



LiVPO₄F/C cathode synthesized by a fast chemical reduction method for lithium-ion batteries



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ABSTRACT

LiVPO₄F/C cathode has been successfully synthesized by a fast chemical reduction method using polyvinylidene fluoride as carbon source. NH₄VO₃ is reduced by oxalic acid at 60 °C in short time. The green color and binding energy peaks around 517.1 eV and 524.7 eV in dried precursors corroborate that element V in NH₄VO₃ is reduced to +3 valence. The crystallite of LiVPO₄F/C is well developed. Nanometer granules with smooth edge aggregate and form micron size LiVPO₄F/C particles. The molar ratio of V:P:F in cathode is 1:0.99:1.02, which is close to stoichiometric. The discharge capacities of LiVPO₄F/C at 0.2 C, 1 C and 2 C are 140.9 mA h g⁻¹, 127.4 mA h g⁻¹ and 122.9 mA h g⁻¹. It is concluded that the fast chemical reduction in this paper can be used to prepare LiVPO₄F/C cathode with stable crystallite structure and excellent performances.

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1. Introduction

Nowadays, lithium-ion batteries are more and more used in the daily life of people, such as the portable electronic devices and the promising energy sources for electric vehicle. LiVPO₄F cathode possesses the high operating voltage platform (4.2 V) [1], stable crystallite structure [2] and excellent thermal stability [3], which are superior to LiCoO₂, LiMn₂O₄, Li(NiMnCo)_{1/3}O₂, LiFePO₄ and Li₃V₂(PO₄)₃.

Since LiVPO₄F was first synthesized [4], it was mainly prepared by a two-step carbothermal reduction method [1,2,5,6]. Unfortunately, this method contains two separated high temperature section (~800 °C). Its production flow is long, complex and energy consumption. And the residual carbon black is difficult to be removed and this will sacrifice the electrochemical performances of cathode.

In order to decrease the above drawbacks, one-step method is developed. Some researchers propose a V₂O₅ hydro-gel method [7–10] where V₂O₅ are reduced by H₂O₂ or melted at 700 °C. Although it is workable, an extra high temperature reaction is introduced. In the others literatures, V₂O₅, oxalic acid and raw

materials are mixed by magnetic stirring-high energy ball milling [11] or agate mortar-ball milling [12,13]. In these researches, V₂O₅ is reduced by oxalic acid and the defects from the preparation of VPO₄ by carbon black are prevented.

However, the high toxicity V₂O₅ is first substituted with NH₄VO₃ [14]. In the one-step method, V₂O₅ or NH₄VO₃ are reduced by oxalic acid at room temperature in 2–4 h time. Moreover, the influences of carbon source are seldom discussed, in which multi-walled carbon nanotubes [15] and graphene [16] only modify LiVPO₄F and V₂O₅ is reduced by citric acid. It is found that the reduction strength of pyrolysis carbon from organic carbon source is much stronger than that of carbon black [17].

In this paper, LiVPO₄F/C cathode was synthesized by a fast chemical reduction method, in which NH₄VO₃ was reduced by oxalic acid at 60 °C in only several minutes. The hydrophobic carbon source of polyvinylidene fluoride (PVDF) was added to the solution of surfactant hexadecyl trimethyl ammonium bromide (CTAB) assisting with ultrasonic dispersion.

2. Experimental

LiVPO₄F/C cathode was synthesized by a fast chemical reduction. NH₄VO₃ was added to deionized water in a polytetrafluorethylene beaker accompanying with magnetic stirred. Then,

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oxalic acid at the molar ratio of 1.5:1 to NH_4VO_3 was used to reduce NH_4VO_3 at 60 °C in 10 min. Next, LiF and $\text{NH}_4\text{H}_2\text{PO}_4$ and PVDF suspension were added to the solution, which was prepared by ultrasonic dispersion the aqueous solution containing PVDF and surfactant CTAB. The water in the solution was evaporated by heated it in a vacuum oven at 80 °C for 6 h. The dried precursor was heated at 400 °C for 5 h and sintered at 800 °C for 6 h in a tubular furnace with flowing argon atmosphere.

The oxidative valence of V was determined by an ESCALAB 250Xi X-ray photoelectron spectroscopy (XPS) from Thermo Fisher-VG Scientific. The crystallite was analyzed by a Rigaku D/MAX 2500 X-ray diffraction (XRD) instrument. The scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS) analysis was conducted by a Navo NanoSEM230 microscopy.

Cathode films were prepared by mixing $\text{LiVPO}_4\text{F/C}$, acetylene black and PVDF at the mass ratio of 80:15:5. The slurries were coated on aluminum current collector and dried at 120 °C for 12 h. The 2016 type cell was assembled in a super (1220/750) glove box. The counter electrode was lithium foil. The electrolyte was 1 mol L^{-1} LiPF_6 in a mixture solvent of ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate (1:1:1, volume). The charge and discharge performances of cathode at different rates were determined by a BT2000 Battery test system in the potential range of 3.0–4.5 V (vs. Li^+/Li).

3. Results and discussion

It is found that the color of NH_4VO_3 solution adding with oxalic acid changes gradually from ivory white to yellow, deep red,

purple and green. The photo image and XPS spectrum of the dried precursor are presented in Fig. 1. The XRD pattern of $\text{LiVPO}_4\text{F/C}$ is also given in it.

It is well known that the color of NH_4VO_3 solution represents different oxidation state of element V. According to chemical knowledge, the state of V is +5 valence in NH_4VO_3 and the final color is green, which shows that Vanadium is reduced to +3 valence by oxalic acid. As can be seen from the figure that the dried precursor still maintain the green color. It shows that the subsequent addition of LiF, $\text{NH}_4\text{H}_2\text{PO}_4$, CTAB and PVDF do not change the oxidation state of Vanadium.

Two peaks at the binding energy of 517.1 eV and 524.7 eV are conformed to the $\text{V } 2p_{3/2}$ and $\text{V } 2p_{1/2}$ and there is no other peaks. They are in accordance with that of V_2O_3 [18] and LiVPO_4F [2,7]. It implies that the valence of Vanadium in the precursor is +3. Combining with the color and the XPS analysis, it is verified that V^{5+} in NH_4VO_3 is completely reduced to V^{3+} by oxalic acid dihydrate at 60 °C in short time.

The reaction rate will increase 2–4 times when the temperature raise 10 K according to Vander Hoff's law. It indicates that the rate at 60 °C will increase at least 9 times compared with room temperature.

The higher the standard electrode potential is, the stronger the oxidizability will be. Then, it is more difficult to be reduced. The standard electrode potential of NH_4VO_3 and KMnO_4 are 1.337 V and 1.491 V. They both possess strong oxidizability. The determination of KMnO_4 by the chemical titration analysis of oxalic acid is always performed at 75–85 °C, which ensure that it can be quickly reduced. Therefore, it is convinced that NH_4VO_3 can be fast reduced by oxalic acid at 60 °C in this paper, where the milling

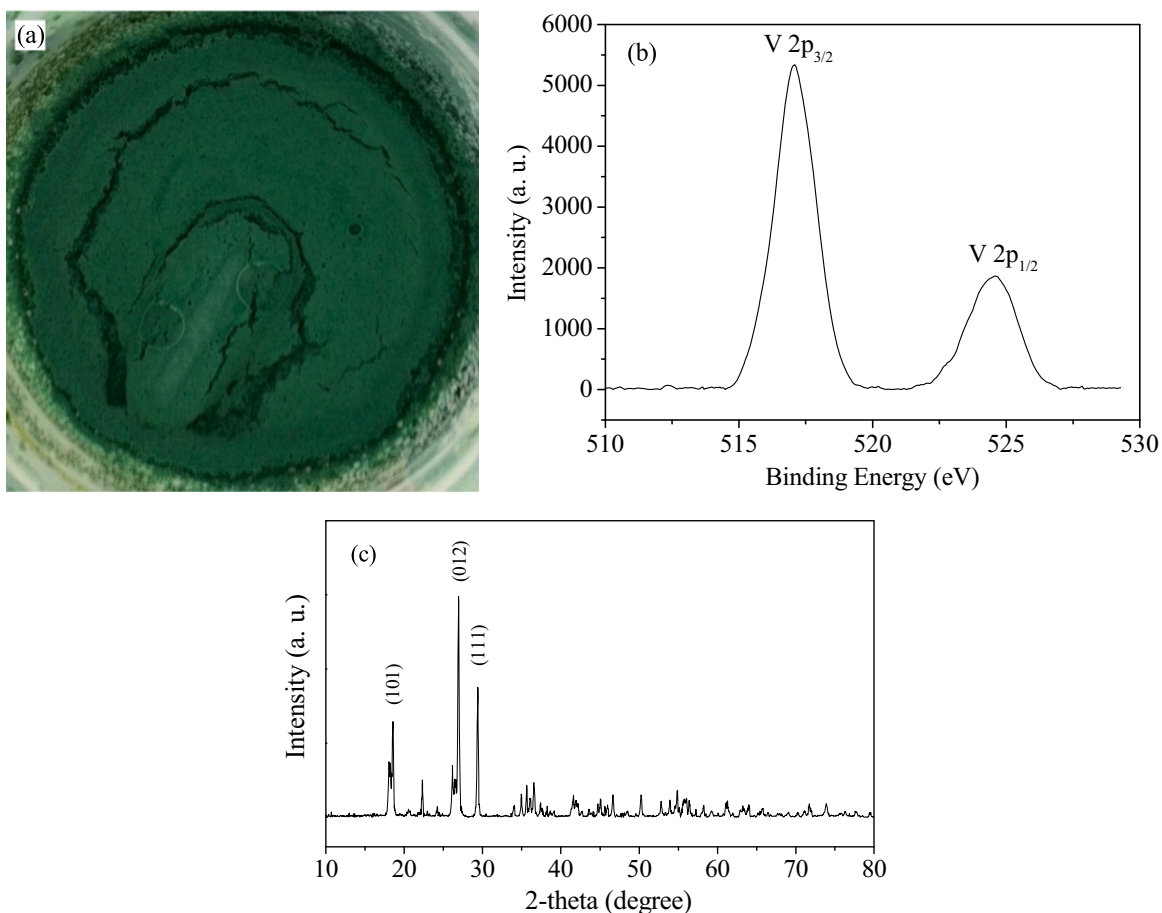


Fig. 1. Color (a) and XPS spectrum of V2p (b) of dried precursor and XRD pattern (c) of $\text{LiVPO}_4\text{F/C}$.

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