Structure Tracking Aided Design and Synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Nanocrystals as High-Power Cathodes for Lithium Ion Batteries

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ABSTRACT

Preparing new electrode materials with synthetic control of phases and electrochemical properties is desirable for battery applications but hardly achievable without knowing how the synthesis reaction proceeds. Herein, we report on structure tracking-aided design and synthesis of single-crystalline $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) nanoparticles with extremely high rate capability. A comprehensive investigation was made to the local structural orderings of the involved phases and their evolution towards forming LVP phase using *in-situ/ex-situ* synchrotron X-ray and electron-beam diffraction, spectroscopy and imaging techniques. The results shed light on the thermodynamics and kinetics of synthesis reactions, and enabled the design of a cost-efficient synthesis protocol for making nanocrystalline LVP, wherein solvothermal treatment is a crucial step leading to an amorphous intermediate with local structural ordering resembling that of LVP, which, upon calcination at moderate temperatures, rapidly transforms into the desired LVP phase. The obtained LVP particles are about 50 nm, coated with thin layer of amorphous carbon, and featured with excellent cycling stability and rate capability — 95% capacity retention after 200 cycles, and 66% theoretical capacity even at high rate of 10 C. The structure tracking based method we developed in this work offers a new way of designing battery electrodes with synthetic control of material phases and properties.

INTRODUCTION

Lithium-ion batteries (LIBs) are the preferred energy-storage devices for portable electronics and now are becoming one of the main power sources for electric vehicles and grids¹. There has been considerable research interest in developing new electrode materials of high energy density and power density for use in next-generation batteries. Polyanion-type cathodes are of particular interest given the open while stable framework, as well as high voltage induced by phosphate groups and the possibility of accessing multiple redox states of transition metals particularly when vanadium is used (eventually enabling the high energy density). In addition to the traditional olivine-based metal phosphates (*i.e.*, LiMPO_4 ; $\text{M}=\text{Fe}, \text{Mn}$), lithium vanadium phosphate, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP), has emerged as a promising cathode material due to its abundance, high thermal-stability, and capability of delivering high capacity at high working potentials ($\sim 4\text{V}$)²⁻⁵. Between the two polymorphs of LVP, *i.e.*, rhombohedral and monoclinic phases^{6,7}, the latter is thermodynamically stable and preferable for the use as high-energy and high-power cathodes owing to its three-dimensional open framework for fast lithium ion diffusion and accommodating up to 3 Li^+ (leading to a capacity of 197 mAh.g^{-1})⁸.

A variety of methods were developed to obtain monoclinic LVP, including solid-state reaction⁹, sol gel⁴, microwave-assisted techniques¹⁰, hydrothermal/solvothermal or sol-gel assisted¹¹⁻¹³, ionothermal synthesis¹⁴ and glass-ceramic processing¹⁵. The solvothermal route is environmentally benign and offers additional flexibility in controlling morphology, grain size, and *in-situ* carbon coating, and thus has been widely used for synthesizing LiFePO_4 ¹⁶. However, there are few report on using solvothermal approach for synthesizing LVP¹¹⁻¹³, and synthetic control of the morphology remains a challenge largely due to the lack of understanding of the synthesis process. In this study, we explored solvothermal approaches for making monoclinic

LVP, starting with investigating the synthesis reactions in a solvothermal environment. A combination of X-ray absorption spectroscopy (both near-edge structure (XANES) and extended fine structure (EXAFS)) of the V K-edge, *in-situ* XRD, along with electron diffraction and high-resolution transmission electron microscopy (TEM) were applied to identify the local structural and chemical ordering in the involved phases. The results from the investigation shed light on the kinetics and thermodynamics of synthesis reactions, indicating that solvothermal treatment is a crucial step leading to a VPO₄-like amorphous intermediate, which, upon calcination, transforms into the desired LVP phase. Through structure tracking to study the whole synthesis process, we were able to design a solvothermal-assisted protocol to synthesize single-crystalline LVP nanoparticles that exhibit excellent rate capability and cycling stability.

EXPERIMENTAL

Structure tracking using Synchrotron and TEM techniques. The XRD measurements were performed at Beamline X14A, National Synchrotron Light Source, Brookhaven National Lab with a wavelength of 0.7780 Å. Rietveld refinements of the X-ray powder diffraction patterns were carried out using the GSAS/EXPGUI package. X ray absorption spectroscopy (XAS) for the V K-edge was collected at Beamline X18A, National Synchrotron Light Source, Brookhaven National Laboratory. Energy calibration was established with the simultaneous absorption measurements on 5 micron meter thick V metal foil inserted between the second and third ionization cell. TEM measurements were performed on a JEOL 2100F operated at 200 kV. The powder sample dispersed on a TEM grid (with an amorphous carbon- membrane support) were loaded on to a TEM holder and then transferred to the TEM column. TEM images and electron diffraction patterns were recorded by a charge-coupled device (CCD, Gatan).

In-situ XRD measurements. Similar to our previous report²³, the intermediate phase after solvothermal treatment was placed in a quartz tube (about 0.7 mm inner diameter) filling about 2 mm of the tube. A small amount of quartz wool was inserted into the tube to keep the powders in place. The quartz tube was sealed with a one-end capped Swagelok elbow under high pure Ar atmosphere in the glove box. The XRD patterns were taken by 2 °/step (2 theta from 4 °-50 °, about 6 minutes per pattern) with a heating rate 3 °C/ minute for the reactor. When the temperature reaches the point at which a pure LVP phase was obtained, the sample was held at that temperature, and the growth of LVP for a prolonged time was examined.

Synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. 0.015 mol LiH_2PO_4 and 0.01mol V_2O_5 were added into 96 mL ethylene glycol under magnetic stirring at 80 °C; subsequently, 1.7 g sucrose was added into the yellow suspension. After vigorous stirring for 30 minutes, the blue solution was transferred into a Teflon vessel (120 mL) in a stainless steel autoclave. The autoclave was then purged with nitrogen, sealed, and placed in an oven at a constant temperature of 230 °C for 10 hours. After the material was cooled to room temperature, the resulting brown suspension was stirred continuously to evaporate the solvent. Finally, the mixture was annealed in an inert atmosphere at 730 °C for 10 hours. VPO_4 -reference was obtained by ball milling the precursor V_2O_5 , $\text{NH}_4\text{H}_2\text{PO}_4$, Li_2CO_3 , and then this mixture was calcinated at 730 °C for 10 hours under H_2/Ar atmosphere.

Electrochemical measurements. The electrodes were prepared by casting slurry of 70 wt.% active materials, 20 wt.% Super-P carbon, and 10wt.% kynar binder on the Al foil. A Li foil was used as the counter electrodes. The electrolyte consisted of 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). Then, 2025-type coin

cells were assembled in an argon-filled glove box and the galvanostatic charge-discharge performance was measured at different current rates using a VMP multi-potentiostat.

RESULTS AND DISCUSSION

In the first step, the precursors LiH_2PO_4 , V_2O_5 and sucrose in an ethylene glycol solution were heated in a sealed autoclave to high temperatures (typically 230 °C) for 10 hours, and then naturally cooled down to room temperature. A brown suspension was obtained, and subsequently dried by continuously stirring (with solvent being evaporated). The product (hereon denoted as the intermediate phase) was a mixture of amorphous phases and Li_3PO_4 (JCPDS 15-0760) from precursors, identified from the tiny peaks in the XRD pattern shown in Figure 1a. TEM images (bright-field mode) and selected-area electron diffraction (SAED) patterns were also collected from local areas of the powders extracted from the intermediate product. The ill-defined particle morphology and presence of broadened diffusive rings in the SAED patterns (Figure 1b) further confirmed the amorphous nature of the intermediate.

The valence state of vanadium and short-range ordering in the intermediate phase were also examined *via* X-ray absorption spectroscopy. The oxidation state of vanadium was determined by X-ray absorption near-edge spectroscopy (XANES) of V K-edge (with V_2O_5 and V_2O_3 as references; Figure 1c). Overall, the energy position of the V K-edge from the intermediate phase is similar to that of V_2O_3 , suggesting the reduction of the precursor V_2O_5 to a valence state close to 3+ after solvothermal treatment (with about a 3 eV chemical shift to a lower energy; indicated by the dot lines). Considering that amorphous vanadium phosphorus oxide, VPO_4 was produced in a hydrothermal treatment¹⁷, and was ever used as an intermediate for the synthesis of $\text{LiVPO}_4\text{F}^{18}$ and $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2^{19}$, we speculate that the amorphous component of the intermediate (after solvothermal treatment) is possibly a VPO_4 -like phase. Thus, we synthesized amorphous

VPO₄ powders using solid-state reaction procedure as reported in the literature¹⁴. The XRD pattern was obtained from the resulting powder, showing that it is indeed amorphous (Figure S1). From the XAS measurements shown in Figure 1c, the XANES spectrum of the intermediate has a similar edge position and shape as that of the synthesized VPO₄. Also shown in Figure 1c, the XANES of the final product LVP resembles those of the intermediate and VPO₄ except for a prominent pre-edge peak around 5470 eV. The pre-edge peak originates from the dipole-forbidden transitions from 1s core levels to 3d states, and is an indication of the distorted VO₆ octahedra in the LVP structure²⁰. Figure 1d is a magnitude plot of the Fourier transformation of the extended X-ray absorption fine structure (FT-EXAFS) spectra for the V K-edge (k^3 -weighted in k -space) of the intermediate phase, in comparison to that of the reference materials, including V₂O₃, V₂O₅, synthesized-VPO₄, and the final product LVP. In the FT-EXAFS of the LVP, there were two dominant peaks. The peak at approximately 1.5 Å is assigned to the single scattering-path from V to the closest oxygen atoms (the V-O bond in VO₆ octahedra), while the peak at $R = \sim 3.0$ Å is attributed to the V-V bonding between two edge-sharing V-O₆ octahedra. It should be noted that the FT-EXAFS spectra are not phase-corrected and the actual bond lengths are longer. The FT-EXAFS of the intermediate phase also shows resemblance to that of LVP and synthesized VPO₄, with the 1st peak being present at about 1.5 Å (V-O bond in V-O₆ octahedra) (Figure 1d). The large-distance bonding (*i.e.*, V-V) is not shown in the FT-EXAFS of the intermediate and VPO₄ due to their amorphous nature. Therefore, the XAS spectra from these amorphous intermediates confirm that it assumes a similar valence state and local structure to that of VPO₄, as well as to the final LVP phase. According to the results from XRD, TEM and XAS analysis, the intermediate is a Li-V-P-O composite containing a mixture of Li₃PO₄, the

amorphous VPO₄-like phase, and carbon (derived from sucrose) as well. The chemical reaction during solvothermal synthesis at temperatures up to 230 °C presumably follows the route:

Additional attempts were made to synthesize the crystalline LVP phase at even higher temperatures (up to 260 °C), but only amorphous intermediates were obtained (along with the residual Li₃PO₄). So it appears that calcination is needed to obtain the final LVP phase (as in Fig. 1a). In order to obtain details of the structural evolution during calcination, *in-situ* time-resolved XRD was performed during heating. The diffraction patterns were recorded every 14 minutes. Representative time-resolved XRD patterns were given in Figure 2a (see also Figure S2 for the index to some of the main peaks). In the early stage of heating (within the first ~3.5 hours), there was no visible change in the Bragg patterns until 630 °C, and thereafter the peaks associated with the Li₃PO₄ precursor began to disappear, and concomitant growth of new peaks associated with LVP phase became apparent. The diffraction peaks, being broad and weak due to nanocrystalline nature, became sharper and stronger with further heating (a trend more obvious in the expanded view in the inset). When the temperature reached 730 °C, pure phase of LVP was obtained, and no obvious change in the diffraction pattern was observed with further constant-temperature heating (730 °C).

In order to track the nucleation and growth processes of the LVP phase, we made refinements on individual XRD patterns, thereby obtaining the width and intensity of the diffraction peaks, from which the particle size and the concentration of the LVP phase as a function of time and temperature were extracted, as shown in Figure 2b. In stage I (below 630 °C), no LVP was formed. With further increase of temperature to about 666 °C (in Stage II), LVP

particles, of about 30 nm, was formed rapidly, within the time needed to complete a single scan (14 minutes or less) although the concentration of LVP was still low. Interestingly, there was little change in the particle size as the temperature rose from 666 °C to 730 °C; while the concentration increased steadily, reaching the maximum value within one hour. Since there is no growth of the particle size, the rapid increase in the concentration of the LVP must be due to the multiplication of the LVP nucleus at the current stage. During the prolonged heating in Stage III at 730 °C (> 5 hours), LVP concentration stayed almost constant and particle size became slightly larger, to about 40 nm, indicating that the growth of the LVP particles was largely hindered, most likely by the carbon coating on their surface since carbon was highly mixed with the V-containing phases in the intermediate.

As discussed above, solvothermal treatment is an essential step towards forming the VPO_4 -like intermediate with a similar local ordering as LVP (Figure 1), both having VO_6 octahedra and PO_4 tetrahedra as building blocks (illustrated in Figure 3). As demonstrated in an earlier work²¹, the similarity in short-range order between the glassy precursor and the crystalline product promotes a bulk nucleation in silicate glasses. So we believe the local structural similarity between the VPO_4 -like intermediate and LVP plays a critical role in the fast nucleation and growth of LVP nanocrystals.

In a recent report,¹⁵ the glass-ceramic processing method was applied for fast synthesis of crystalline LVP. Contrary to their high temperature (1000 °C) melting step to generate the glassy intermediate, our solvothermal treatment at mild temperature (230 °C) is much more cost-efficient. And importantly, the solvothermal step not only leads to the amorphous intermediate with desirable local ordering, but also implements the reduction of the vanadium cations and the fine mixture of carbon, which are critical for producing the carbon-coated LVP nanocrystals.

Another important aspect in producing pure LVP is the processing of the intermediate during which the evaporation of the solvent after the solvothermal reaction was found to be critical in retaining stoichiometry. If only the solid powders were collected using filter papers after solvothermal treatment, impurities of V_2O_3 were found in the final product, likely due to the loss of the PO_4 -containing components. The chemical reaction taking place in the calcination process presumably follows the route (2nd step shown in Figure 3):

Such a solvothermal-assisted synthetic process in producing LVP, namely solvothermal treatment followed with calcination, apparently differs from the one-pot solvothermal synthesis of the $LiFePO_4$ analogues²⁰. However, our latest *in-situ* investigation of the solvothermal synthesis of $LiFePO_4$, shows that a two-step, interface-coupled dissolution-reprecipitation process actually took place,²¹ and the intermediate phase possesses a long-range ordering, with high resemblance to that of the final $LiFePO_4$. But during synthesis of LVP, the 1st step of solvothermal treatment only leads to an amorphous intermediate stage with short-range ordering, which is presumably due to the insufficiency of energy to activate the precipitation of LVP under solvothermal conditions (below 260 °C in our experiment). By combining the XAS, *in-situ* XRD and TEM examinations of the structure of all the involved phases and their re-organization from the precursor (LiH_2PO_4 , V_2O_5), to the intermediate (VPO_4 , Li_3PO_4), and to the final phase ($Li_3V_2(PO_4)_3$), we can now summarize the whole reaction process, as illustrated in Figure 3.

Using the developed solvothermal-assisted synthetic protocol, *i.e.*, solvothermal treatment at 230 °C followed by calcination at 730 °C, we obtained phase-pure LVP powders with a monoclinic structure (Space group P21/n; cell parameters $a=8.6088(1)$ Å, $b=8.5985(1)$ Å,

$c=12.0488(2)$ Å, $\beta=90.546(1)^\circ$) (Figure 4a). The crystallographic information and reliability from the refinements are given in the supporting information, Table S1. The particle size is highly uniform, about 50 nm in diameter, as examined by scanning electron microscopy (SEM; Figure 4b, c). These particles are single-crystalline and coated with amorphous carbon (less than 5 nm thick) according to high-resolution TEM image and Fast Fourier transform (Figure 4d). About 6.5 wt% of carbon in the powder was measured using thermogravimetric analyzer (TGA), by heating the materials in the air from RT to 600 °C (Figure 4e). This supports the observations from *in-situ* XRD measurements, indicating that the presence of carbon that actually hindered the agglomeration and growth of the particles during calcinations, eventually leading to uniform size distribution of the LVP particles.

The as-obtained carbon-coated LVP particles were further assessed as cathodes in a half cell (with Li as counter electrodes). Figure 5a shows their cyclic voltammetry behavior in different voltage windows (3.0 - 4.3 V, and 3.0 - 4.8 V) at a scan rate of 0.1 mV.s⁻¹. During the charge process (lithium extraction) between 3.0 - 4.3 V, there are three obvious electrochemical signatures around 3.63 V, 3.71 V, 4.13 V, which correspond to a series of phase transitions. Correspondingly, we observed three cathodic peaks at 4.0 V, 3.62 V, and 3.53 V during discharge process (lithium re-insertion). Despite the similarity of overall cycling behaviors to earlier reports^{5, 19}, the CV curves show striking features of low polarization and sharp anodic- and cathodic peaks, indicating the high electrochemical activity and fast reaction kinetics of the LVP electrodes. Nevertheless, the current peak at 4.58 V corresponding to extraction of the third lithium ($V^{4+} \rightarrow V^{5+}$) has a boarder shape with lower intensities, being consistent with previous reports^{8, 24}. Nazar *et al.*²⁴ ascribed this to the lower electronic/ionic conductivity of $V_2(PO_4)_3$ and thus, it has slow reaction kinetics and low electrochemical activity. Interestingly, during the

lithium reinsertion, in contrast to the lower voltage features, a solid solution behavior is initially observed with a characteristic S-shape curve. Subsequently, two electrochemical plateaus were observed at 3.63 V and 3.55 V, respectively, and should be related to the reinsertion of the last lithium. This characteristic can be attributed to Li^+ disordering with the lack of V^{n+} ordering till sufficient Li^+ repopulation and the associating vanadium reduction takes place⁵.

The capacity-retention performances during 200 cycles are presented in Figure 5b. With full (de)lithiation between 3.0 - 4.8 V, it shows an initial charge-capacity of $186 \text{ mAh}\cdot\text{g}^{-1}$ (close to theoretical value, $197 \text{ mAh}\cdot\text{g}^{-1}$) but there is a gradual fading of capacity during elongated cycling, to $105 \text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles. This decline may reflect structural degradation during phase transition between $\text{Li}_{1.0}\text{V}_2(\text{PO}_4)_3$ and $\text{V}_2(\text{PO}_4)_3$ ⁵, and the instability of the solid electrolyte interphase (SEI) formed above 4.5 V versus Li^+/Li ^{3,25}. Moreover, this could also be ascribed to formation of dendrite-like and granular lithium at the counter electrode lithium metal side²⁶, which leads to inhomogeneous ionic and electronic conductivity in the cell.

When this operation voltage window is restricted to 3.0 - 4.3 V (with only 2 lithium being cycled) at the same current rate ($19.7 \text{ mA}\cdot\text{g}^{-1}$), the cycling performance significantly improved with an initial discharge capacity of $120 \text{ mAh}\cdot\text{g}^{-1}$, with only about 5% capacity decay after 200 cycles (to $114 \text{ mAh}\cdot\text{g}^{-1}$). The rate performance was also tested *via* galvanostatic cycling at a current density of $1.33 \text{ A}\cdot\text{g}^{-1}$ (equivalent to 10 C) (Figure 5c) and different charge-discharge current rates (Figure S3). It demonstrates negligible capacity decay, from initial $90 \text{ mAh}\cdot\text{g}^{-1}$ to $86 \text{ mAh}\cdot\text{g}^{-1}$ after 200 cycles. Such a rate performance of this carbon-coated LVP is remarkable, and outperforms the micron-size C/LVP obtained *via* conventional solid-state reactions, in which a capacity of $80 \text{ mAh}\cdot\text{g}^{-1}$ at 1 C, and capacity of $10 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C was obtained (Figure S4a-c). On the other hand, the nanosized LVP has a much lower polarization in the charge-discharge

curves even at such a high rate (inset of Figure 5c), which may be due to the small charge-transfer resistance (Figure S4d).

The rate capability is among the best-performed LVP cathodes as reported in the literature^{4, 9-15, 22}. For example, the capacity at 10 C is 2-3 times higher than that of the carbon-coated LVP synthesized *via* hydrothermal-assisted solid-state reactions (as being recently reported by Sun *et al.*)¹¹, where a discharge capacity of only 30 mAh·g⁻¹ at 10 C was demonstrated. Such outstanding electrochemical performance may not be explained solely by enhanced electronic conductivity (with carbon coating), but also by the nano-size effect, particularly on minimizing the lithium transport route. We also applied CV techniques to estimate the lithium diffusion in the LVP electrodes (Figure 5d). The variation of peak current (I_p) is linear with the square root of the scanning rate ($v^{1/2}$), as shown in Figure S5. The apparent chemical-diffusion coefficient of lithium is about 10^{-10} cm²·s⁻¹ as determined by Randles-Sevik equation (see details in the Supporting Information). It is one order of magnitude higher than the theoretical coefficient of lithium diffusion at room temperature (10^{-11} cm²·s⁻¹)²⁷, and 2-4 orders higher than that of traditional LiFePO₄ (10^{-14} cm²·s⁻¹)²⁸ and LiNi_{0.5}Mn_{1.5}O₄ (10^{-12} cm²·s⁻¹)), which may be explained by the three-dimensional lithium diffusion pathways, eventually leading to the high rate capacity.

CONCLUSIONS

In summary, aided by the structure tracking investigation of the synthesis reactions, we developed a solvothermal-assisted synthetic protocol for making monoclinic LVP nanocrystals, namely *via* solvothermal treatment, to obtain amorphous intermediate and subsequent calcination to get a pure LVP phase. Through X-ray absorption spectroscopy (XANES and EXAFS) and TEM imaging/diffraction studies, was the local structural ordering, with high resemblance to that of final LVP phase, identified; whilst *in-situ* XRD studies provided details of the crystal growth

during calcination, revealing, for the first time, the rapid crystallization of LVP nanocrystals at a temperature as low as 666 °C. The results from this study also suggested that one-pot synthesis of LVP in a low-temperature solvothermal environment may not be thermodynamically allowed.

The solvothermal-assisted protocol design was applied to synthesis of carbon-coated single-crystalline LVP nanoparticles, which deliver excellent cycling retention with only about 5% capacity decay after 200 cycles. Good rate capability with a discharge capacity of $86 \text{ mAh}\cdot\text{g}^{-1}$ was also obtained in the voltage window 3.0 - 4.3 V at 10 C as a result of the surface carbon coating and nanosize that ensure a low charge-transfer resistance and a high lithium diffusion coefficient of $10^{-10} \text{ cm}^2\cdot\text{s}^{-1}$.

ASSOCIATED CONTENT

Supplementary Information

Supplementary information was provided on the synthesis and XRD measurements of VPO_4 powder, rate performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ at different rates, the morphology and electrochemistry of the micron-sized $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ by solid-state reactions, diffusivity extraction from CV curves, and atomic sites of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ from refinement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Figure 1. Structure tracking of the intermediate and final products in preparing $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP). (a) X-ray diffraction patterns of the precursor (black), intermediate phase (blue; with all the peaks associated with the Li_3PO_4 phase) and final product (red), (b) bright-field TEM image and selected area electron-diffraction pattern (inset; recorded from the areas labeled by the green circle) of the intermediate phase, (c-d) XANES spectra and Fourier transformation magnitude of the EXAFS of V K-edge from intermediate (blue), final LVP (red), precursor V_2O_5 (grey), and reference compounds of VPO_4 (purple), and V_2O_3 (green). Vertical dashed lines were used to indicate the edge positions of the intermediate phase (blue), and precursor V_2O_5 (grey).

Figure 2. Real time tracking of the crystal growth of LVP during calcination by *in-situ* XRD. (a) Time-resolved XRD patterns of the intermediate during heating from RT (25 °C) to 730 °C under an Ar atmosphere, (b) evolution of the crystal size (red square) and concentration of LVP (black circle) with time obtained from refinement of the XRD patterns, showing no formation of crystalline LVP below 630 °C, and rapid growth of LVP starting at 666 °C, followed with a slowdown of the growth at 730 °C during a prolonged time of constant-temperature heating.

Figure 3. Local structural ordering during the solvothermal-assisted synthesis process, starting from (a) the precursor (V_2O_5 , LiH_2PO_4), (b) amorphous intermediate (VPO_4 -like, Li_3PO_4) to (c) final monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ crystalline phase.

Figure 4. Structural properties of the synthesized LVP nanocrystals. (a) Synchrotron XRD pattern and Rietveld refinement with observed data points (red points), calculated data (black line), Bragg positions (green bars) for as-obtained LVP ($R_{wp}=2.81\%$, $R_{exp}=1.73\%$, $R_p=2.16\%$), (b) SEM image of LVP nanoparticles, (c) size distribution obtained from diameter measurements of 100 particles, (d) high-resolution TEM image and corresponding Fourier Transform (inset) of LVP, indicating its single-crystallinity, (e) thermo-gravimetric analyzer (TGA) curve of LVP during heating in air.

Figure 5. Electrochemical properties of LVP nanocrystals. (a) Cyclic voltammetry curves (CV) in the two different voltage windows of 3.0 - 4.8 V (black) and 3.0- 4.3 V (red) at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$, (b) cycling performance in the windows of 3.0- 4.8 V (black) and 3.0 -4.3 V (red) at current rate of 0.1 C for 200 cycles, (c) cycling performance and charge-discharge curve (inset) at 10 C in the window of 3.0 -4.3 V, (d) evolution of the CV curves of LVP as a function of scan rates (from 0.1 to $10 \text{ mV}\cdot\text{s}^{-1}$).

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