



# Morphology Dependency of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Cathode Material Regarding to Rate Capability and Cycle Life in Lithium-ion Batteries



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## ABSTRACT

Transition-metal phosphates have been extensively studied as potential electrode materials for lithium-ion batteries. For this application, high rate capability and cycling performance are required. In this work, we present a one-pot solvothermal synthesis process in combination with in situ carbonization for the tailoring of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  morphologies with improvements of the electrochemical performance. These include an unstructured cluster, a needle-like microstructure, a flake-like microstructure and a hollowsphere microstructure. We demonstrate a significant impact of the particle morphology with respect to the electrochemical performance. The results obtained include, for instance, needle-like  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  showing a superior rate capability of about 72% ( $\sim 96 \text{ mAh g}^{-1}$ ) of its theoretical capacity being maintained at 30 C, whereas the flake-like  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  exhibits outstanding cycling performance with a capacity retention of 97.1% ( $\sim 112 \text{ mAh g}^{-1}$ ) of its initial capacity after 1000 cycles at 2 C. Our work demonstrates that the morphology of cathode particles defines a highly selective parameter to improve the electrochemical properties. Accordingly, strategies to selectively tailor particle morphology for a given application become feasible.

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## 1. Introduction

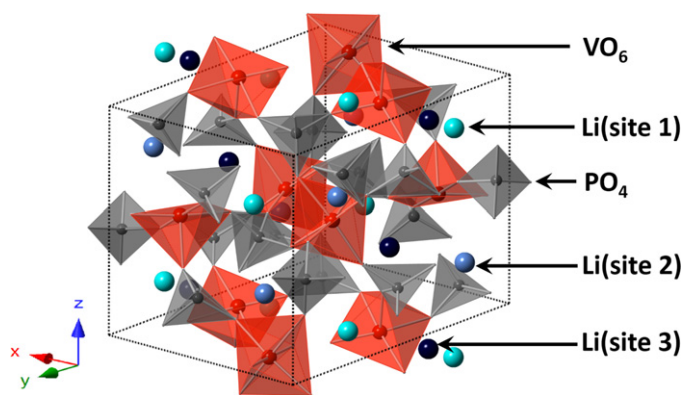
Lithium-ion batteries (LiBs) are universal devices for energy storage issues, both for mobile and stationary applications, owing to their high energy density and long cycle life.[1,2] However, concerns are now being raised regarding the suitability of LiBs for electric vehicles, electric power storage systems, smart grids, etc.[3–6] These large-scale applications require tremendously high energy densities and an excellent thermal stability, which cannot be fulfilled by today's LiBs systems. A reason therefore is the limited energy/power density of the current cathode materials, which are typically spinel- $\text{LiMn}_2\text{O}_4$ , [7–9] and layered- $\text{LiMO}_2$  ( $\text{M} = \text{Co}, \text{Mn}, \text{Ni}$ ). [10–12] New candidates of cathode materials such as  $\text{Li}_x\text{M}_y(\text{PO}_4)_3$ , [13–15]  $\text{Li}_x\text{M}_y\text{PO}_4\text{F}$ , [16,17] and  $\text{Li}_x\text{M}_y\text{SiO}_4$ , [18,19] have recently attracted much attention because more than two Li-ions per formula unit can possibly intercalate/deintercalate

into/from their host crystal structure during (dis)charge with a moderate working voltage.

On the basis of the crystal structure in the newly developed cathode materials, the use of phosphate polyanions  $(\text{PO}_4)^{3-}$  is considered as a potential alternative to oxide-based cathodes. The strong P–O bonds and the three-dimensional solid framework in  $(\text{PO}_4)^{3-}$  anions can guarantee both the dynamic and thermal stabilities required to fulfill the safety requirements in high-power applications.[18] Among these transition-metal phosphates, lithium vanadium phosphate  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  (LVP) is a promising candidate which crystallizes in two different structure types: the rhombohedral structure and the thermodynamically more stable monoclinic structure.[20,21] In the rhombohedral structure of LVP, only two of the lithium ions can be de-/intercalated in a single two-phase transition.[21–23] This leads to a lower gravimetric capacity compared to the monoclinic LVP structure, which exhibits stable phase transitions of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{V}_2(\text{PO}_4)_3$  in combination with the (de)-intercalation of Li-ions. Thus, this article focuses on the monoclinic structure of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

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**Fig. 1.** Polyhedral representation of monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

As shown in Fig. 1, the host framework  $\text{V}_2(\text{PO}_4)_3$  of monoclinic LVP forms a three dimensional network of octahedrally coordinated metal ions and tetrahedrally coordinated phosphates sharing oxygen vertices. The guest Li-ions (denoted as site 1, site 2 and site 3) are mobile in the interstitial space. Monoclinic LVP can be operated in two electrochemical windows, 3.0–4.3 V vs.  $\text{Li}^+/\text{Li}$  and 3.0–4.8 V vs.  $\text{Li}^+/\text{Li}$ , resulting in different theoretical gravimetric capacities of  $133 \text{ mAh g}^{-1}$  and  $197 \text{ mAh g}^{-1}$ , which corresponds to intercalation of 2 Li-ions from  $\text{LiV}_2(\text{PO}_4)_3$  to  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  or the intercalation of 3 Li-ions starting from pure  $\text{V}_2(\text{PO}_4)_3$ , respectively. However, LVP has a poor electronic conductivity ( $2.4 \times 10^{-7} \text{ S cm}^{-1}$  at room temperature), which limits its rate capability and restricts its use in LiBs so far.[22] It is generally believed that small particle size,[23,24] carbon coating,[18,22–25] and aliovalent doping[26–29] is beneficial for improving the electronic conductivity. However, these strategies still remain questionable with respect to potentially occurring unwanted side effects. For instance, the reduction of the particle size can significantly shorten the diffusion distance, enabling a fast lithium ion/electron transfer in LVP, whereas the low volume density of nanosized cathode materials can also decrease the electrochemical performance. Carbon coating is a traditional way to improve the electronic conductivity of electrode active materials, but the carbon amount and homogeneity of carbon surface need to be considered and controlled carefully. Moreover, a thicker carbon layer may hinder  $\text{Li}^+$  diffusion. Although the conductivity can be increased in some degree by aliovalent doping, introducing guest atoms into the crystal lattice of LVP may also be deleterious.[26–29]

One efficient way to solve the conductivity problem is the controlled synthesis of LVP/C composites with optimized morphology and particle size together with carbon surface modification. Moreover, the solvothermal synthesis route offers additional flexibility in controlling morphology, grain size, and in-situ carbon coating and thus has been used for synthesizing transition metal phosphates like  $\text{LiFePO}_4$  and  $\text{LiTi}_2(\text{PO}_4)_3$ . [17,30–32] However, there are few reports on the solvothermal synthesis of LVP, and applying the method for the tuning of particle morphologies remained a challenge.[22,33,34]

In this work, we introduce an effective and direct solvothermal route in combination with annealing process for LVP synthesizing with uniform carbon coating. More importantly, different morphologies of LVP/C, including small unstructured clusters, needle-like microstructure, flake-like microstructure and hollow sphere microstructure, can be deliberately produced by our method. The formation mechanism of LVP/C with different morphologies and the influence of LVP/C morphologies on the electrochemical performance are being elucidated in detail.

## 2. Experimental section

### 2.1. Synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ powders

All chemical reagents were purchased from Sigma-Aldrich and were used as received. For the preparation of the precursor solution for the solvothermal reaction, 0.05 mol ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ,  $\geq 99.0\%$ ) and oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ,  $\geq 99.0\%$ ) in a stoichiometric ratio of 1:3 were first dissolved in a mixture of deionized water and ethanol (4:1 *vol/vol*) and afterwards magnetically stirred at  $50^\circ\text{C}$  for 12 h until a dark blue solution was formed. Stoichiometric amounts of lithium acetate dehydrate ( $\text{LiCOOCH}_3 \cdot 2\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ) and ammonium dihydrogenphosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\geq 99.999\%$ ) were dissolved in the water and ethanol mixture solution, separately, and then added to the dark blue solution slowly under continuous stirring. 3 wt% of one of the surfactants, hexadecyltrimethylammonium bromide (CTAB,  $\geq 99\%$ ), polyoxyethylenesorbitan monolaurate (TWEEN<sup>®</sup> 20, Mw  $\sim 1228$ ) or a triblock copolymer Pluronic<sup>®</sup> P123 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), Mw  $\sim 5800$ ) were then dissolved in the prepared solution. The solution was flushed with argon for 30 minutes and immediately used for the solvothermal process afterwards. As a comparison, the blank precursor without surfactant was also prepared and applied to the solvothermal reaction.

For the solvothermal method, a commercial high-pressure reactor BR-300 with Teflon liner was used (Berghof GmbH, Germany). The as-prepared solution was transferred into a 500 ml vessel with Teflon lining. The filling ratio of the solvothermal reactor for all the reactions was set to 70%, in order to have a similar self-generated pressure during reaction for all the samples. The initial pressure was set to 50 bar by filling argon into the reactor vessel before the reaction was started, while the stirring speed was set to 400 rpm during the whole reaction process. The reaction temperature was kept at  $80^\circ\text{C}$  for 3 h, to fully mix the dissolved raw materials. Afterwards, the temperature was subsequently increased to  $120^\circ\text{C}$  and kept for 24 h then heated to  $180^\circ\text{C}$  and held for another day. The maximum pressure of all the reactions was detected by the reactor to be around 120 bar. After the reaction, the system was allowed to cool to room temperature freely. A stable wet Li-V-P-O-C powder precursor was obtained by centrifugation. Importantly, the carbon amounts of the Li-V-P-O-C powder precursors obtained after the solvothermal reaction were different for different surfactants in the solvothermal reaction. During the solvothermal reaction, the oxalic acid was used as a chelating agent and during the annealing process as a carbon source.  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  powders were obtained by annealing of the Li-V-P-O-C powder precursor at  $850^\circ\text{C}$  under  $\text{N}_2$  gas flow in a tube furnace for 8 h. The gas flow rate was optimized in order to obtain the same thickness of the carbon coating for all morphologies.

### 2.2. Details of instrumental analysis

The crystallinity and phase analysis was carried out using powder X-ray diffraction (XRD) measurements between  $10^\circ$  and  $70^\circ$  in Bragg-Brentano-geometry with an EMPYREAN (Panalytical, Netherlands) X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation operating at 40 kV, 40 mA. Scanning electron microscopy (SEM) images were taken using a Quanta FEG 650 (FEI, USA) environmental scanning electron microscope operated at a voltage of 20 kV. Thermogravimetric analysis (TGA) was performed on a NETZSCH TGA/STA-QMS 403D thermoanalyzer (Germany) from room temperature to  $800^\circ\text{C}$  with a heating rate of  $3 \text{ K min}^{-1}$  under  $\text{O}_2$  flow. The specific surface area was determined in Brunauer–Emmet–Teller (BET) measurements by  $\text{N}_2$  adsorption.

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