



Synthesis and electrochemical characterization of high rate capability $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ prepared by using poly(acrylic acid) and D-(+)-glucose as carbon sources



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HIGHLIGHTS

- $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ obtained by using poly(acrylic acid) and glucose as carbon sources.
- Poly(acrylic acid) is a good dispersing agent to obtain sub-micron particles.
- High specific discharge capacity has been obtained at high C-rates.
- High cycle stability and long cycle life displayed over 1000 cycles at 100C.
- Excellent performances at low temperatures (0, -20°C) and high C-rates (30C).

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ABSTRACT

Submicron-structured $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ has been synthesized by carbon-thermal reduction method with poly(acrylic acid) and D-(+)-glucose as carbon sources. The pure monoclinic structure of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ has been confirmed by XRPD and Rietveld refinement, scanning electron microscopy, and transmission electron microscopy. The specific capacity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ as cathode has been evaluated, between 3.0 and 4.3 V vs Li^+/Li , in the two different electrolytes: 1 M solution of LiPF_6 in EC:DMC (1:1) at room temperature and in EC:DMC:DEC (1:1:1) at low temperature (0 and -20°C). Because of the submicron-size dimensions of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and of the good carbon coating, the material discharge capacities as high as 103, 98 and 81 mAh g^{-1} at 40, 60 and 100C rates, retains 93% of the initial discharge capacity after 1000 cycles at 100C. The performances even at low temperature are also good with values of the order of 84, 40, 23, 19 mAh g^{-1} at 0°C and 69, 24, 19, 15 mAh g^{-1} at -20°C at 3, 7.5, 15, 30 C-rates, respectively.

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1. Introduction

Nowadays, Li-ion batteries (LIBs) are considered very promising power sources that can move the ground transportation from the fossil fuels toward the electric vehicles (EVs). This change is needed to reduce the use of fossil fuel for the transportation as quickly as possible due to the limited nonrenewable resources and the environmental constraints [1]. Furthermore, LIBs are the first candidates as energy storage systems thanks to their high energy density and long cycle life [2]. From the first commercial cathode LiCoO_2 [3], several intercalation compounds have been developed, including layered compounds LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{etc.}$), spinel

type compounds LiM_2O_4 ($M = \text{Mn}, \text{etc.}$), and olivine compounds LiMPO_4 ($M = \text{Fe}, \text{Mn}, \text{Ni}, \text{Co}, \text{etc.}$) [4]. Several high voltage cathode materials such as silicates Li_2MSiO_4 ($M = \text{Fe}, \text{Mn}$) [5] and borates LiMBO_3 ($M = \text{Mn}, \text{Fe}, \text{Co}$) with high specific capacity have also been tested [6]. However, due to a variety of reasons, most of the attention has been focused to lithium transition metal phosphates as LiMPO_4 ($M = \text{Fe}, \text{Co}, \text{Ni}, \text{Mn}$) [7–10] and $\text{Li}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{V}, \text{Fe}$) [11,12] that are considered very interesting cathode materials for their good electrochemical and thermal stability and high operation potentials [13–15].

The energy/power density of LIBs strongly depends on the redox potential couples and on the number of lithium ions that can be exchanged [4]. To this respect, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) is a good candidate able to exchange three lithium ions at relatively high potential [11]. In LVP all the three lithium ions can be reversibly deintercalated/intercalated when operated over the potential range (3.0–4.8 V).

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The deintercalation occurs through four steps corresponding to a sequence of phase transition process in which x in $\text{Li}_x\text{V}_2(\text{PO}_4)_3$ assumes the values $x = 3.0, 2.5, 2.0, 1.0$ and 0 , leading to the final member $\text{V}_2(\text{PO}_4)_3$, where the formal valence of V is 4.5 [11,16]. The theoretical capacity is 197 mAh g^{-1} with a voltage on the fourth plateau around 4.6 V vs Li/Li^+ [17,18]. On the reverse process, three plateaus corresponding to a single phase region between $x = 0$ and $x = 2.0$, and a two phase region between $x = 2.0$ and $x = 3.0$ are present. The compound has in general a high rate capability and stability that, as reported in several studies [19,20], can be enhanced if the material is operated in the potential range $3.0\text{--}4.3 \text{ V}$. This avoids the extraction of the third Li^+ that is kinetically slow because of the reduced ionic/electronic conductivity of $\text{V}_2(\text{PO}_4)_3$ whose framework is completely empty. In this case no solid solution phase region is observed and the charge/discharge curves are characterized by three reversible plateaus associated with the two phase transition processes: $\text{Li}_3\text{V}_2(\text{-PO}_4)_3 \leftrightarrow \text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$, $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{Li}_2\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_2\text{V}_2(\text{-PO}_4)_3 \leftrightarrow \text{LiV}_2(\text{PO}_4)_3$ at potentials of about $3.6, 3.7$ and 4.1 V , respectively. The theoretical capacity of LVP in this potential range is 133 mAh g^{-1} , but the capacity retention is generally higher because adverse phenomena, such as for instance the decomposition of the electrolyte and the increase of impedance at high voltage [2,21], are minimized.

Compared with other lithium transition metal phosphates, LVP has a Li^+ diffusion coefficient (D_{Li^+}) (i.e., $10^{-9}\text{--}10^{-10} \text{ cm}^2 \text{ s}^{-1}$) [22], six order of magnitude higher than D_{Li^+} of LiFePO_4 (i.e., $10^{-14}\text{--}10^{-16} \text{ cm}^2 \text{ s}^{-1}$) [23]. Furthermore, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has a higher electronic conductivity (i.e., $10^{-7} \text{ S cm}^{-1}$) [24] than LiFePO_4 (i.e., $3.7 \cdot 10^{-9} \text{ S cm}^{-1}$) [25]. In spite of this, the electronic conductivity of LVP remains the main limiting factor of the rate performance. This problem can be addressed through three main routes: reduction of the particle dimension [26,19], doping of the structure with alien transition metal ions like Al^{3+} [27], Fe^{3+} [28], Ti–Mn and Ti–Fe [29], Ni^{2+} [30] and by carbon coating [11,31]. In this way, the rate capability and the capacity retention of this material are enhanced making it suitable for high power and high energy applications [32].

The electrochemical performances of LVP are strongly affected by the nature of the carbon source [33]. For example, the study of Rui et al. [34] compared four different carbon precursors used in a solid state reaction process: citric acid, glucose, PVDF and starch as both reducing agent and carbon source. All the composites have a comparable particle size, with a carbon content very low in the case of citric acid (1.33%) and the same order of magnitude in the range $10\text{--}13 \%$ for the other cases. The best results are those obtained using PVDF that presents a favorable morphology, with a sub-micron LVP particle size embedded in a continuous carbon network, resulting in a decreased impedance and in a discharge specific capacity of 95 mAh g^{-1} at 5C , between 3.0 and 4.3 V .

Recently there has been an increasing interest toward the use of polymeric precursors such as PVA [35] and PEG [36]. Good results have been obtained by Qiao et al. [37] by using PVA-124, with good rate performance both at high and low temperatures. On the same line this paper describes the preparation and electrochemical characterization of high pure crystalline LVP/C by using poly(acrylic acid) ($M_w = 1800$, PAA) and D-(+)-glucose as carbon sources. The choice of low molecular weight PAA was done on the basis of its peculiar physical-chemical properties. Low molecular PAA is a water-soluble polyanionic polymer at $\text{pH} \geq 7$ [38] that behaves as a strong ligand that coordinates the precursors to the polymer chains [39]. This leads to a good dispersion that reduces the growth of the LVP particles during the annealing step. At the same time the decomposition of the polymer backbone creates a fairly good conductive carbon coating at the particles surface. The D-

(+)-glucose acts as strong reducing agent and as additional source of amorphous carbon [40]. The prepared LVP/C has been characterized by XRD, scanning and transmission electron microscopy and electrochemical measurements at room and low temperature ($0, -20 \text{ }^\circ\text{C}$).

2. Experimental

2.1. Synthesis of LVP/C

LVP/C was synthesized by ball-milling and carbon-thermal reduction method as schematically depicted in Fig. 1. First lithium carbonate (7.35 mmol , 99.0%), ammonium metavanadate (9.80 mmol , 99.9%), and ammonium dihydrogen phosphate (14.70 mmol , 99.9%), with a molar ratio of (Li:V:P) of $3:2:3$ were added to 20 ml of ethanol together with PAA (0.29 mmol), and D-(+)-glucose (1.12 mmol) that act as carbon sources and reducing agents. The mixture was ball-milled with 20 agate spheres for 8 h at 350 rpm . Milling was interrupted after every 1 h for 30 min in order to avoid the heating of the solution. The solvent was evaporated under reduced atmosphere at $60 \text{ }^\circ\text{C}$ for 30 min and the remaining powder was ground with mortar and pestle for 1 h and finally annealed in two steps in Ar:H_2 atmosphere ($95:5$). The first step was performed at $350 \text{ }^\circ\text{C}$ for 5 h , with a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$; the second step was performed at $800 \text{ }^\circ\text{C}$ for 8 h , with a heating rate of $3 \text{ }^\circ\text{C min}^{-1}$. The final gray powder was ground again with mortar and pestle for 1 h . The carbon content of the final product, as evaluated from TGA analysis, was about 4.1% .

2.2. Structural and morphological characterization

The crystal structure of the as-synthesized sample was characterized by X-ray powder diffraction (XRPD) with an automated Philips Bragg-Brentano diffractometer equipped with graphite monochromator. The long-fine focus Cu tube was operated at 40 kV and 25 mA . Spectrum was recorded in the 2θ range $13\text{--}140^\circ$ with a 0.02° step and 9 s counting time. The structure was refined with the program GSAS [41]. The peaks shape was modeled with a Pseudo-Voigt function; the FWHM (Full Width Half Maximum) was refined as a function of 2θ taking into account both Gaussian and Lorentzian broadening. The refinement was carried out in the space group $P2_1/n$ and the starting atomic coordinates were the ones reported by Yin et al. [42]. The atom sites were designated fully occupied. The background was modeled with a 12-terms polynomial function. Cell parameters, scale factor, and the background

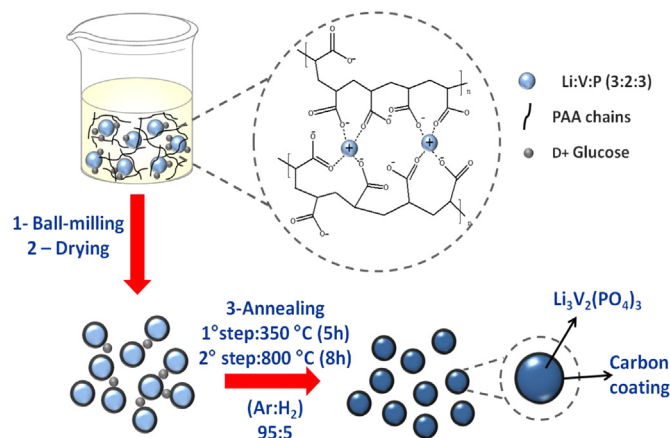


Fig. 1. Schematic diagram of the synthesis of core-shell structure cathode LVP/C.

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