# Facile Synthesis of LiFePO<sub>4</sub> Nanoparticles Coated by Few Layers of PAS with Quasi-Graphene Structure

Jing Liu<sup>1,\*</sup>, Xianfa Zhang<sup>2</sup>, Rongshun Wang<sup>3</sup>, Jingping Zhang<sup>3</sup>

 <sup>1</sup> Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, and School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, PR China.
<sup>2</sup> Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Heilongjiang University, Harbin 150080, PR China
<sup>3</sup> Institute of Functional Materials, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, PR China
\*E-mail: jingliu@sdu.edu.cn

Received: 18 October 2012 / Accepted: 16 November 2012 / Published: 1 December 2012

A facile method has been developed to synthesize LiFePO<sub>4</sub> nanoparticles that are coated by 5-10 layers (2-4 nm thickness) of polyacenic semiconductor (PAS) with quasi-graphene structure. The PAS is produced from the windward pyrolysis of phenol-formaldehyde (PF) resin gas, and this solid-gas reaction process allows few layers of PAS to be coated on the surface of LiFePO<sub>4</sub> homogeneously. Such a thin and homogeneous PAS coating greatly enhances the electronic conductivity of LiFePO<sub>4</sub>, so does the electrochemical performance. At the rate of 0.1 C, the discharge capacity of the prepared LiFePO<sub>4</sub>/PAS composite is 166 mAh g<sup>-1</sup>, closing to the theoretical value. At a high rate of 5 C, the discharge capacity is as high as 116 mAh g<sup>-1</sup>. In addition, this composite shows an excellent long-term cyclability, retaining over 96.5% of its original discharge capacity beyond 500 cycles at the rate of 1 C.

**Keywords:** Few layers; Quasi-graphene structure; Solid-gas reaction; Conductivity; Lithium-ion battery

# **1. INTRODUCTION**

Since the pioneer work of prof. Goodenough and co-workers [1], LiFePO<sub>4</sub> has attracted extensive interest as a cathode material for lithium-ion battery because of its many advantages, such as the high energy density, low cost, environmental friendliness and excellent thermal safety [2].

However, the intrinsic poor electronic conductivity combined with the slow lithium ion diffusion rate leads to a poor rate performance of LiFePO<sub>4</sub>.

Strategies to solve these problems focused on doping with foreign atoms [3, 4], minimizing the particle size [5, 6] and coating with conductive layers [7-10]. In particular, carbon coating is an easy and successful strategy to enhance the electrochemical performance of LiFePO<sub>4</sub> [11]. However, the electrochemical performance of LiFePO<sub>4</sub>/C is strongly dependent on the structure  $(sp^2/sp^3 ratio)$ , the homogeneity, and the thickness of the carbon layer. Higher electronic conductivity of LiFePO<sub>4</sub>/C composite resulted from lower disordered/graphene (D/G) and increased  $sp^2/sp^3$  ratios in carbon was reported continuously in recent decade [12-17]. Dominko et al [18] and Cho et al [19] investigated the impact of carbon coating thickness on the electrochemical properties of LiFePO<sub>4</sub>/C composites, respectively, and similar conclusions were obtained that the reversible capacity decreased with thicker carbon coating. Dominko et al [18] ascribed this to increasingly hindered electrolyte transport and increased amount of inactive of Fe (III) species (presumably Fe<sub>3</sub>P) with thicker carbon coating. Moreover, as an electrochemical inactive material, too much carbon will undoubtedly decrease the energy density of lithium-ion battery. Therefore, an optimized coating carbon layer for LiFePO<sub>4</sub> should be thin, homogeneous and with more  $sp^2$  structure, which can not only enhance the electronic conductivity but also contribute to the power density of lithium-ion battery.

Graphene, a monolayer of carbon atoms connected by  $sp^2$ -bonded, should be the most promising coating carbon for its high conductivity and structural flexibility. Recently, a LiFePO<sub>4</sub> wrapped by graphene with 3-5 monolayer thickness was reported by Liu's group [20]. The composite could deliver a discharge capacity of 70 mAh·g<sup>-1</sup> at a high rate of 60C and showed a long-term cyclability at high rates. Unfortunately, the synthesis process of graphene is complicated and gives a very low yield, so the cost of graphene is expensive. By contrast, the polyacenic semiconductor (PAS), which shows a quasi-graphene structure [21], has advantages of facile synthesis, low cost, and good environmental compatibility [22, 23]. Therefore, PAS is a better choice for the optimized carbon coating.

In this work, a LiFePO<sub>4</sub> material coated by few layers of PAS with quasi-graphene structure has been synthesized by a facile method. Performance improvements over LiFePO<sub>4</sub> are observed in this study, and the chemical/physical characterization of these coatings provides insight into the morphology and conductivity improvement mechanism of the LiFePO<sub>4</sub>/PAS.

## 2. EXPERIMENTAL PART

The LiFePO<sub>4</sub>/PAS composite was synthesized using FePO<sub>4</sub>·4H<sub>2</sub>O (self-made according to our previous report [24]) and LiOH·H<sub>2</sub>O. Equimolar solutions of FeSO<sub>4</sub>·7H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> were mixed and stirred continuously, and concentrated hydrogen peroxide solution was added slowly until all the

bivalent iron ions were oxidized. Then the yellowish precipitate was filtered and washed with distilled water for several times.

Stoichiometric of FePO<sub>4</sub>·4H<sub>2</sub>O and LiOH·H<sub>2</sub>O were ball-milled for 10 h in the ethanol and then dried. Then the precursor and appropriate amount of PF resin were put into quartz boats, separately. Note that the quartz boat with PF resin was close to the gas atmosphere inlet. The thermal treatment was performed at 450 °C for 3 h and 700 °C for 10 h under the flowing nitrogen atmosphere with a 10 mL min<sup>-1</sup> gas flow rate. The final black power was the LiFePO<sub>4</sub>/PAS composite.

The carbon content in the LiFePO<sub>4</sub>/PAS composite was determined by the VarioEL III (elementar, Germany) element analyzer. The electronic conductivity was measured with a Four-Point Probe Meter (SDY-5, Guangzhou). Resonant Raman scattering spectra were recorded at room temperature with a JY HR-800 Lab Ram confocal Raman microscope in a backscattering configuration, with an excitation wavelength of 325 nm. The phase purity and structure were detected with powder X-ray diffraction (XRD, Bruker, D8 Advance) using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). Lattice parameters and the mean crystallite size were obtained from the full pattern matching refinements via the software of MDI Jade 5.0. The particle morphology was observed by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM, JEM-2010).

The electrochemical performance of the cathode was characterized on experimental cells with lithium metal as the counter electrode. The slurry with 84 wt.% host material, 8 wt.% super P, and 8 wt.% polyvinylidene fluoride (PVDF) dispersed in N-methylpyrrolidinone (NMP) was coated on the Al foil and dried in a vacuum oven at 120 °C for 12 h. The resulting cathode film was pressed and punched into a disc. Celgard 2400 was used as a separator. The electrolyte was 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume). All cells were assembled in an argon-filled glove box and tested at room temperature over the voltage range 2.5-4.2 V. 1 C = 170 mA g<sup>-1</sup>.

# **3. RESULTS AND DISCUSSIONS**



Figure 1. Scheme of the whole synthesis process of the LiFePO<sub>4</sub>/PAS composite.

The whole synthesis process of the LiFePO<sub>4</sub>/PAS composite is shown in Figure 1. The PF resin in a single quartz boat is close to the gas atmosphere inlet. With the increasing of temperature, the PF resin sublimes windward, so the whole quartz tube is filled with the PF resin vapor. And the precursor (mixture of FePO<sub>4</sub> and LiOH) is also surrounded by the PF resin vapor. The flow rate of nitrogen atmosphere is limited at 10 mL min<sup>-1</sup> to make sure not all the PF resin vapor overflow the quartz tube. By the further increasing of temperature, the pyrolysis of PF resin gas takes place, and produces the PAS with quasi-graphene structure combined with a quantity of H<sub>2</sub>. Therefore, the LiFePO<sub>4</sub> forms under this reducing atmosphere. Furthermore, this solid-gas reaction process allows few layers of PAS to be coated on the surface of LiFePO<sub>4</sub> homogeneously, and the *in situ* formed PAS plays an important role in inhibiting the crystal growth of LiFePO<sub>4</sub>. It is notable that the prepared LiFePO<sub>4</sub>/PAS powder is black rather than gray, and the inner wall of the whole quartz tube is adhered by the black PAS with metallic luster.



Figure 2. XRD patterns of the LiFePO<sub>4</sub>/PAS composite.

Figure 2 shows the XRD patterns of the prepared LiFePO<sub>4</sub>/PAS composite. The diffraction peaks are well consistent with the olivine LiFePO<sub>4</sub> in the JCPDS file (no. 83-2092), indexing to be an orthorhombic crystal structure (space group Pnma) with a = 10.315(3) Å, b = 6.000(6) Å, and c = 4.686(9) Å. The strong diffraction peaks indicate a good crystallinity of LiFePO<sub>4</sub>. No additional diffraction peaks belonging to the crystal modification of the PAS can be observed from the XRD

patterns, which should be attributed to its low concentration. Element analysis shows that the carbon content in the LiFePO<sub>4</sub>/PAS composite is 4.95 %.

Figure 3 shows the Raman spectrum of the LiFePO<sub>4</sub>/PAS composite. The group of peaks at 1120-100 cm<sup>-1</sup> is attributed to the vibrations of Fe-O and PO<sub>4</sub><sup>3-</sup> in LiFePO<sub>4</sub> [25, 26]. Two groups of characteristic peaks of PAS are observed, including the peak at ~1350 cm<sup>-1</sup> (D-band) assigned to the disorder-induced phonon mode, and one strong peak at ~1600 cm<sup>-1</sup> (G-band) corresponding to the  $E_{2g}$  mode.



Figure 3. Raman spectra of the LiFePO<sub>4</sub>/PAS composite.

The low intensity ratio of D and G bands (about 0.7 for  $I_D/I_G$ ) indicates a high electronic conductivity of the LiFePO<sub>4</sub>/PAS composite. The electronic conductivity of the LiFePO<sub>4</sub>/PAS composite is tested as  $5.4 \times 10^{-1}$  S cm<sup>-1</sup> by Four-Point Probe Meter, which is nearly eight orders of magnitude greater than that of pure LiFePO<sub>4</sub> (10<sup>-9</sup> S cm<sup>-1</sup>). Otherwise, instead of characteristic peaks of carbon materials only [13, 15, 17, 24], characteristic peaks of both LiFePO<sub>4</sub> and PAS can be observed clearly from our Raman spectrum, indicating that the thickness of PAS layer is ultrathin.

The morphology of the prepared LiFePO<sub>4</sub>/PAS composite is shown in Figure 4. The SEM image in Figure 4A shows that the typical size of these LiFePO<sub>4</sub>/PAS particles is in the range of 100-200 nm. Figure 4B shows a TEM image including several primary particles, and the PAS films distributed in interstices of LiFePO<sub>4</sub> particles can be observed clearly. These PAS films closely connect LiFePO<sub>4</sub> particles thus form a conductive network to enhance the electronic conductivity. The

unique morphology of PAS, as observed from Figure 4C, is a quasi-graphene layered structure rather than an amorphous coating. These PAS films also show a flexible structure that they are packing and/or folding by several layers with random shapes. A particle embedded in the PAS films is shown in Figure 4C. It can be observed clearly that the LiFePO<sub>4</sub> particle is highly crystalline and is surrounded by few layers of PAS films (7 layers at the marked place, about 2.5 nm). The boundary of a LiFePO<sub>4</sub> particle is shown in Figure 4D. About 10 layers of PAS films are tightly coated on the surface of LiFePO<sub>4</sub>, which perfectly fits the shape of particle without any gaps. These PAS films ensure that each spot on the particle surface is able to accept the electron rapidly, which can also contribute to the electrical continuity between LiFePO<sub>4</sub> crystallites.



**Figure 4.** Characterization of the LiFePO<sub>4</sub>/PAS composite: (A) SEM images; (B) TEM images including several primary crystallites; (C)-(D) typical HRTEM images of primary LiFePO<sub>4</sub> crystallites. (E)-(F) TEM and HRTEM images of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/PAS.

This result could promote the development of a novel method to synthesize nano-sized lithium intercalated compounds with greatly improved electronic conductivities by several layers of quasi-graphene films coating. Following this line, we also successfully synthesized nano-sized  $Li_4Ti_5O_{12}$  particles completely coated by few layers of PAS films by calcining at 800 °C for 10 h (See Figure 4E and Figure 4F). This  $Li_4Ti_5O_{12}$ /PAS composite shows a typical size of 100-200 nm, and its electronic conductivity is as high as  $8.7 \times 10^{-1}$  S cm<sup>-1</sup>.

Galvanostatic charge and discharge measurements of the as-prepared LiFePO $_4$ /PAS composite are carried out.



**Figure 5.** Electrochemical performance of the prepared LiFePO<sub>4</sub>/PAS composite: (A) chargedischarge curves at different rates; (B) cycle performance at different rates.



**Figure 6.** Cycle performance of the LiFePO<sub>4</sub>/PAS composite at the rate of 1 C, inset is its chargedischarge curves at different cycle number.

As shown in Figure 5A, at a rate of 0.1 C, the discharge curve of the LiFePO<sub>4</sub>/PAS composite displays a flat plateau at 3.40 V, and the discharge capacity is as high as 166 mAh g<sup>-1</sup>, closing to the theoretical value. At higher rates of 1 C, 2 C and 5 C, the material delivers discharge capacities of 141 mAh g<sup>-1</sup>, 129 mAh g<sup>-1</sup> and 116 mAh g<sup>-1</sup> with flat plateaus at 3.37 V, 3.35 V and 3.19 V, respectively. The LiFePO<sub>4</sub>/PAS also shows good cycling performances at different rates, as shown in Figure 5B. Even at the high rate of 5 C, it exhibits stable capacity retention in 50 cycles without any fading.

Moreover, the prepared LiFePO<sub>4</sub>/PAS composite reveals an excellent cycling performance with more than 96.5% capacity retention after 500 cycles with a depth of discharge (DOD) of 84% at the rate of 1 C, as shown in Figure 6. Inset is its charge-discharge curves at different cycle numbers. The  $\Delta V$ , which is calculated from the difference of charge and corresponding discharge voltage plateaus, increases only 0.034 V from the 1<sup>st</sup> to the 500<sup>th</sup> cycle, indicating a small polarization and a high cycling stability. Therefore, this thin and homogeneous PAS coating is a facile and effective way to improve the electrochemical performance of LiFePO<sub>4</sub>.

### **4. CONCLUSIONS**

In summary, a simple method has been developed to synthesize several layers of PAS films on the surface of LiFePO<sub>4</sub>. The PAS distributed at the boundary/interstitial of LiFePO<sub>4</sub> particles effectively enhances the electronic conductivity as well as the electrochemical performance. We believe our demonstration of this synthesis method gives an efficient strategy for other electrode materials towards high conductivity and high performance.

#### ACKNOWLEDGEMENTS

This work was supported by the financial support from China Postdoctoral Science Foundation (No. 2012M511490), and the Special Fund for Postdoctoral Innovation Program of Shandong Province (No. 201102022). We also thank the financial support from the National Key Technologies R&D Program (Grant No. 2009BAG19B00).

### References

- 1. A.K. Padhi, K.S. Nanjundaswamy and J.B. Goodenough, J. Electrochem. Soc., 144 (1997) 1188.
- 2. B.L. Ellis, K.T. Lee and L.F. Nazar, Chem. Mater., 22 (2010) 691.
- 3. S.-Y. Chung, J.T. Bloking and Y.M. Chiang, Nat. Mater., 1 (2002) 123.
- 4. C. Ban, W.-J. Yin, H. Tang, S.-H. Wei, Y. Yan and A.C. Dillon, *Adv. Energy Mater.*, 2 (2012) 1028.
- 5. S. Woon Oh, Z.-D. Huang, B. Zhang, Y. Yu, Y.-B. He and J.-K. Kim, *J. Mater. Chem.*, 22 (2012) 17215.
- 6. F. Brochu, A. Guerfi, J. Trottier, M. Kopeć, A. Mauger, H. Groult, C.M. Julien and K. Zaghib, J. *Power Sources*, 214 (2012) 1.

- 7. Z. Lu, H. Cheng, M. Lo and C.Y. Chung, Adv. Funct. Mater., 17, (2007) 3885.
- 8. Y.-S. Hu, Yu-Guo Guo, Robert Dominko, Miran Gaberscek, Janko Jamnik and Joachim Maier, *Adv. Mater.*, 19 (2007) 1963.
- 9. S.W. Oh, S.-T. Myung, S.-M. Oh, K.H. Oh, K. Amine, B. Scrosati, and Y.-K. Sun, *Adv. Mater.*, 22 (2010) 4842.
- 10. M.M. Rahman, J.-Z. Wang, R. Zeng, D. Wexler and H.K. Liu, J. Power Sources, 206 (2012) 259.
- 11. Y. Wang, Y. Wang, E. Hosono, K. Wang and H. Zhou, Angew. Chem. Int. Ed., 47 (2008) 7461.
- R. Kostecki, B. Schnyder, D. Alliata, X. Song, K. Kinoshita and R. Kötz, *Thin Solid Films*, 396 (2001) 36.
- 13. M.M. Doeff, Y. Hu, F. McLarnon and R. Kostecki, *Electrochem. Solid-State Lett.*, 6 (2003) A207.
- 14. K.-F. Hsu, S.-Y. Tsay and B.-J. Hwang, J. Power Sources, 146 (2005) 529.
- 15. M.M. Doeff, J.D. Wilcox, R. Kostecki and G. Lau, J. Power Sources, 163 (2006) 180.
- 16. G.L. Yang, A.F. Jalbout, Y. Xu, H.Y. Yu, X.G. He, H.M. Xie and R.S. Wang, *Electrochem. Solid-State Lett.*, 11 (2008) A125.
- 17. G.T.-K. Fey, K.-P. Huang, H.-M. Kao and W.-H. Li, J. Power Sources, 196 (2011) 2810.
- 18. R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, S. Pejovnik and J. Jamnik, J. *Electrochem. Soc.*, 152 (2005) A607.
- 19. Y.-D. Cho, G.T.-K. Fey and H.-M. Kao, J. Power Sources, 189 (2009) 256.
- 20. X. Zhou, F. Wang, Y. Zhu and Z. Liu, J. Mater. Chem., 21 (2011) 3353.
- 21. T. Yamabe, M. Fujii, S. Mori, H. Kinoshita and S. Yata, Synth. Met., 145 (2004) 31.
- 22. S. Yata, S. Mori, H. Satake and H. Kinoshita, J. Electrochem. Soc., 154 (2007) A221.
- 23. A. Yoshino, T. Tsubata, M. Shimoyamada, H. Satake, Y. Okano, S. Mori and S. Yata, *J. Electrochem. Soc.*, 151 (2004) A2180.
- 24. J. Liu, F. Liu, G. Yang, X. Zhang, J. Wang and R. Wang, Electrochim. Acta, 55 (2010) 1067.
- 25. C.M. Burba and R. Frech, J. Electrochem. Soc., 151, (2004) A1032.
- 26. M.-H. Lee, J.-Y. Kim and H.-K. Song, Chem. Commun., 46, (2010) 6795.

© 2012 by ESG (www.electrochemsci.org)