



Short communication

## Novel synthesis of $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ composite cathode material by aqueous precipitation and lithiation

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### ABSTRACT

$\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  composite cathode material is synthesized by aqueous precipitation of  $\text{FeVO}_4 \cdot x\text{H}_2\text{O}$  from  $\text{Fe}(\text{NO}_3)_3$  and  $\text{NH}_4\text{VO}_3$ , following chemical reduction and lithiation with oxalic acid as the reducer and carbon source. Samples are characterized by XRD, SEM and TEM. XRD pattern of the compound synthesized at  $700^\circ\text{C}$  indicates olivine-type  $\text{LiFePO}_4$  and monoclinic  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  are co-existed. TEM image exhibits that  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  particles are encapsulated with a carbon shell 5–10 nm in thickness. The  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  compound cathode shows good electrochemical performance, and its discharge capacity is about 139.1 at 0.1 C, 135.5 at 1 C and 116  $\text{mAh g}^{-1}$  at 3 C after 30 cycles.

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## 1. Introduction

Lithium transition-metal phosphates have received wide attention recently as promising positive electrodes because of their high theoretical capacity and reversibility, good electrochemical performance and thermal stability [1–3]. It has been reported that two phosphate structure types are superior than the currently commercialized layered oxide, especially at the aspect of capacity,  $\text{LiCoO}_2$ . Exhibits  $130 \text{ mA h g}^{-1}$ , while, Olivine-type  $\text{LiFePO}_4$  exhibits a capacity close to theoretical ( $170 \text{ mA h g}^{-1}$ ) of  $150\text{--}165 \text{ mA h g}^{-1}$  [4,5], and a NASICON-related structure  $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  can exhibits a nearly theoretical capacity of  $197 \text{ mA h g}^{-1}$  [3]. However, the low electrical conductivity of  $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$  has been a serious obstacle to the development of practical cathode material [1,6].

Many efforts including metal doping [7–10], coating with the electronically conductive materials like carbon, metal, and metal oxide [5,11–13], and optimization of particles with suitable preparation procedures have been made to improve the performance of  $\text{LiFePO}_4$  and  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  cathode materials. Recently, Wang [14] prepared a series of compounds  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  through a rheological phase reaction method, using  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{FePO}_4\cdot 4\text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5$  and  $\text{HO}(\text{C}_2\text{O}_4)_n\text{H}$  as the starting material, and reported that the electronic conductivity of the  $\text{LiFePO}_4$  could be

enhanced by adding some  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ . Yang [15] used  $\text{V}_2\text{O}_5$ , iron metal,  $\text{LiNO}_3$ ,  $(\text{NH}_4)_2\text{HPO}_4$  as the starting material and synthesized  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ , and also found that the conductivity of the  $\text{LiFePO}_4$  was greatly enhanced by the introduction of  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ .

In this work, we reported a new way to synthesize  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  composite cathode material. We use  $\text{NH}_4\text{VO}_3$  and  $\text{Fe}(\text{NO}_3)_3$  as starting materials to synthesize fine precursor  $\text{FeVO}_4$ , then synthesize  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  by chemical reduction and lithiation [16,17]. We believe the  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized by this new method would show good electrochemical performance.

## 2. Experimental

$\text{FeVO}_4 \cdot x\text{H}_2\text{O}$  was prepared by a wet chemical process. An equimolar solution of  $\text{Fe}(\text{NO}_3)_3$  (99 wt.%) and  $\text{NH}_4\text{VO}_3$  (99 wt.%) was mixed under stirring and maintained at  $60^\circ\text{C}$  for 1 h. The pH value of the solution was adjusted to 4 by using ammonia water. Then a yellow precipitate spontaneously appeared and remained. Amorphous  $\text{FeVO}_4$  precursor was washed several times in de-ionized water and dried in an oven at  $60^\circ\text{C}$ . Then stoichiometric ratio of  $\text{FeVO}_4$  precursor (annealed at  $600^\circ\text{C}$  before mixing with other components),  $\text{Li}_2\text{CO}_3$  (99.9 wt.%),  $\text{NH}_4\text{H}_2\text{PO}_4$  (99 wt.%) and oxalic acid was mixed by ball milling for 4 h in alcohol, the oxalic acid is the reducer as well as carbon source. Then the resulting mixture was dried at  $\sim 60^\circ\text{C}$  and subsequently fired in argon atmosphere. Finally the  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  was obtained.

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The powder X-ray diffraction (Rint-2000, Rigaku) measurement using Cu K $\alpha$  radiation was employed to identify the crystalline phase of the synthesized materials. The samples were observed by SEM (JEOL, JSM-5600LV) and a Tecnai G12 transmission electron microscope (TEM). Elemental carbon analysis of LiFePO $_4$ /C was performed by C–S analysis equipment (Eltar, Germany). The metals content of samples was analyzed using inductively coupled plasma emission spectroscopy (ICP, IRIS intrepid XSP, Thermo Electron Corporation).

The electrochemical characterizations were performed using CR2025 coin-type cell. Typical positive electrode loadings were in the range of 2–2.5 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 $^{-1}$  LiPF $_6$  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 cyler, between 2.5 and 4.5 V versus Li/Li $^+$  electrode at room temperature.

### 3. Results and discussion

#### 3.1. FeVO $_4$ ·xH $_2$ O

The Fe/V molar ratio of the dried yellow solid at 60 °C was determined to be 0.99 by ICP, confirming the stoichiometry of iron orthovanadate species. The XRD patterns of the yellow solid dried at 60 and 600 °C are shown in Fig. 1. It can be seen that there is no evidence of diffraction peaks in Fig. 1a, indicating the synthesized material is amorphous. After been calcined at 600 °C for 12 h, the compound shows a series of diffraction peaks in its XRD pattern, as shown in Fig. 1b. The crystal structure is identified to be triclinic FeVO $_4$  structure, which is consistent with that reported by Refs. [18,19].

Fig. 2 shows the SEM images of the FeVO $_4$ ·xH $_2$ O synthesized at 60 and 600 °C. It can be seen that the particle size of the FeVO $_4$ ·xH $_2$ O synthesized at 60 °C is very small, and the particles have no obvious morphology. When the calcined temperature increased to 600 °C, fine particles can be observed, and the particle sizes are about

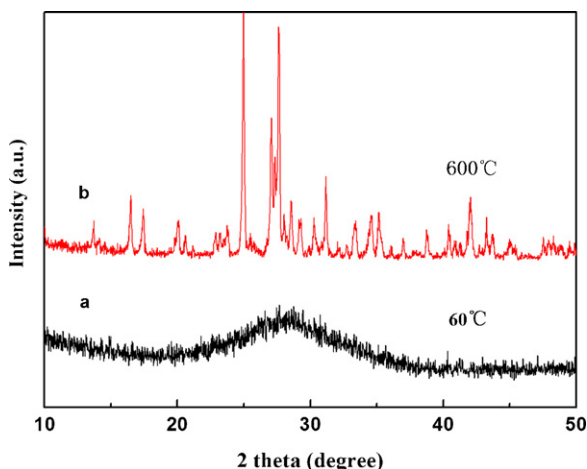


Fig. 1. XRD patterns of the FeVO $_4$ ·xH $_2$ O synthesized at different temperatures (a: 60 °C and b: 600 °C).

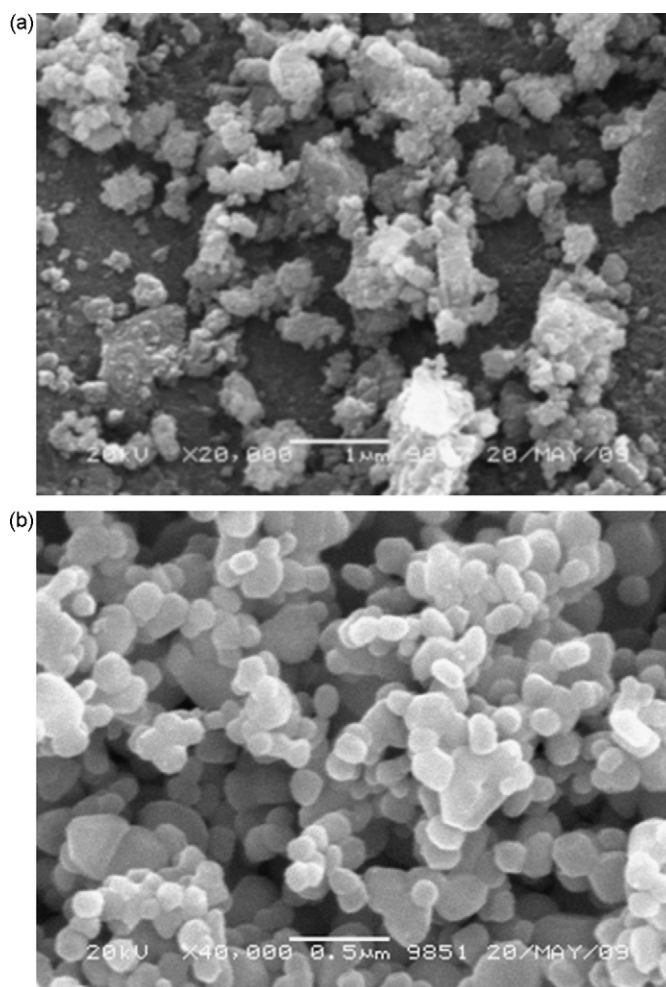


Fig. 2. SEM images of FeVO $_4$ ·xH $_2$ O calcined at different temperatures (a: 60 °C and b: 600 °C).

100 nm. Meanwhile the ball-like particles are extremely homogeneous. In the following work, we use FeVO $_4$  synthesized at 600 °C to prepare LiFePO $_4$ –Li $_3$ V $_2$ (PO $_4$ ) $_3$ .

#### 3.2. LiFePO $_4$ –Li $_3$ V $_2$ (PO $_4$ ) $_3$

LiFePO $_4$ –Li $_3$ V $_2$ (PO $_4$ ) $_3$  was prepared by chemical reduction and lithiation [16,17] between Li $_2$ CO $_3$ , FeVO $_4$ , NH $_4$ H $_2$ PO $_4$  and oxalic acid (a nominal composition of Li:Fe:V:P=2.5:1:1:2.5). The raw materials reacted as the follows:

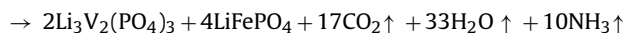


Fig. 3 is the XRD pattern of LiFePO $_4$ –Li $_3$ V $_2$ (PO $_4$ ) $_3$  synthesized at 700 °C for 12 h. The diffraction peaks of the synthesized compound are composed of both LiFePO $_4$  and Li $_3$ V $_2$ (PO $_4$ ) $_3$ , indicating the synthesized compound is a mixture of LiFePO $_4$  and Li $_3$ V $_2$ (PO $_4$ ) $_3$ , which is consistent with that reported by Refs. [14–16]. The amount of carbon in the LiFePO $_4$ –Li $_3$ V $_2$ (PO $_4$ ) $_3$ /C composite is about 0.5 wt.% determined by C–S analysis method. The SEM image of LiFePO $_4$ –Li $_3$ V $_2$ (PO $_4$ ) $_3$  synthesized at 700 °C for 12 h is shown in Fig. 4a. Fine particles can be observed. Fig. 4b is the TEM image of the LiFePO $_4$ –Li $_3$ V $_2$ (PO $_4$ ) $_3$  synthesized at 700 °C for 12 h, it can be seen that the primary particle size is about 100 nm, and coated by nano-carbon webs, forming a core–shell structure. The thickness of carbon shell is about 5–10 nm. Core–shell nanostructured

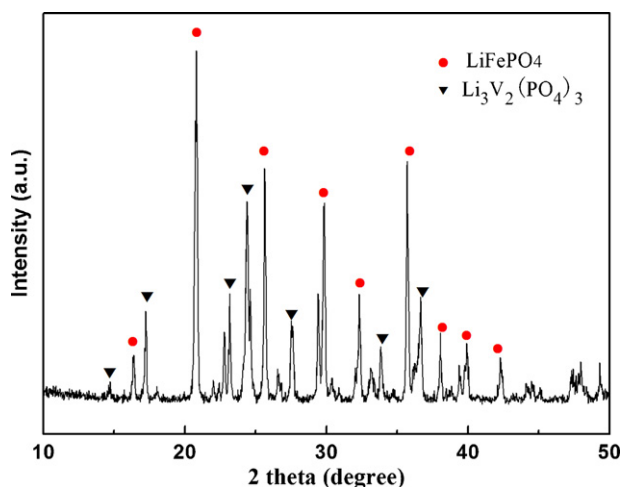


Fig. 3. XRD pattern of  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized at  $700^\circ\text{C}$  for 12 h.

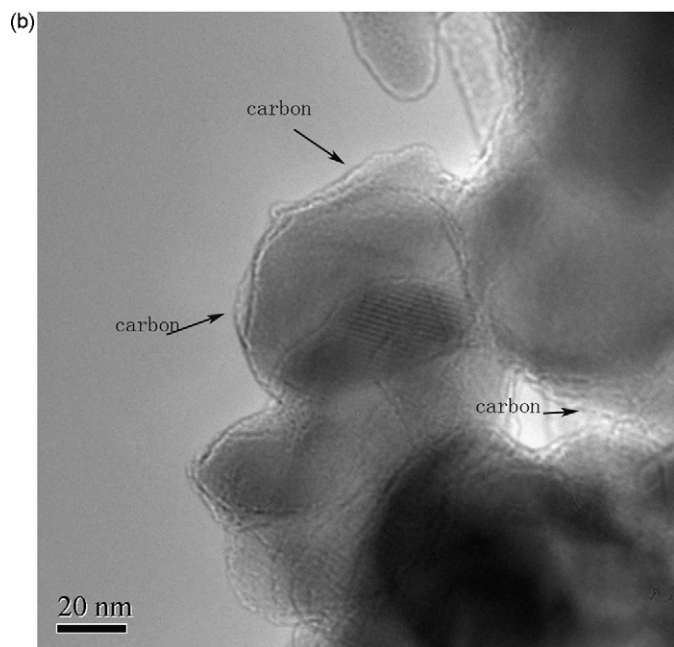
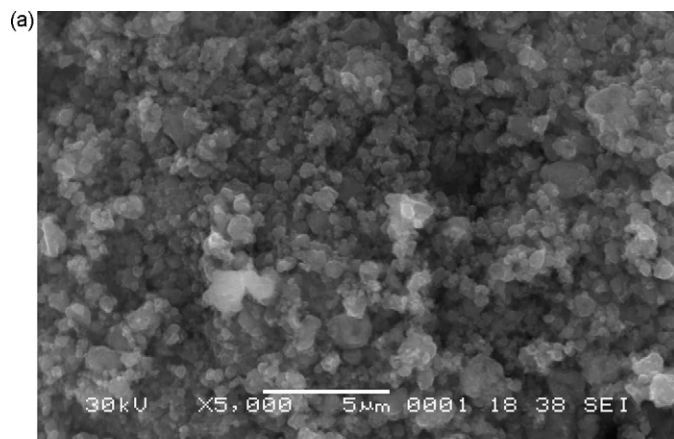


Fig. 4. (a) SEM image of  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized at  $700^\circ\text{C}$  for 12 h. (b) TEM image of  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized at  $700^\circ\text{C}$  for 12 h.

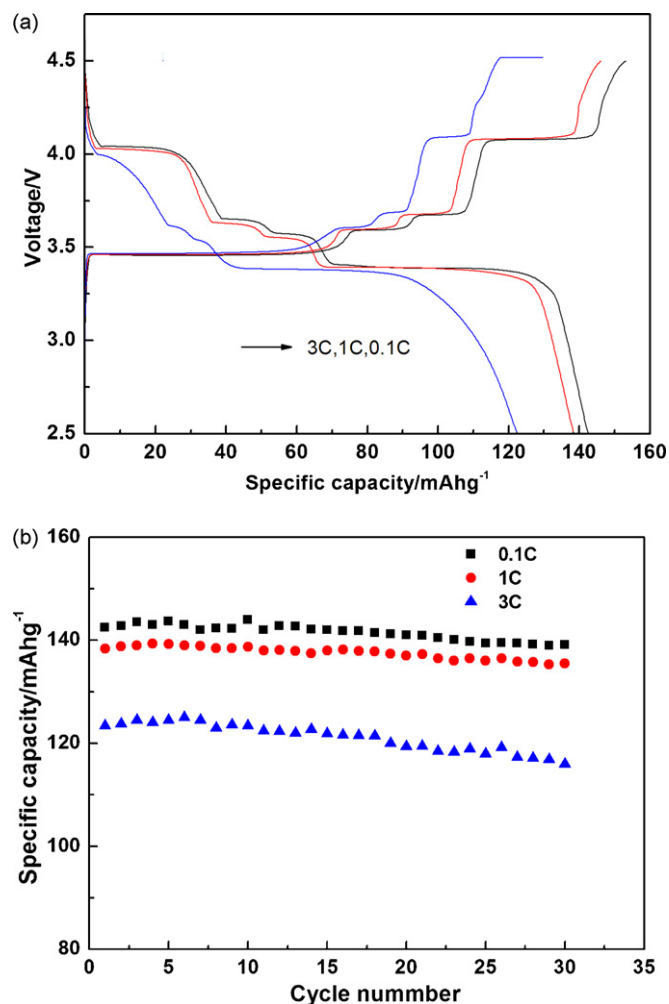


Fig. 5. (a) Rate performance of  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized at  $700^\circ\text{C}$  for 12 h. (b) Cycle performance of  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  synthesized at  $700^\circ\text{C}$  for 12 h.

materials are very effective for promoting transition-metal phosphates as cathode materials in Li-ion batteries [20–22].

Fig. 5a shows the first charge/discharge curves of  $\text{Li}/\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  cells at different rates. The curves all contain four plateaus, with three plateaus for  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and the other one for  $\text{LiFePO}_4$ . As seen in Fig. 5, the initial discharge capacity of  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  at the rate of 0.1 C, 1 C and 3 C is about 142.5, 138.4 and 123.4  $\text{mAh g}^{-1}$ , and the discharge capacity is about 139.1, 135.5 and 116  $\text{mAh g}^{-1}$  after 30 cycles. The cell retains 97.6%, 97.9% and 94.0% of its initial discharge capacity, respectively. The results are better than that reported by Ref. [15]. Besides, the discharge plateaus of the  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  at different rates are almost at the same voltage, however, the discharge plateaus of individual component  $\text{LiFePO}_4$  and  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  at different rates are fading obviously, which can be observed in our previous reports [17,23].

#### 4. Conclusion

$\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  composite cathode material was synthesized by aqueous precipitation of  $\text{FeVO}_4$  from  $\text{Fe}(\text{NO}_3)_3$  and  $\text{NH}_4\text{VO}_3$ , following chemical reduction and lithiation with oxalic acid as the reducer and carbon sources. The  $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$  compound synthesized at  $700^\circ\text{C}$  for 12 h showed good electrochemical performance, and its discharge capacity is about 139.1 at 0.1 C, 135.5 at 1 C and 116  $\text{mAh g}^{-1}$  at 3 C after 30 cycles.

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