



# Conducting polyaniline-wrapped lithium vanadium phosphate nanocomposite as high-rate and cycling stability cathode for lithium-ion batteries



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## ABSTRACT

This work introduces a facile strategy to improve the high-rate capability and cycling stability for carbon-free  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  by coating with conducting polymer polyaniline. Core-shell  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /polyaniline nanocomposite with typical sizes of 200 nm has been synthesized via a microwave heating assisted sol-gel method followed by a self-assembly process. The highly conductive and uniform polyaniline layer coated on the surface of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  nanoparticles significantly enhances the electrochemical performance of the electrode, which exhibits better rate capability and excellent cycling stability compared with the pristine  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . The resultant nanocomposite exhibits a high initial discharge capacity of  $130.7 \text{ mAhg}^{-1}$  at 0.1 C within a voltage range of 3.0–4.3 V. When cycled at a rate of 10 C the capacity can reach up to  $101.5 \text{ mAhg}^{-1}$ , and the capacity retention is 87.3% after 500 cycles. The likely contributing factor to the excellent electrochemical performance of core-shell  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /polyaniline could be related to the uniform conducting polymer layer, which can improve the electrical conductivity of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

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## 1. Introduction

In the past decades, lithium-ion batteries are widely considered to be among the most promising rechargeable batteries for the rapid development of mobile devices and electric vehicles [1–3], owing to their high energy and power density, as well as long cycle life. Among the candidate materials for rechargeable lithium-ion batteries, the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  exhibits high power density, thermal stability, low toxicity and low cost, and has been regarded as a prospective alternative cathode material for a wide range of green applications [4,5].

Monoclinic-phase  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  represents a promising high theoretical specific capacity and high operating voltage electrode material, being capable of storing more charges, approximately  $197 \text{ mAhg}^{-1}$ , all three lithium-ions can be completely extracted and inserted between 3.0 and 4.8 V [6–11]. Nevertheless, the low intrinsic electronic conductivity ( $2.4 \times 10^{-7} \text{ S cm}^{-1}$ ) and low lithium-ion diffusion coefficient ( $10^{-10}$ – $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ) of pristine  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

lead to a poor high rate performance, which thus limit its developments in large-scale application [12]. Up to now, a variety of approaches have been developed to improve the electrochemical performance of the pristine  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  electrode material. The intrinsic low conductivity of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  can be enhanced by doping an appropriate amount of other alien ions to form a continuous conductive path in the electrode, thus promoting the rate capability [8,13–21]. Carbon coating is an economic and feasible technique to improve the apparent conductivity of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , and is helpful to restrict the growth of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  particles to some degree during the sintering process [22–29]. The smaller particles can shorten the diffusion length for both electrons and lithium-ions, and also increase the effective interface area for enhancing electrode kinetics. Simultaneously, surface coating with other oxides such as  $\text{SiO}_2$  [30] and  $\text{MgO}$  [31] et al. can enhance the structural stability of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  electrode. After modified through the above approaches, the as-synthesized samples exhibit excellent high-rate performance as well as long cyclability.

In recent years, conductive polymers such as polypyrrole [32], polythiophene [33], poly(3,4-ethylenedioxythiophene) [34,35], polyaniline [36–45], have been used as attractive coating agents for electrode surfaces, because it not only improves the electrical conductivity but also mechanical flexibility, which improves the

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electrode stability. Among the above conductive polymers, the polyaniline possesses high conductivity, fast electrochemical switching and environmental stability [46–49]. Up to the present, many materials including  $\text{LiFePO}_4$  [37],  $\text{Li}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Fe}_{1/3})\text{O}_2$  [36],  $\text{LiV}_3\text{O}_8$  [39,41],  $\text{V}_2\text{O}_5$  [40],  $\text{Si}$  [38],  $\text{TiO}_2$  [42] and  $\text{NiO}$  [43], have been modified via using polyaniline as coating material, which exhibit satisfactory electrochemical performance. For example, Chen et al. [37] employed a self-assembly process with APS (ammonium persulfate) as oxidizer for aniline polymerization to prepare polyaniline-modified  $\text{LiFePO}_4/\text{C}$ , and they found that the as-prepared composite exhibited enhanced rate capability and cyclability which could be ascribed to the conductive polymer coating. In another study, Gao et al. [39] fabricated conducting polyaniline-coated  $\text{LiV}_3\text{O}_8$  nanorods by a simple chemical method, which achieved a discharge capacity of  $204 \text{ mAhg}^{-1}$  after 100 cycles and had a better rate capability. Obviously, these results prove that improved rate capability and cyclability can be achieved when electrode materials are supported by conductive polymer polyaniline.

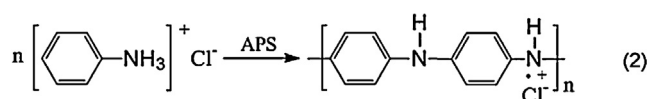
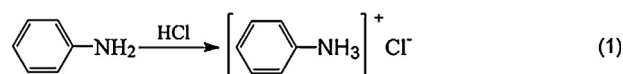
To the best of our knowledge, as a typical conductive polymer, there has been no report on polyaniline-modified  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  composite as cathode for rechargeable lithium-ion batteries. Herein, the uniform coating of the conductive polyaniline on  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  was synthesized for the first time via a microwave heating assisted sol-gel method followed by a self-assembly process and did not form any harmful gases, in contrast to carbon-coating based on decomposition of organic compounds. The  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  product with typical sizes of 200 nm can be obtained within 5 minutes via the microwave heating assisted sol-gel route. During the self-assembly process, the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  was coated by conductive polyaniline without destroying the structure. This conducting polyaniline can remarkably enhance the conductivity of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ , and the obtained polyaniline-coated  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  exhibits superior rate capability and cyclability. The structure, morphology and electrochemical activity of the pristine and polyaniline-coated  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  samples are investigated in detail. The synthesis and modification route present here offer a simple, rapid and green method to obtain high-performance cathode materials for lithium-ion batteries.

## 2. Experimental

The nanosized pristine  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  (abbreviated as LVP) was synthesized via a microwave heating assisted sol-gel method. The typical synthesis process is shown in Fig. 1 (a). Firstly, the oxalic

acid and  $\text{V}_2\text{O}_5$  in a stoichiometric ratio were dissolved in deionized water at  $70^\circ\text{C}$  under stirring to form the  $\text{VOC}_2\text{O}_4$  solution. Secondly, the mixed solution of  $\text{Li}_2\text{CO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  were slowly dropped into the  $\text{VOC}_2\text{O}_4$  solution. The mixtures were heated gently with continuous stirring to remove the excess water at  $70^\circ\text{C}$  until the gel formed. Thirdly, the obtained gel was dried in air in an oven at  $60^\circ\text{C}$  for 2 days. Then, the gel was preheated at  $350^\circ\text{C}$  in an  $\text{N}_2$  atmosphere for 20 min under microwave heating. Finally, the obtained precursor was ground in ethanol for 4 h and annealed at  $750^\circ\text{C}$  for 5 min in flowing  $\text{N}_2$  by using microwave tube furnace.

The fabrication process of polyaniline-coated  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  composite (abbreviated as PANI-LVP) is schematically illustrated in Fig. 1(b). The LVP powder was sonicated for 30 min in HCl solution and to get homogenous dispersion. The aniline monomer (abbreviated as ANI) was dissolved into the suspension and magnetically stirred for 60 min at room temperature. Then, a precooled ammonium persulfate (abbreviated as APS) aqueous solution was slowly added into the above suspension together with diluted HCl. The concentration of HCl acid is about  $0.01 \text{ mol dm}^{-3}$ . The reaction was carried out in an iced bath ( $0\text{--}5^\circ\text{C}$ ) over 6 h. The polymerization of ANI follows the well-known oxidative mechanism (1–2).



After that, the precipitate was filtered and washed several times with deionized water, ethanol and acetone successively. Finally, it was dried for 24 h in a vacuum at room temperature to get a composite product. Calculated from the weight increment, the content of PANI in the nanocomposite was about 6 wt%.

The crystal structures of LVP and PANI-LVP powders are characterized by X-ray diffraction measurement (XRD, Phillips, PW1700) equipped with  $\text{Cu K}\alpha$  radiation ( $\lambda=0.15406 \text{ nm}$ ). Scanning electron microscopy (SEM, JEOL JSM-6390) and transmission electron microscopy (TEM, JEOL JEM-200CX) were performed to observe the morphologies and microstructures of the as-synthesized powders.

The electrochemical performances of the as-synthesized samples were examined using CR2025 coin-type cells. The working electrodes were fabricated by compressing a mixture of the active

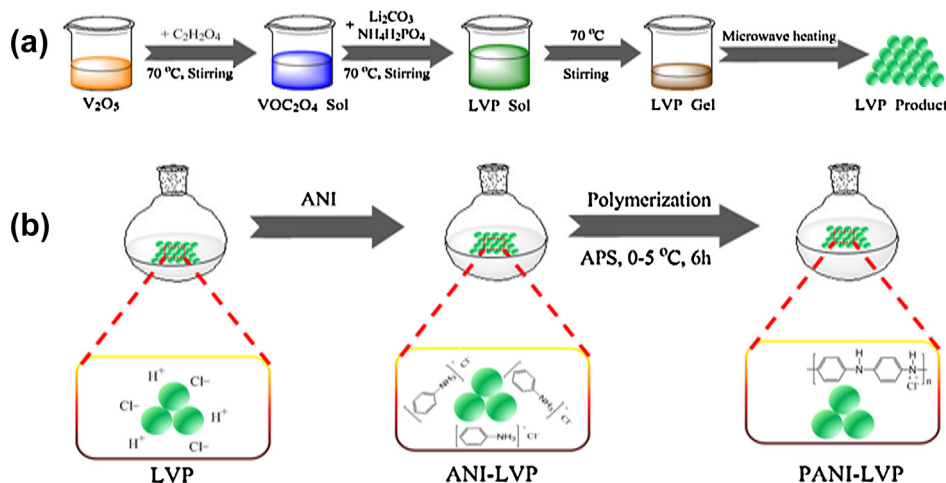


Fig. 1. Schematic illustration of the fabrication process of (a) LVP and (b) PANI-LVP samples.

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