



Short communication

Li₃V₂(PO₄)₃ cathode material synthesized by chemical reduction and lithiation method

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ABSTRACT

The monoclinic-type Li₃V₂(PO₄)₃ cathode material was synthesized via calcining amorphous Li₃V₂(PO₄)₃ obtained by chemical reduction and lithiation of V₂O₅ using oxalic acid as reducer and lithium carbonate as lithium source in alcohol solution. The amorphous Li₃V₂(PO₄)₃ precursor was characterized by using TG–DSC and XPS. The results showed that the V⁵⁺ was reduced to V³⁺ by oxalic acid at ambient temperature and pressure. The prepared Li₃V₂(PO₄)₃ was characterized by XRD and SEM. The results indicated the Li₃V₂(PO₄)₃ powder had good crystallinity and mesoporous morphology with an average diameter of about 30 nm. The pure Li₃V₂(PO₄)₃ exhibits a stable discharge capacity of 130.08 mAh g⁻¹ at 0.1 C (14 mA g⁻¹).

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1. Introduction

Since LiFePO₄ was proposed as cathode material for lithium-ion batteries, considerable studies have been performed to the transition metal polyanion material based on PO₄³⁻, such as LiMnPO₄, LiCoPO₄, Li₃M₂(PO₄)₃ (M = V, Fe) and LiVPO₄F because of their high capacity and thermal stability [1–8]. Among these, the monoclinic Li₃V₂(PO₄)₃ is a highly promising material proposed as a cathode for higher voltage lithium-ion batteries because it possesses high reversible capacity, high operate voltage, good ion mobility [9–11], and so on.

Usually, monoclinic Li₃V₂(PO₄)₃ materials were obtained through solid-state reaction [12–14] and sol–gel route [15,16]. In this investigation, to obtain Li₃V₂(PO₄)₃ materials, we developed a new method using Li₂CO₃, V₂O₅, NH₄H₂PO₄, and oxalic acid as reduce agent. Amorphous Li₃V₂(PO₄)₃ can be obtained by lithiation of V₂O₅ in alcohol by using oxalic acid as a novel reducer. The V⁵⁺ was reduced to V³⁺ by oxalic acid at ambient temperature and pressure. The monoclinic-type Li₃V₂(PO₄)₃ powders were easily obtained by heating amorphous Li₃V₂(PO₄)₃.

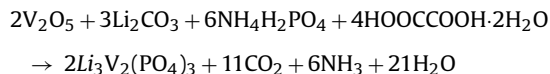
2. Experimental

2.1. Preparation of Li₃V₂(PO₄)₃

Li₃V₂(PO₄)₃ was synthesized by chemical reduction and lithiation method, the process steps were:

- (1) the stoichiometric Li₂CO₃, V₂O₅, NH₄H₂PO₄ and HOCCOOH·2H₂O (all chemical 99% purity) initially mixed by magnetic stirring together as a slurry in alcohol at room temperature for 2 h, (2) ball milling for 4 h at room temperature, (3) drying in oven at 80 °C for 24 h in the air, (4) thermal treatment in argon atmosphere.

The chemical reaction may occur as follows:



2.2. Sample characterization

The surface elements' content of Li₃V₂(PO₄)₃ powders was determined by an X-ray photoelectron spectrometer (XPS, Kratos Model XSAM800) equipped with an Mg Kα achromatic X-ray source (1235.6 eV). Structural and crystalline phase analyses of the products were taken from the powder X-ray diffraction (XRD, Rint-2000, Rigaku) using Cu Kα radiation. The particle size and morphology of the Li₃V₂(PO₄)₃ powders were measured by scanning electron

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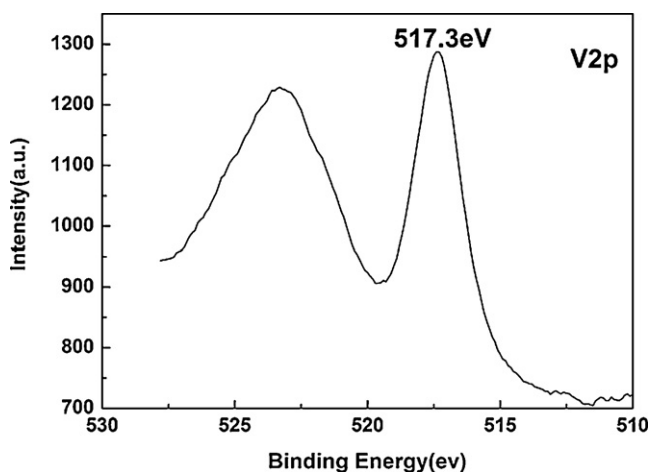


Fig. 1. XPS spectra of V2p.

microscope (JEOL, JSM-5612LV). Thermo gravimetric (TG) analysis of the precursor was measured on a SDT Q600 TG-DTA apparatus at the temperature between 25 and 1000 °C with a heating rate of 10 °C min⁻¹ under nitrogen flow.

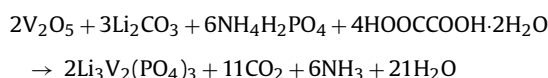
2.3. Electrochemical tests

The electrochemical characterizations were performed using CR2025 coin-type cell. Typical positive electrode loadings were in the range of 1.95–2 mg cm⁻², and an electrode diameter of 14 mm was used. For positive electrode fabrication, the prepared powders were mixed with 10% of carbon black and 10% of polyvinylidene fluoride in *N*-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries were pasted onto an aluminum current collector, and the electrode was dried at 120 °C for 12 h in the air. The test cell consisted of the positive electrode and lithium foil negative electrode separated by a porous polypropylene film, and 1 mol L⁻¹ LiPF₆ in EC, EMC and DMC (1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. Electrochemical tests were carried out using an automatic galvanostatic charge–discharge unit, NEWARE battery cycler, between 3.2 and 4.4 V versus Li/Li⁺ electrode at room temperature.

3. Results and discussion

3.1. Li₃V₂(PO₄)₃ precursor

Raw material V₂O₅, NH₄H₂PO₄, Li₂CO₃ and HOOC(2H₂O) were under ball milling at ambient temperature and pressure reacted as the follows:



The color of the raw material changed from buff to aqua as the reaction went on, which is one of the proofs for the V⁵⁺ being reduced by HOOC(2H₂O). Fig. 3 is the XRD patterns of Li₃V₂(PO₄)₃ prepared by chemical reduction and lithiation method at different temperature. No evidence of diffraction peaks in the XRD pattern of the Li₃V₂(PO₄)₃ prepared at ambient temperature and pressure can be observed in Fig. 3, indicating the synthesized Li₃V₂(PO₄)₃ is amorphous.

The XPS spectra of the amorphous Li₃V₂(PO₄)₃ precursor sample are illustrated in Fig. 1. It shows that the binding energy for the V2p is 517.3 eV, matching well with that observed in V₂O₅ (517.3 eV), it was also reported that the binding energy for the V2p in Li₃V₂(PO₄)₃

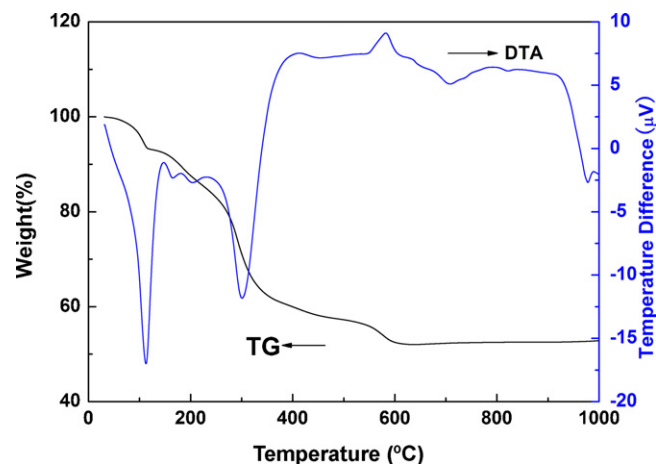


Fig. 2. TG and DTA profiles for precursor of Li₃V₂(PO₄)₃ in argon atmosphere.

was 517.2 eV [17]. Hence it can be concluded that the oxidation state of V in the amorphous Li₃V₂(PO₄)₃ precursor is V³⁺. The transfer of V⁵⁺ to V³⁺ in the material originate from the reduction effect of oxalic acid.

Fig. 2 shows TG–DSC curves of the precursor mixture of the Li₃V₂(PO₄)₃ compound. The TG curves show four weight loss main stages. The first one attributed to the release of little physical adsorbed water within the range from ambient temperature to around 110 °C can be observed in the TG curve, corresponding with an obvious endothermic peak in the DSC curve. The weak weight loss from 110 to 190 °C in the TG curve should be due to the decomposition of oxalic acid. The weight loss from 190 to 300 °C in the TG curve should be due to the release of NH₃ for NH₄H₂PO₄. The steep weight loss, which occurs between 310 and 600 °C in the TG curve can be ascribed to the formation of crystalline Li₃V₂(PO₄)₃. The reaction stopped at 600 °C. According this result, we choose 550, 650, 750 as heating temperature.

3.2. Li₃V₂(PO₄)₃

XRD patterns of Li₃V₂(PO₄)₃ material synthesized at different temperature are shown in Fig. 3. For the sample synthesized at 650, all the peaks correspond to a single phase and are indexed with monoclinic structure with space group 14(*P*2₁/*n*) which agrees well with the values reported previously [9]. But a minor impu-

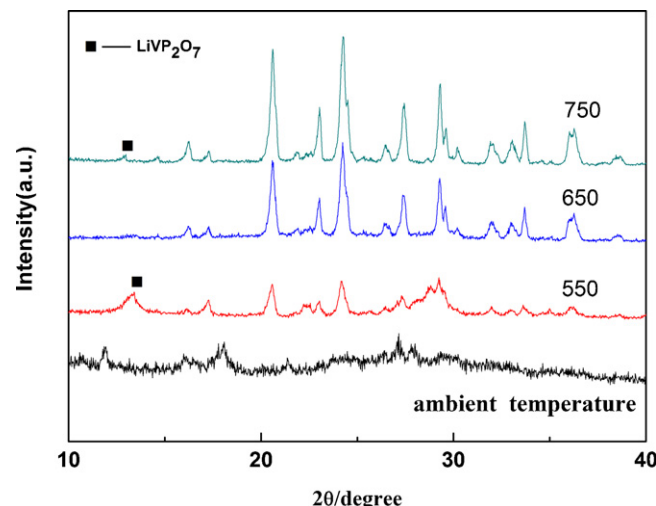


Fig. 3. XRD patterns of Li₃V₂(PO₄)₃ synthesized at different temperature.

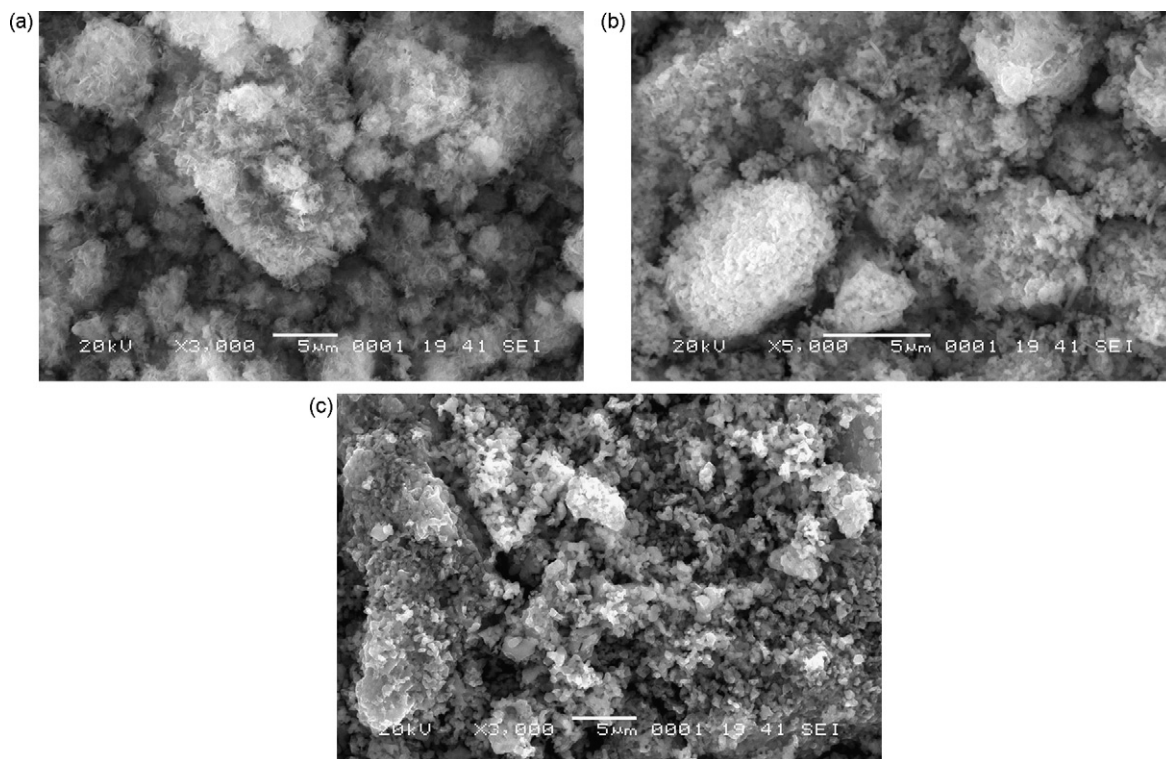


Fig. 4. SEM images of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized at different temperature (a) 550, (b) 650 and (c) 750 °C.

ity phase, which is LiVP_2O_7 appeared when the temperature is 550 and 750 °C. When sintering temperatures were increased, the peaks of the samples became sharper, indicate the crystallinity of the synthesized material was improved. The size of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ crystallites was estimated to be about 14.7, 28.5, 28.8 nm using Scherrer's relation $t = 0.9\lambda/\beta_{1/2}\cos\theta$, where λ is the X-ray wavelength, θ is the Bragg angle and $\beta_{1/2}$ is the angular full-width-half maximum of the chosen (1 2 1) reflection in radian. The grain size is much smaller than those prepared through conventional solid-state reactions [17]. The average size synthesized by solid-state reaction is always micrometer level [12,13]. Fig. 4 are the SEM images of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders prepared at different temperature. It can be seen that the primary particle sizes are nano-scale, some of them agglomerate together and forming larger mesoporous particles. The particle sizes increase when the synthesis temperature

increases, which is accordance with the data calculated by Scherrer formula.

Fig. 5a shows the first charge/discharge curves of $\text{Li}/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cells. Charge/discharge performances were measured in the voltage ranges of 3.2–4.4 V. These data were collected at 0.1 C (14.0 mA g^{-1}) for charge and discharge at room temperature. The voltage profiles exhibit three charge plateaus and the corresponding three discharge ones, which corresponds to three compositional regions of $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$, that is, $x = 0.0\text{--}0.5$, $0.5\text{--}1.0$ and $1.0\text{--}2.0$, and the theoretical capacity values for these various Li^+ ions insertion steps are 32.80, 32.80 and 65.70 mAh g^{-1} , respectively. The voltage plateau in each region implies the two-phase character of the electrochemical reaction in the corresponding stoichiometric range [13]. A highest discharge specific capacity of $130.08 \text{ mAh g}^{-1}$ at 0.1 C was obtained when the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was synthesized at 650 °C, reach-

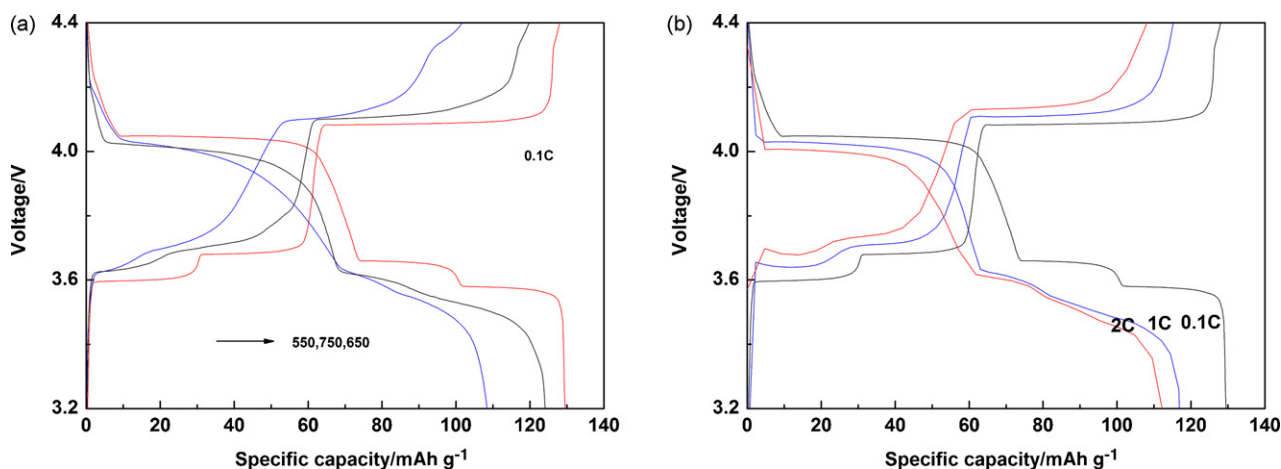


Fig. 5. (a) Charge/discharge performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized at different temperature and (b) rate performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized at 650 °C.

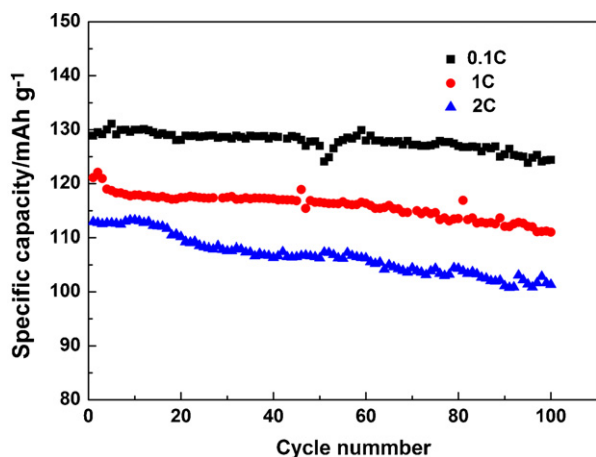


Fig. 6. Cycle performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized at 650°C .

ing 99.07% of its theoretical capacity (132 mAh g^{-1}). It delivers a capacity of 32.58, 32.50 and 65.00 mAh g^{-1} , which is corresponded to the lithium insertion as the following stoichiometric ranges: $x=0.0\text{--}0.5$, $0.5\text{--}1.0$ and $1.0\text{--}2.0$ in $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$, respectively, it reaches 99.32%, 99.08% and 98.9% of its theoretical capacity. The powders also show a good performance at higher rate, as shown in Figs. 5b and 6, the initial discharge capacity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at the rate 1 and 2 C is about 118.00 and $113.12 \text{ mAh g}^{-1}$, respectively. These results are better than Chen [18] reported.

The cycle life of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized at 650°C at different C rates to a cut off voltage between 3.2 and 4.4 V is shown in Fig. 6. The capacity retention is very good. As seen in the Fig. 6, the initial discharge capacity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at the rate 0.1, 1 and 2 C is about 130.08, 118.00 and $113.12 \text{ mAh g}^{-1}$, and the discharge capacity is about 124.43, 101.35, 89.69 mAh g^{-1} after 100 cycles. The cell retains 95.7%, 94.06% and 89.69% of its initial discharge capacity.

4. Conclusions

Nano-crystalline $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was synthesized via calcining amorphous $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ obtained by chemical reduction and lithi-

ation of V_2O_5 using oxalic acid as a novel reducer. X-ray diffraction results are indexed as monoclinic structure with space group $14(P2_1/n)$. Nano-particles are in principle easier to bring into the electrical contact between particles than micro-particles. Reducing the size of particles can improve the discharge capacity of the materials. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized at 650°C for 12 h exhibits a discharge capacity of 130.08, 118.00, $113.12 \text{ mAh g}^{-1}$ at 0.1, 1, 2 C, respectively. The discharge capacity was held to be $101.35 \text{ mAh g}^{-1}$ at 2 C rate after 100 cycles, 89.69% of its initial discharge capacity. The good electrochemical performance attribute to the nano-size and the mesoporous surface of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles synthesized by this new synthetic route.

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