Design and Synthesis of Nano-sized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Particles Embedded in Boron-doped Graphene Sheets for Lithium-ion Batteries

Yisheng Hu ^{a,1}, Yifan Xing ^{b,c,1}, Jinhui Zhao ^{d,e,*}

^a State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China

^b Shenzhen Quantum Wisdom Culture Development Co., Ltd., Shenzhen 518035, China

^c Department of Physics and Material Sciences, City University of Hong Kong, Hong Kong

^d College of Mechanical & Electrical Engineering, China Jiliang University, Hangzhou 310018, China

^e Alliance Manchester Business School, The University of Manchester, Manchester M15 6PB, UK

¹ These authors contributed equally to this work.

Corresponding author

E-mail: jinhui Zhao_mc@sina.com

Abstract

The boron-doped graphene decorated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite ($\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$) has been successfully synthesized for the first time using a facile method. The effects of B-GS on the structure, morphology and electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode are investigated. The results show that the nano-sized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles are about 80 nm on an average and are uniformly dispersed on the conducting B-GS. This combined favorable

structure is helpful to facilitate the electron and Li^+ transmission, leading to the excellent rate capability and cycling stability. The improved battery performance indicates that the obtained $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite can be a potential cathode candidate for the application of high-performance lithium-ion batteries.

Keywords: High-voltage cathode; $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; B-doped graphene; Electrochemical performance; Lithium-ion batteries

1. Introduction

Nowadays, rechargeable lithium-ion batteries are the most popular power source for electric vehicles [1]. In the battery systems, the high-voltage and high-capacity cathode materials hold the key to meeting future high energy density requirements. Among the various explored materials, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is considered as one of the most promising cathodes due to its good Li^+ mobility, excellent thermal stability, high safety and low cost [2,3]. Meanwhile, it can completely extract three Li^+ when charged to a high voltage of 4.8 V, leading to a theoretical capacity of 197 mAh g^{-1} [4]. Unfortunately, the major challenge for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode is the poor cycling stability due to the low electronic conductivity ($2.0 \times 10^{-8} \text{ S cm}^{-1}$) [5]. Over the past decade, several approaches have been adopted to overcome this obstacle such as scaling down the particle size, doping with metal ions or coating with conducting materials [6-8].

As one of the promising carbon materials, graphene has been proved to be a good substrate to host electrode materials for energy applications, owing to its large surface area, high electronic conductivity, flexibility and chemical stability [9]. Recently, preparation of

graphene-decorated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composites and their applications for lithium-ion batteries have been vastly reported [10]. Meanwhile, it has been proved that boron-doping can further improve the properties of carbon materials [11]. However, to the best of our knowledge, no research was reported on the preparation of boron-doped graphene-modified $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode.

In this work, the boron-doped graphene sheets wrapping modification approach is initially applied to improve the electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ for lithium-ion batteries. The structure, morphology and battery property of the as-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite are investigated and compared with that of the bare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

2. Experimental

The graphene oxide (GO) sheets were firstly prepared from natural graphite by using a modified Hummers method [12]. To prepare the boron-doped graphene sheets (B-GS), a general strategy could be achieved with boric acid (H_3BO_3) as the dopant. In a typical process, the B-GS was obtained by mixing 5 wt% H_3BO_3 with GO and thermally treating the mixture at 2450 °C for 30 min using a graphite furnace in an argon atmosphere.

The $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite was synthesized through a hydrothermal-assisted sol-gel route as described previously [5]. As illustrated in Fig. 1, the obtained B-GS was firstly dispersed in deionized water and continuously sonicated for 30 min to form a homogeneous suspension. Then, the V_2O_5 , $\text{NH}_4\text{H}_2\text{PO}_4$, Li_2CO_3 and glucose were added to the B-GS solution and magnetically stirred at room temperature for 2 h before being transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed and kept at 180

°C for 24 h. After cooling to room temperature, the obtained mixture was heated on a hot plate at 80 °C with stirring to evaporate the water. Finally, the precursor was preheated at 350 °C for 5 h and then calcined at 750 °C for 10 h under a flow of N₂ atmosphere to obtain the Li₃V₂(PO₄)₃/B-GS composite. For comparison, the bare Li₃V₂(PO₄)₃ sample was also synthesized using the similar procedure without adding the B-GS.

Fig. 1. Schematic procedure for the nanosized Li₃V₂(PO₄)₃ grown on B-GS as cathode for high-performance lithium-ion batteries.

The as-synthesized B-GS, Li₃V₂(PO₄)₃ and Li₃V₂(PO₄)₃/B-GS products were studied by X-ray diffraction (XRD, Rigaku D/max 2500v/pc) using Cu K α radiation ($\lambda=0.154$ nm). The morphologies of Li₃V₂(PO₄)₃ and Li₃V₂(PO₄)₃/B-GS were characterized by scanning electron microscopy (SEM, Hitachi, S-4800). The microstructure of Li₃V₂(PO₄)₃/B-GS was investigated by transmission electron microscopy (TEM, Tecnai, F-20). The electronic conductivities for the as-synthesized samples were measured with an RTS-8 linear four-point probe measurement system. Raman spectra of Li₃V₂(PO₄)₃/B-GS composite was analyzed by using a Renishaw Invia Raman microscope with the 532 nm line of an Ar⁺ laser as the excitation source. The surface chemical composition of Li₃V₂(PO₄)₃/B-GS was investigated by X-ray photoelectron spectroscopy (XPS, PHI-5300) equipped with an Mg K α achromatic X-ray source.

For the electrochemical measurement, the working electrode was prepared by mixing 85 wt% active material, 10 wt% carbon black and 5 wt% polyvinyl difluoride (PVDF) dispersed in 1-methyl-2-pyrrolidinone (NMP). The average mass of the active material was about 3.7 mg. The coin-type cells (CR2032) were fabricated with lithium foil as the counter electrode and Celgard 2300 film as the separator in a glove box filled with pure argon. The electrolyte was 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (1:1 in volume). Cells were galvanostatically cycled on a Land BT2000 battery test system (Wuhan, China) at various current rates in the voltage range of 3.0-4.8 V (vs. Li/Li^+) at 25 °C. In describing batteries, charge and discharge current is often expressed as a C-rate. A C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. Note that the charge and discharge capacities of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ were calculated based on the content of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

3. Results and Discussion

The crystallographic phases of B-GS, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ samples were identified by XRD as shown in Fig. 2. A broad peak ascribed to the (002) crystal plane appears at around 26° in the B-GS, which is consistent with the previously reported results [13]. Strong diffraction peaks can be observed in the XRD patterns of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$. All the patterns are well indexed as monoclinic structure with the space group of $\text{P2}_1/\text{n}$ (JCPDS No.: 80-1515). The results are similar with that of previous literatures [6-8,10,14]. Moreover, no diffraction peak related to B-GS can be detected based on the XRD analysis, which may be due to the low content of the added B-GS. In all, the XRD results reveal that the B-GS in the preparing process does not influence the structure

of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

Fig. 2. XRD patterns of B-GS, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ samples.

The Raman spectrum of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ is illustrated in Fig. 3a. The characteristic peaks of the D band and G band for the composite are observed at 1355 cm^{-1} and 1582 cm^{-1} , respectively. The D band corresponds to the vibrations of sp^3 carbon atoms in edge or structural defects; the G band is related to the vibrations of sp^2 carbon atoms in graphite [15,16]. The intensity ratio value of D band and G band (I_D/I_G) for $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ is about 1.05. The high value of I_D/I_G indicates that the boron-doping can increase the defects and randomness of graphene. Meanwhile, the boron atoms have great potential as an efficient doping agent for engineering the physical and chemical properties of graphene

sheets [17]. XPS test was performed to determine the chemical composition of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$. It can be noted from Fig. 3b that the Li, V, P, O, C and B elements are existed in the XPS curve. As shown in Fig. 3c, the prominent C 1s peak at 285 eV corresponds to the graphite-like sp^2 hybridized state. Additionally, according to Fig. 3d, a new peak at around 191 eV is the B 1s emission [18] which confirms the boron atoms have been doped into the graphene sheet.

Fig. 3. (a) Raman spectrum, (b) survey XPS spectra, (c) XPS C 1s and (d) XPS B 1s spectra of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite.

Fig. 4 SEM images of (a) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ powders.

The morphologies of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ were characterized by SEM in Fig. 4. The SEM images of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (Fig. 4a) show regular particles with sizes of 70-150 nm. For the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ sample (Fig. 4b), it can be clearly seen that the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles are dispersed on the B-GS. Meanwhile, the presence of B-GS can prevent the particle growth during the calcining process [19]. Fig. 5 gives the TEM images

of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite. Obviously, the B-GS are clearly visible and the nanosized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles are anchored onto the surface of B-GS. The B-GS can not only increase the electronic conductivity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, but also make the electrode more stable against the electrolyte etching [20]. It should be noted that the electronic conductivities of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ are 4.5×10^{-5} and $9.6 \times 10^{-4} \text{ S cm}^{-1}$, respectively, indicating that the B-GS plays an important role in enhancing the electronic conductivity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ material. According to the elemental analysis, the B-GS content in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite is about 4.7 wt%.

Fig. 5 TEM images of the as-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite.

The initial charge/discharge curves and cycling performances for the bare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ electrodes at a low rate of 0.1 C between 3.0 and 4.8 V (vs. Li/Li^+) are shown in Fig. 6. For both cathode materials (Fig. 6a), there are four voltage plateaus in the charge process which corresponds to the extraction of three Li-ions from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ over four two-phase transformation, while the corresponding discharge curves present three plateaus due to the solid state solution behavior of insertion of Li-ions into the $\text{V}_2(\text{PO}_4)_3$ structure [3,21]. The initial discharge capacities for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ are 167.2 and 188.6 mAh g^{-1} , respectively. As shown in Fig. 6b, the specific capacity of the bare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrode drops rapidly during the cycling process. On the contrary, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite exhibits superior cycling stability with capacity retention ratio of 98.9% over 30 cycles.

Fig. 6 (a) Initial charge/discharge curves and (b) cycling performances of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ electrodes at 0.1 C in the voltage range of 3.0-4.8 V (vs. Li/Li^+).

Fig. 7 (a) The dependence of specific capacity on the current density and (b) cycling stability at various current rates between 3.0 and 4.8 V (vs. Li/Li⁺) for the Li₃V₂(PO₄)₃ and Li₃V₂(PO₄)₃/B-GS electrodes.

The rate performances for Li₃V₂(PO₄)₃ and Li₃V₂(PO₄)₃/B-GS at different rates in the voltage range of 3.0-4.8 V (vs. Li/Li⁺) are also investigated. Fig. 7a compares the rate

capabilities of the two electrodes at various current rates from 1 C to 10 C. Obviously, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ shows higher specific capacity than the bare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at each current rate. It delivers specific capacities of 183.2, 178.0, 166.9 and 153.6 mAh g^{-1} at 1, 2, 5 and 10 C, respectively. Furthermore, the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite exhibits superior cycling performance (Fig. 7b) with capacity retention ratio of 98.5% at 10 C after 50 cycles. When the current rate was reduced back to 1 C, the specific capacity can almost recover its initial capacity value, whereas the bare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ returns to only 86% of its initial capacity. It has been proved that the bad rate performance of the bare $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrode can be attributed to the poor electronic conductivity [5,22], and the enhanced battery performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ is due to the added conducting B-GS which can significantly increase the electronic conductivity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ material.

4. Conclusions

Herein, we have developed an effective approach to improve the electrochemical property of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode for lithium-ion batteries via uniform B-GS wrapping. The as-synthesized $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{B-GS}$ composite delivers excellent Li storage performances (3.0-4.8 V) in terms of remarkable specific capacity (188.6 mAh g^{-1} at a low rate of 0.1 C), rate capability (153.6 mAh g^{-1} at 10 C) and cycling performance (151.2 mAh g^{-1} remained after 50 cycles at 10 C). Such superior electrochemical properties are mainly attributed to the high electronic conductivity of B-GS as well as the features of nano-sized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles. The present work demonstrates that the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nanoparticles combined with conducting B-GS is a promising cathode material for lithium-ion batteries.

Acknowledgments

This work was supported by the National Science Foundation of China (No.61403356). Research on membrane computing based multi mode optimization algorithms and application in gasoline producing and scheduling.

References

- [1] Z.Q. Zhu, S.W. Wang, J. Du, Q. Jin, T.R. Zhang, F.Y. Cheng, J. Chen, Ultrasmall Sn nanoparticles embedded in nitrogen-doped porous carbon as high-performance anode for lithium-ion batteries, *Nano Lett.* 14 (2014) 153-157.
- [2] J. Kim, J. Yoo, Y. Jung, K. Kang, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /conducting polymer as a high power 4 V-class lithium batteries electrode, *Adv. Energy Mater.* 3 (2013) 1004-1007.
- [3] X. Rui, Q. Yan, M. Skyllas-Kazacos, T.M. Lim, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials for lithium-ion batteries: A review, *J. Power Sources* 258 (2014) 19-38.
- [4] S. Yin, H. Grondy, P. Strobel, M. Anne, L. Nazar, Electrochemical property: structure relationships in monoclinic $\text{Li}_{3-y}\text{V}_2(\text{PO}_4)_3$, *J. Am. Chem. Soc.* 125 (2003) 10402-10411.
- [5] W.C. Duan, Z. Hu, K. Zhang, F.Y. Cheng, Z. Tao, J. Chen, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ @C core-shell nanocomposite as a superior cathode material for lithium-ion batteries, *Nanoscale* 5 (2013) 6485-6490.
- [6] C.Y. Lai, J.J. Wei, Z. Wang, Q.J. Xu, Y.F. Lu, H.X. Li, $\text{Li}_3\text{V}_2(\text{PO}_4)_3/(\text{SiO}_2+\text{C})$ composite with better stability and electrochemical properties for lithium-ion batteries, *Solid State Ion.* 272 (2015) 121-126.
- [7] Y.L. Wang, L.H. Wang, Z.Z. Hou, W.X. Mao, Effects of Nd-doping on the structure

and electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ synthesized using a microwave solid-state route, *Solid State Ion.* 261 (2014) 11-16.

[8] L.Q. Mai, L. Xu, C.H. Han, X. Xu, Y.L. Luo, S.Y. Zhao, Y.L. Zhao, Electrospun ultralong hierarchical vanadium oxide nanowires with high performance for lithium ion batteries, *Nano Lett.* 10 (2010) 4750-4755.

[9] M. Ghosh, G. Venkatesh, G. Mohan Rao, Surface modification of vertically aligned graphene nanosheets by microwave assisted etching for application as anode of lithium ion batteries, *Solid State Ion.* 296 (2016) 31-36.

[10] K. Cui, S. Hu, Y. Li, Nitrogen-doped graphene nanosheets decorated $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanocrystals as high-rate and ultralong cycle-life cathode for lithium-ion batteries, *Electrochim. Acta* 210 (2016) 45-52.

[11] J. Paraknowitsch, A. Thomas, Doping carbons beyond nitrogen: an overview of advanced heteroatom doped carbons with boron, sulphur and phosphorus for energy applications, *Energy Environ. Sci.* 6 (2013) 2839-2855.

[12] W.S. Hummers, R.E. Offeman, Preparation of graphite oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.

[13] Q.H. Wang, L.F. Jiao, H.M. Du, Y.J. Wang, H.T. Yuan, Fe_3O_4 nanoparticles grown on graphene as advanced electrode materials for supercapacitors, *J. Power Sources* 245 (2014) 101-106.

[14] H. Han, F. Qiu, Z.T. Liu, X.E. Han, ZrO_2 -coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ nanocomposite: A high-voltage cathode for rechargeable lithium-ion batteries with remarkable cycling performance, *Ceram. Int.* 41 (2015) 8779-8784.

[15] X. Xu, S. Ji, M. Gu, J. Liu, In situ synthesis of MnS hollow microspheres on reduced

graphene oxide sheets as high-capacity and long-life anodes for Li- and Na-ion batteries, ACS Appl. Mater. Interfaces 7 (2015) 20957-20964.

[16] J.L. Yang, J.J. Wang, X.F. Li, D.N. Wang, J. Liu, G.X. Liang, M. Gauthier, Y.L. Li, D.S. Geng, R.Y. Lia, X.L. Sun, Hierarchically porous LiFePO_4 /nitrogen-doped carbon nanotubes composite as a cathode for lithium-ion batteries, J. Mater. Chem. 22 (2012) 7537-7543.

[17] Y. Kim, K. Fujisawa, H. Muramatsu, T. Hayashi, M. Endo, T. Fujimori, K. Kaneko, M. Terrones, J. Behrends, A. Eckmann, C. Casiraghi, M. Dresselhaus, Raman spectroscopy of boron-doped single-layer graphene, ACS Nano 6 (2012) 6293-6300.

[18] H. Wang, Y. Zhou, D. Wu, L. Liao, S.L. Zhao, H.L. Peng, Z.F. Liu, Synthesis of boron-doped graphene monolayers using the sole solid feedstock by chemical vapor deposition, Small 9 (2013) 1316-1320.

[19] H.D. Liu, P. Gao, J.H. Fang, G. Yang, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /graphene nanocomposites as cathode material for lithium ion batteries, Chem. Commun. 47 (2011) 9110-9112.

[20] J.R. He, Y.F. Chen, P.J. Li, F. Fu, J.B. Liu, Z.G. Wang, Facile fabrication of RGO wrapped LiMn_2O_4 nanorods as a cathode with enhanced specific capacity, RSC Adv. 5 (2015) 80063-80068.

[21] M. Saidi, J. Barker, H. Huang, J. Sowyer, G. Adamson, Performance characteristics of lithium vanadium phosphate as a cathode material for lithium-ion batteries, J. Power Sources 119 (2003) 266-272.

[22] S. Lee, S.S. Park, Atomistic simulation study of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a cathode material for lithium ion batteries: structure, defect chemistry, lithium ion transport pathway, and dynamics, J. Phys. Chem. C 116 (2012) 25190-25197.