, the oxidation and reduction peaks for the LiFePO₄-CNT composite appear at around 3.51 and 3.38 V, respectively, corresponding to a potential interval of 0.13 V. This reduced potential interval highlights the improved reversibility and reactivity of the LiFePO₄-CNT composite compared to the unmodified LiFePO₄ material. Fig. S2 compares the impedance spectra of the pristine LiFePO₄ and LiFePO₄-CNT composite electrodes. The impedance spectra can be explained on the basis of an equivalent circuit (as shown in the insert of Fig. S2) with uncompensated resistance (*R*_u), (*C*₁*R*₁) parallel elements corresponding to the SEI film, electrode roughness and inhomogeneous reaction at the surface, and (*C*₂(*R*₂*Z*_w)) elements relating to the electronic and ionic resistance between electrode and electrolyte and Warburg resistance associated with diffusion.²⁴ Compared to the pristine material, the reasonably good fitting results showed both greatly decreased *R*₁ (~222 ohm of the composite vs. ~420 ohm of the pristine) and *R*₂ (~56 ohm of the composite vs. ~505 ohm of the pristine) components for the composite, indicating increased charge transfer and reaction kinetics. The inclined lines in the low frequency range are attributed to a Warburg impedance, which may be associated with lithium-ion diffusion within the LiFePO₄ electrode. From the inclined lines in the Warburg region, the lithium-ion diffusion coefficient may be estimated using the following equation:²⁶

$$D = (R^2 T^2) / (2A^2 n^4 F^4 C^2 \sigma^2) \quad (1)$$

Where *R* is the gas constant, *T* is the absolute temperature, *A* is the surface area of the cathode, *n* the number of electrons per molecule during oxidation, *F* the Faraday constant, *C* the concentration of lithium-ion (7.69×10^{-3} mol cm⁻³), and σ the Warburg factor associated with *Z*_{re} or -*Z*_{im},

$$Z_{re} \text{ (or } -Z_{im}) \propto \sigma \omega^{-1/2} \quad (2)$$

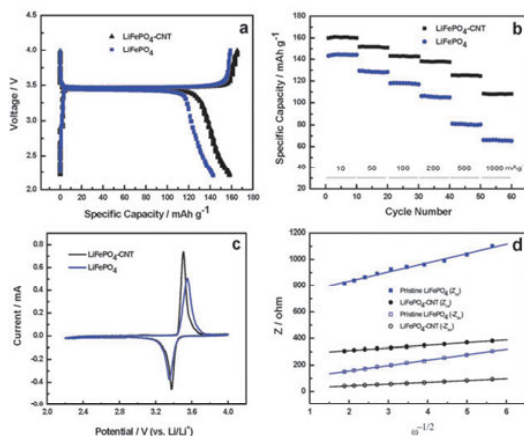


Fig. 3 (a) Charge/discharge profiles; (b) rate performance; (c) cyclic voltammograms; and (d) variations and fittings between Z_{re} , $-Z_{im}$ and reciprocal square root of the angular frequency at low frequency region of porous LiFePO_4 (blue) and LiFePO_4 -CNT composite (black).

From eqn (2), the Warburg factor σ could be obtained by linear fitting the relation plot between Z_{re} (or $-Z_{im}$) and reciprocal square root of the angular frequency (as shown in Fig. 3d), then the diffusion coefficient could be obtained from eqn (1). The lithium-ion diffusion coefficients of pristine LiFePO_4 and LiFePO_4 -CNT composites were calculated to be $\sim 4.9 \times 10^{-14}$ and $6.3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ (σ 70.48 and 19.69) using Z_{re} ; $\sim 1.5 \times 10^{-13}$ and $1.4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ (σ 40.95 and 13.36) using $-Z_{im}$, respectively, which are comparable to the reported values (for example, $9.9 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for LiFePO_4 and $1.6 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for doped LiFePO_4 ,²⁷ and $1.7 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for carbon coated LiFePO_4 ²⁸). These results indicated that the diffusion of lithium-ion, which is considered to be the slowest process, has been drastically promoted in the composites. The decreased charge transfer resistance and the increased lithium-ion diffusion in the LiFePO_4 -CNT are consistent with the superior capacity and rate characteristics observed for this composite material. We hypothesize that high porosity in combination with the electrical connectivity provided by the LiFePO_4 -CNT composite material increases the area that is simultaneously accessible to both electrons and Li-ions, thereby greatly reducing the “inert” zones^{14,27} and leading to lower charge transfer resistance, higher specific capacity and better rate performance. This hypothesis is consistent with many of the recent models proposed to explain the two-phase reaction of LiFePO_4 such as the shrinking core,¹⁴ platelet-type, miscibility gaps, and domino cascade concepts (ref. S1-S3, ESI)[†] which incorporate morphology or homogeneity characteristics to explain electrode performance.

In summary, hierarchically structured composites based on porous LiFePO_4 with CNT networks present significantly improved specific capacity and rate performance in comparison to unmodified porous LiFePO_4 when used in lithium ion batteries. This performance enhancement effect is attributed to the improved electrochemical accessibility and decrease in inert “dead” zones provided by the interpenetrating conductive

CNT networks present in the composite structure. This strategy demonstrated here could be potentially extended to other materials, for example by investigating conductive metal nanowire/tubes and alternative electro-active porous materials (including anode electrode materials), and therefore presents an intriguing route to design enhanced electrode structures for a wide variety of applications in electrochemical energy storage and conversion.

This work was supported by the National 973 Basic Research Program of China under contract No. 2007CB209704 and the New Century Excellence Program of the Chinese Ministry of Education.

Notes and references

- 1 M. Armand and J. Tarascon, *Nature*, 2008, **451**, 652.
- 2 P. G. Bruce, B. Scrosati and J.-M. Tarascon, *Angew. Chem., Int. Ed.*, 2008, **47**, 2930.
- 3 L.-F. Cui, R. Ruffo, C. K. Chan, H. Peng and Y. Cui, *Nano Lett.*, 2009, **9**, 491.
- 4 Y. S. Hu, Y. G. Guo, R. Dominko, M. Gaberscek, J. Jamnik and J. Maier, *Adv. Mater.*, 2007, **19**, 1963.
- 5 K. Saravanan, M. V. Reddy, P. Balaya, H. Gong, B. V. R. Chowdari and J. J. Vittal, *J. Mater. Chem.*, 2009, **19**, 605.
- 6 R. Dominko, M. Bele, J. M. Goupil, M. Gaberscek, D. Hanzel, I. Arcon and J. Jamnik, *Chem. Mater.*, 2007, **19**, 2960.
- 7 L. Kavan, I. Exnar and M. Graetzel, *Chem. Mater.*, 2008, **20**, 3163.
- 8 C. A. J. Fisher and M. S. Islam, *J. Mater. Chem.*, 2008, **18**, 1209.
- 9 L.-F. Cui, Y. Yang, C.-M. Hsu and Y. Cui, *Nano Lett.*, 2009, **9**, 3370.
- 10 S. Hamelet, P. Gibot, M. Casas-Cabanas, D. Bonnin, C. P. Grey, J. Cabana, J. B. Leriche, J. Rodriguez-Carvajal, M. Courty, S. Levasseur, P. Carlach, M. van Thournout, J. M. Tarascon and C. Masquelier, *J. Mater. Chem.*, 2009, **19**, 3979.
- 11 H. Yang, X. L. Wu, M. H. Cao and Y. G. Guo, *J. Phys. Chem. C*, 2009, **113**, 3345.
- 12 A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon and W. V. Schalkwijk, *Nat. Mater.*, 2005, **4**, 366.
- 13 G. Armstrong, A. R. Armstrong, P. G. Bruce, P. Reale and B. Scrosati, *Adv. Mater.*, 2006, **18**, 2597.
- 14 A. K. Padhi, K. S. Nanjundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 1188.
- 15 L. Kavan, I. Exnar, J. Cech and M. Graetzel, *Chem. Mater.*, 2007, **19**, 4716.
- 16 C. M. Doherty, R. A. Caruso, B. M. Smarsly and C. J. Drummond, *Chem. Mater.*, 2009, **21**, 2895.
- 17 K. S. Park, S. B. Schougaard and J. B. Goodenough, *Adv. Mater.*, 2007, **19**, 848.
- 18 K. Wang, R. Cai, T. Yuan, X. Yu, R. Ran and Z. P. Shao, *Electrochim. Acta*, 2009, **54**, 2861.
- 19 Q. Wang, S. M. Zakeeruddin, D. Wang, I. Exnar and M. Grätzel, *Angew. Chem., Int. Ed.*, 2006, **45**, 18197.
- 20 H. M. Xie, R. S. Wang, J. R. Ying, L. Y. Zhang, A. F. Jalbout, H. Y. Yu, G. L. Yang, X. M. Pan and Z. M. Su, *Adv. Mater.*, 2006, **18**, 2609.
- 21 S. Y. Lim, C. S. Yoon and J. P. Cho, *Chem. Mater.*, 2008, **20**, 4560.
- 22 X. J. Zhu, L. B. Cheng, C. G. Wang, Z. P. Guo, P. Zhang, G. D. Du and H. K. Liu, *J. Phys. Chem. C*, 2009, **113**, 14518.
- 23 L. Q. Sun, M. J. Li, R. H. Cui, H. M. Xie and R. S. Wang, *J. Phys. Chem. C*, 2010, **114**, 3297.
- 24 R. Amin, P. Balaya and J. Maier, *Electrochem. Solid-State Lett.*, 2007, **10**, A13.
- 25 G. Brumfiel, *Nature*, 2003, **424**, 246.
- 26 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, 2nd edn, 2001.
- 27 H. Liu, Q. Cao, L. J. Fu, C. Li, Y. P. Wu and H. Q. Wu, *Electrochem. Commun.*, 2006, **8**, 1553.
- 28 X. Z. Liao, Z. F. Ma, Q. Gong, Y. S. He, L. Pei and L. J. Zeng, *Electrochem. Commun.*, 2008, **10**, 691.