

Available at [www.sciencedirect.com](http://www.sciencedirect.com)

SciVerse ScienceDirect

journal homepage: [www.elsevier.com/locate/carbon](http://www.elsevier.com/locate/carbon)

Letters to the Editor

## The effect of graphene wrapping on the performance of LiFePO<sub>4</sub> for a lithium ion battery

Wei Wei <sup>a</sup>, Wei Lv <sup>a,c</sup>, Ming-Bo Wu <sup>b</sup>, Fang-Yuan Su <sup>c</sup>, Yan-Bing He <sup>c</sup>, Baohua Li <sup>c</sup>, Feiyu Kang <sup>c</sup>, Quan-Hong Yang <sup>a,c,\*</sup>

<sup>a</sup> School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

<sup>b</sup> State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China

<sup>c</sup> Engineering Laboratory for Functionalized Carbon Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

### ARTICLE INFO

#### Article history:

Received 24 October 2012

Accepted 27 January 2013

Available online 8 February 2013

### ABSTRACT

Graphene wrapping is used to experimentally understand how a carbon coating works in improving the electrochemical performance of the LiFePO<sub>4</sub> cathode for a lithium ion battery. A full wrapping of LiFePO<sub>4</sub> by graphene is realized by a self-assembly driven by the electrostatic interaction in a graphene oxide suspension. Results indicate that a partial graphene wrapping provides a balance between increased electron transport and fast ion diffusion while full graphene wrapping isolates LiFePO<sub>4</sub> from the electrolyte and retards ion diffusion. This indicates that steric hindrance for ion diffusion should be considered together with electron transport in constructing a carbon coating layer.

© 2013 Elsevier Ltd. All rights reserved.

Carbon coating is an efficient approach for improving electrochemical performance of the cathode in a lithium ion battery (LIB) by notable electronic conductivity improvement, and a highly graphitic carbon coating is desirable for its excellent electronic conductivity [1]. However, a most recent report indicates that Li<sup>+</sup> diffusion through a defect-free perfect graphitic plane is rather limited [2], and that is, leaving an unimpeded ion diffusion pathway should be considered together with the electronic conductivity improvement when constructing a carbon coating layer around the cathode materials. The rise of graphene [3] gives us an opportunity to understand the graphitic carbon coating layer in-depth since the flexible graphene may act as a very thin graphitic carbon coating on cathode materials like LiFePO<sub>4</sub> (LFP). Our group has proved that graphene nanosheets (GNs), as the conducting additives, may largely improve the conductivity of LFP through forming an effective “plane-to-point” conductive

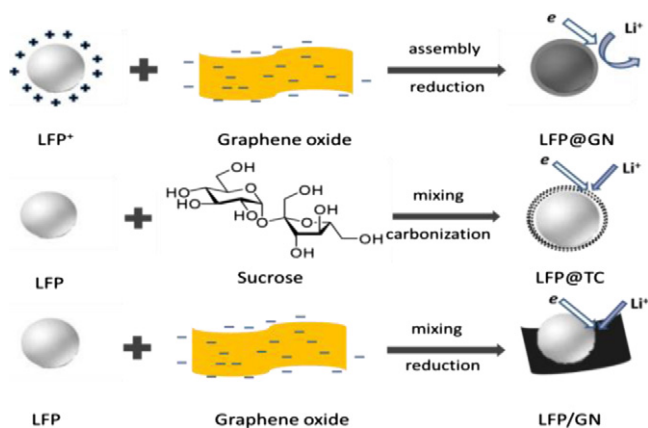
network [4], but show a steric hindrance effect for the Li<sup>+</sup> diffusion due to the planar structure of graphene [5]. Herein, with less defected graphitic structure, flexible graphene is used as a model structure to construct graphitic wrapping layers, and probe how carbon coating works in improving the electrochemical performance of LFP. Two typical graphitic carbon coatings, which are respectively formed through partial and full wrapping of graphene around LFP, show entirely different electrochemical performance. LFP/GN (partial wrapping) shows a capacity as high as 150 mAh g<sup>-1</sup>, while LFP@GN (full wrapping) exhibits a much lower capacity of 40 mAh g<sup>-1</sup>. The results indicate that although with improved electronic conductivity, a full and tight coating of highly graphitic carbon is not favorable for cathode materials due to the steric hindrance effect for Li<sup>+</sup> diffusion and therefore, an ideal coating structure should provide a balance between increased electron transport and fast ion diffusion.

\* Corresponding author at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Fax: +86 755 26036113.

E-mail addresses: [qhyangcn@tju.edu.cn](mailto:qhyangcn@tju.edu.cn), [yang.quanhong@sz.tsinghua.edu.cn](mailto:yang.quanhong@sz.tsinghua.edu.cn) (Q.-H. Yang).

0008-6223/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved.

<http://dx.doi.org/10.1016/j.carbon.2013.01.070>

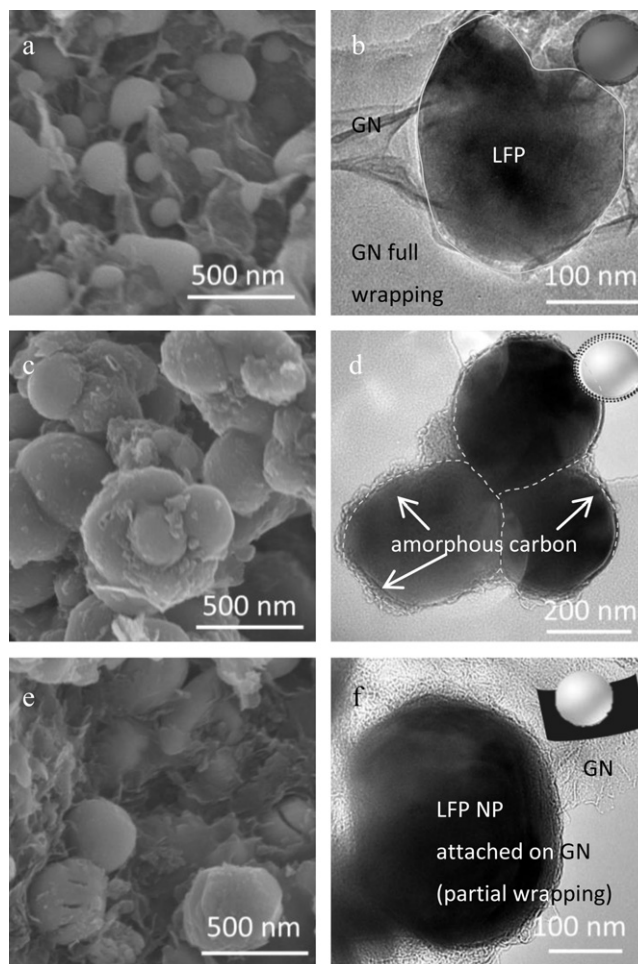


**Fig. 1 – Scheme of fabrication and electrochemistry reaction of LFP@GN, LFP@TC and LFP/GN.**

The overall preparation procedure of LFP@GN, LFP@TC and LFP/GN are schematically represented in Fig. 1. In order to form a full wrapping structure, we developed a self-assembly process driven by the electrostatic interaction. Firstly, the surface of LFP nanoparticles (LFP NPs) was positively charged by the adsorption of hexadecyl trimethyl ammonium bromide (CTAB) under sonication in an aqueous solution. After the pH value was adjusted to  $<7$  using hydrochloric acid, the positively charged LFP NPs were mixed and tightly wrapped by the negatively charged graphene oxide nanosheets (GONs) by the electrostatic interaction. GONs were then reduced to GNs by hydrazine, and the residual surfactant was removed by washing and thermal decomposition at  $600\text{ }^{\circ}\text{C}$  for 2 h, finally resulting in LFP@GN. Note that the encapsulation process can be realized only at  $\text{pH} < 7$ , where LFP NPs and GONs are oppositely charged. Perfect wrapping structure cannot be obtained in the similar preparation free from CTAB (other conditions are exactly the same) where there is no efficient driving force to promote the full wrapping, and LFP/GN is obtained. Meanwhile sucrose-derived amorphous carbon coated LFP (LFP@TC) is also investigated for reference and LFP@TC was obtained by carbonization of sucrose on the LFP NPs.

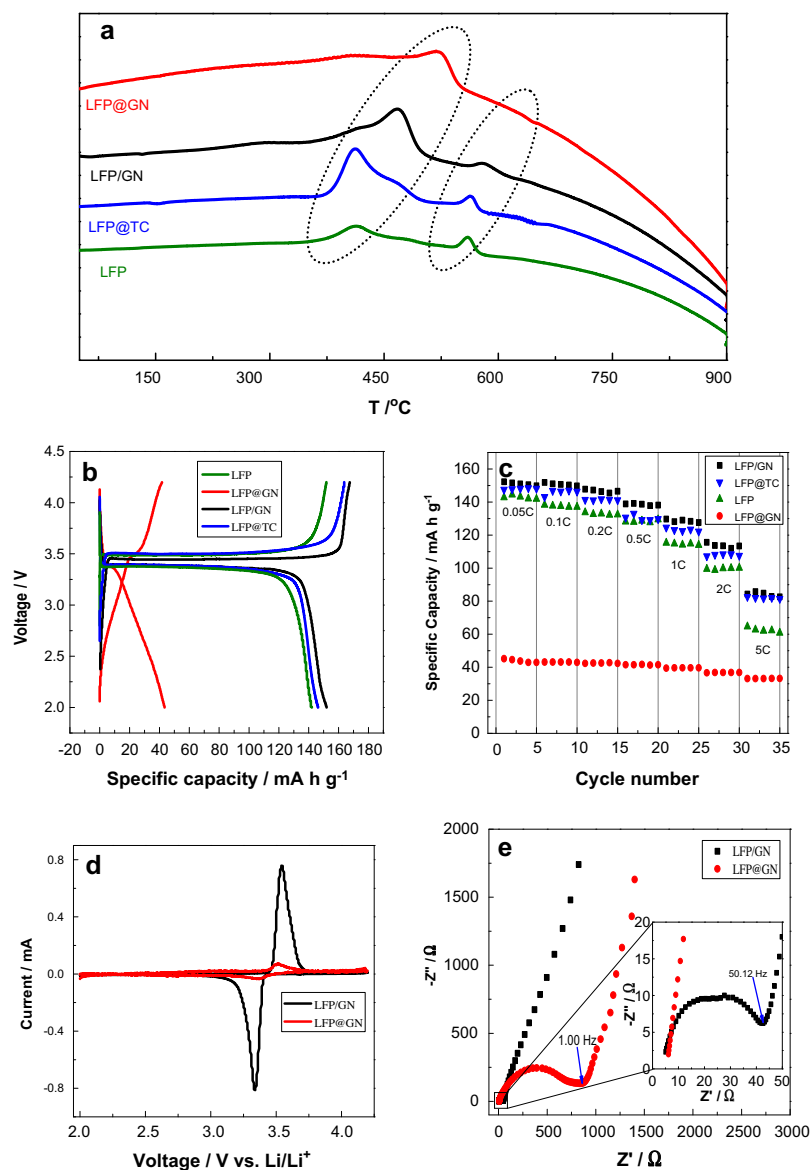
As shown in Fig. 2a and b, the scanning electron microscope (SEM) and transmission electron microscope (TEM) images of LFP@GN reveal that the LFP NPs are fully wrapped by the crinkled, thin and flexible GNs. The morphology and microstructure of LFP@TC are shown in Fig. 2c and d, from which we can clearly identify that the LFP NPs are coated by a thin layer amorphous carbon, which is derived from the sucrose carbonization. The SEM and TEM images of the LFP/GN (Fig. 2e and f) indicate that the LFP NPs are partially wrapped by the GNs (attached on GNs). Compared with the case of LFP@GN shown in Fig. 2b, the boundary between LFP NP and GN in the LFP/GN sample is clear and distinguishable, showing a partial wrapping structure. A simple resistance measurement confirms the difference between LFP@GN and LFP/GN, and with full wrapped structure, the former possesses the resistivity much lower than the latter and close to the GNs prepared by the same method as that for GN coating in LFP@GN (see the details in ESI).

Such different wrapping structures have also been confirmed by the thermal analyses. Thermogravimetric differen-



**Fig. 2 – Structure and microscopic characterization of different carbon coating structures. (a) SEM and (b) TEM images of LFP@GN; (c) SEM and (d) TEM images of LFP@TC; (e) SEM and (f) TEM images of LFP/GN. The insets of (b), (d) and (f) show the schematic diagram of the corresponding carbon coating structure.**

tial scanning calorimetry (DSC) results are presented in Fig. 3a and two oxidation-derived exothermic peaks of LFP are observed for all four samples in the range of  $380\text{--}560\text{ }^{\circ}\text{C}$  [6]. For uncoated LFP, two typical exothermic peaks appear at  $\sim 400$  and  $\sim 520\text{ }^{\circ}\text{C}$ , and LFP@TC possesses almost unshifted two peaks. This indicates that LFP NPs in the two cases show the similar oxidation reaction activity and the amorphous carbon coating with concentrated defects does not hinder the oxygen diffusion onto the LFP surface. In a sharp contrast, as compared to the uncoated LFP case, both exothermic peaks in the cases of LFP/GN and LFP@GN upshift to a higher temperature and LFP@GN demonstrates much larger shifts. That is, graphene coating retards oxygen diffusion to the inside LFP surface, and increases the oxidation temperature of LFP. Furthermore, full and tight coating of graphene in LFP@GN suppresses the oxidation reaction of the inside LFP to a larger extent than the case of LFP/GN, since full carbon coating totally isolates LFP from the atmospheric oxygen and cuts off the mass transport pathway towards the inside LFP while par-



**Fig. 3** – Thermal and electrochemical properties of various carbon coating structures: (a) DSC curves; (b) Charge/discharge profiles; (c) Rate performances; (d) Cyclic voltammograms; (e) EIS presented as Nyquist plots, and the inset shows the plots in the high frequency region. The weight fractions of LFP in all cases of LFP@GN, LFP@TC and LFP/GN are in the range of 95–97% according to the TG measurements.

tial coating leave LFP exposure to the atmospheric oxygen to some extent.

The above DSC results indicate the cut-off effect of full graphene wrapping where GNs retard mass transport into the inside LFP. Herein, the electrochemical measurements are performed to experimentally probe whether  $\text{Li}^+$  can go through the graphene coating. Their capacity performance (Fig. 3b) is obtained at the current density of 0.05C, which is low enough to ensure  $\text{Li}^+$  diffusion from the bulk electrolyte to the material surfaces. The discharge capacity of LFP/GN is up to  $\sim 150 \text{ mAh g}^{-1}$ , while the capacity is only  $\sim 40 \text{ mAh g}^{-1}$  for LFP@GN (even much lower than the uncoated LFP), which indicates that partial or full wrapping results in entirely different electrochemical behaviors, and the first Coulombic efficiencies of LFP/GN and LFP@GN are 90.7% and 96.1%,

respectively. Note that the specific capacity is based on the mass of LFP contained in the active materials (95.5 wt.% for LFP/GN, 95.9 wt.% for LFP@GN). The capacity of LFP@TC is  $145 \text{ mAh g}^{-1}$ , which is slightly lower than the LFP/GN case. It can be clearly seen the typical voltage plateau along 3.4 V (vs.  $\text{Li}^+/\text{Li}$ ) which is associated with the redox processes of LFP/GN and LFP@TC, while the voltage plateau of LFP@GN almost disappears, where the redox process of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  may not occur sufficiently since the GNs act as a barrier to cut off the  $\text{Li}^+$  diffusion pathway. In the case of LFP/GN, partial wrapping leaves pathway for the  $\text{Li}^+$  diffusion and the GNs provide effective conducting network, inducing better electrochemical performance. For LFP@TC, the coating layer is the amorphous carbon, which possesses concentrated defects and can absorb the electrolyte, guaranteeing the smooth ion

transport together with acceptable electronic conductivity. As shown in Fig. 3c, LFP/GN demonstrates acceptable rate performances though partial graphene wrapping limits the ion diffusion to inside LFP to some extent. Fig. 3d shows the cyclic voltammetry curves of LFP@GN and LFP/GN (scanning rate:  $0.1 \text{ mV s}^{-1}$ ). The lower and weaker redox peaks of LFP@GN than the LFP/GN cases indicate a lower electrochemical reactivity of LFP@GN which is resulted from the slower  $\text{Li}^+$  diffusion, which is in accordance with the DSC results. Based on the electrochemical impedance spectroscopy (EIS) profiles (Fig. 3e), it is found that the charge-transfer resistance of LFP@GN is much larger than that of LFP/GN, which is related to the  $\text{Li}^+$  extraction and insertion reactions. This result further suggest that partial graphene wrapping is beneficial to the performance of LFP, while the full and tight graphene wrapping is resistive to the  $\text{Li}^+$  transport, resulting in the large charge transfer resistance.

In this study, we use graphene as an ideal model to probe how carbon coating works in the enhancement of the electrochemical performance of LIB. The results indicate that a partial graphene coating provides a balance between increased electron transport and fast ion diffusion which shows an improved electrochemical performance, while full and tight graphene wrapping totally isolates active materials from the electrolyte and retards ion diffusion. Generally, an ideal carbon coating for LIB cathode should be characterized by highly graphitic structure guaranteeing excellent electron transport property together with the unimpeded path for fast ion diffusion.

### Acknowledgments

We appreciate the supports from NSFC (No. 51072131), State Key Laboratory of Heavy Oil Processing, NSF of Tianjin China

(No. 12JCZDJC27400), Shenzhen Basic Research Project (No. JC201104210152A) and Joint Project for Guangdong-MOE-MOST (No. 2011B090400342).

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2013.01.070>.

### REFERENCES

- [1] Wang J, Sun X. Understanding and recent development of carbon coating on  $\text{LiFePO}_4$  cathode materials for lithium-ion batteries. *Energy Environ. Sci.* 2012;5(1):5163–85.
- [2] Yao F, Güneş F, Ta HQ, Lee SM, Chae SJ, Sheem KY, et al. Diffusion mechanism of lithium ion through basal plane of layered graphene. *J. Am. Chem. Soc.* 2012;134(20):8646–54.
- [3] Geim AK. Graphene: status and prospects. *Science* 2009;324(5934):1530–4.
- [4] Su FY, You CH, He YB, Lv W, Cui W, Jin FM, et al. Flexible and planar graphene conductive additives for lithium-ion batteries. *J. Mater. Chem.* 2010;20(43):9644–50.
- [5] Su FY, He YB, Li BH, Chen XC, You CH, Wei W, et al. Could graphene construct an effective conducting network in a high-power lithium ion battery? *Nano Energy* 2012;1(3):429–39.
- [6] Cao YL, Yu LH, Li T, Ai XP, Yang HX. Synthesis and electrochemical characterization of carbon-coated nanocrystalline  $\text{LiFePO}_4$  prepared by polyacrylates-pyrolysis route. *J. Power Sources* 2007;172(2):913–8.

## Charge carrier transport control in activated carbon fibers

Wojciech Kempniński <sup>a,\*</sup>, Damian Markowski <sup>a</sup>, Mateusz Kempniński <sup>b</sup>,  
Małgorzata Śliwińska-Bartkowiak <sup>b</sup>

<sup>a</sup> Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

<sup>b</sup> Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

### ARTICLE INFO

Article history:

Received 3 August 2012

Accepted 31 January 2013

Available online 9 February 2013

### ABSTRACT

We present the results of measurements of electronic transport in an activated carbon fiber performed over a wide temperature range. The fiber had been subjected to the adsorption of various molecules, one type at a time. The presence of guest molecules inside the fiber's pores causes significant changes in the electronic transport which has been observed to depend on the molecules' dipole moment. Results show the possibility of controlling the charge carrier transport through the fiber by using specific adsorbents.

© 2013 Elsevier Ltd. All rights reserved.

\* Corresponding author.