Journal of Power Sources 282 (2015) 100–108

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Synthesis and electrochemical performance of lithium vanadium phosphate and lithium vanadium oxide composite cathode material for lithium ion batteries

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HIGHLIGHTS

- A novel $2Li_3V_2(PO_4)_3 \cdot LiV_3O_8$ composite is synthesized in this paper.
- XRD results prove the coexistence of both single phase.
- The cyclic stability and discharge capacity are better than both single phase.
- $2Li_3V_2(PO_4)_3 \cdot LiV_3O_8$ composite shows high Li-ion diffusion coefficient.

ARTICLE INFO

Article history:
Received 31 January 2015
Accepted 9 February 2015
Available online 10 February 2015

Keywords:
Lithium vanadium phosphate
Lithium vanadium oxide
Composite cathode
Lithium ion battery

ABSTRACT

A novel $2Li_3V_2(PO_4)_3 \cdot LiV_3O_8$ composite with short rod and thin plate shapes is synthesized through sol–gel method followed by hydrothermal and solid–state reaction. LiV_3O_8 is used as an additive to improve the capacity of $Li_3V_2(PO_4)_3$. In the composite cathode, active impurity phase $Li_{0.3}V_2O_5$ is also present, which has little impact on the whole electrochemical properties. The $2Li_3V_2(PO_4)_3 \cdot LiV_3O_8$ composite delivers a high initial capacity of 162.8 mAh g^{-1} at a current density of 100 mA g^{-1} in the voltage range of 2.0–4.3 V. Furthermore, the composite with high crystallinity also shows high electrochemical reversibility and good rate capability. The diffusion coefficient of Li ions in the composite is in the range of 10^{-11}–10^{-9} cm^2 s^{-1} obtained from galvanostatic intermittent titration technique.

1. Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronic devices and hybrid vehicles because of their excellent electrochemical performances, such as high operating voltage, light weight, eco-friend property and long cycling life [1–3]. While the development of higher power and/or energy density as well as safety relies on the advancement of new electrode materials used in them [1,4]. During the past few years, several cathode materials have been studied for LIBs, such as $LiMnPO_4$ [5,6], Li–V–O compounds [7–13], $LiCoPO_4$ [14], $Li_3V_2(PO_4)_3$ [15–22], and so on.

Monoclinic $Li_3V_2(PO_4)_3$ (LVP) is a highly promising candidate because of good security and excellent thermal stability [23–26]. In the voltage range of 3.0–4.3 V, it can remove the first half, the second half and the second Li^+ ions at the redox potentials of 3.6, 3.7 and 4.1 V (vs. Li/Li^+), and obtain capacities of 120–133 mA h g^{-1}. When charged to 4.8 V, the third Li^+ ion can be extracted at 4.55 V, corresponding to a high capacity of 197 mAh g^{-1} [16,22,27]. However, the practical LIBs take the operating potential below 4.3 V for the instability of electrolyte at high voltage. Therefore, it becomes significant to seek out an efficient way to improve the electrochemical performance of LVP in the voltage range of 3.0–4.3 V. Besides, LVP suffers drawbacks of low electronic conductivity (2.4×10^{-7} S cm^{-1}) [28–30], and low ionic conductivity (10^{-13}–10^{-8} cm^2 s^{-1}) [31], which need to be improved as well. Many efforts have been paid to overcome its shortage and improve its properties, such as cation doping [32–37], carbon and conductive material coatings [38–41], *etc.*

Although these methods have improved some electrical electrochemical properties, there still exists room for capacity between 3.0 and 4.3 V to grow higher than its theoretical capacity. It is expected that by using two or more materials with different merits to

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http://dx.doi.org/10.1016/j.jpowsour.2015.02.051
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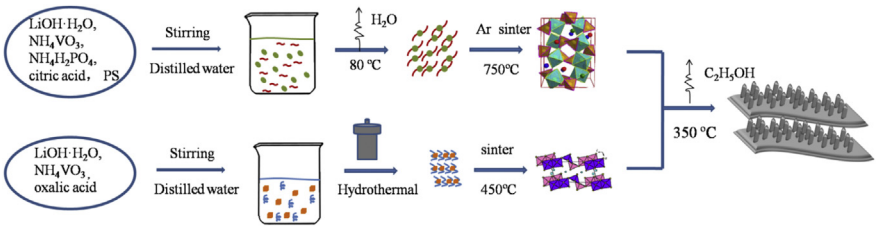

Scheme 1. Schematic illustration of synthetic process of nanoplate/rod like 2LVP·LVO composites.

form a new composite, the synergy among these components may cause a diversity of complex effects and result in complementary advantages.

LiV_3O_8 (LVO) has a layered monoclinic structure which consists of two basic structural units of VO_6 octahedra and VO_5 trigonal bipyramids, and the $V_3O_8^-$ layers are held together through the interaction with the interlayered Li^+ ions. It shows high specific capacities because vanadium has multiple valence states, which cause a multiple discharge plateaus during the Li^+ intercalation of LVO [42,43]. However, the poor stability of its layered structure and incompelete reversible phase transformation during the insertion/de-insertion of lithium, makes the compound suffer from poor rate capability and serious capacity loss [44–46]. In this present work, we adopt LVO as an additive to prepare a $2Li_3V_2(PO_4)_3 \cdot LiV_3O_8$ (2LVP·LVO) composite cathode material. It is expected that LVO and LVP could offset their weaknesses, and obtain high capacity and good cyclic stability simultaneously. The electrochemical properties of 2LVP·LVO were compared with those of the as-prepared LVP and LVO electrodes in the voltage of 2.0–4.3 V.

2. Experimental

2.1. Material synthesis

Stoichiometic amounts of $LiOH \cdot H_2O$, NH_4VO_3, $NH_4H_2PO_4$, citric acid (the molar ratio of citric acid and V is 1) and polystyrene (10 wt.% of the product mass) were used as starting materials for synthesizing LVP. First of all, NH_4VO_3 and citric acid were dissolved in appropriate de-ionized water under mechanical stirring at 80 °C for 0.5 h. Then, a mixture of $LiOH \cdot H_2O$, $NH_4H_2PO_4$ and polystyrene was added into the above solution with stirring for 5 h. After evaporating the water at 80 °C, the solution became a gel. The resulting gel was dried in a vacuum oven at 60 °C overnight, and then annealed in Ar flow at 350 °C for 4 h, finally calcined at 750 °C for 6 h in Ar atmosphere to yield LVP.

$LiOH \cdot H_2O$, NH_4VO_3 and oxalic acid were used as raw materials for preparing LVO. Appropriate ratio of NH_4VO_3 and oxalic acid (the molar ratio of oxalic acid and cation is 2) were put into a beaker containing 80 mL de-ionized water with mechanical stirring until the color of the solution turned into blue. After a few hours, $LiOH \cdot H_2O$ was added into the resulting solution and kept stirring for another 0.5 h. Subsequently, the mixture was transferred into a 100 mL polytetrafluoroethylene (PTFE) container. After the container was sealed, it was heated in an oven at 140 °C for 12 h, and then cooled to the room temperature. Afterward, the obtained precursor was dried at 100 °C, and calcined at 450 °C for 6 h to yield the rufous product LVO.

1 mmol LVP and 0.5 mmol LVO were uniformly mixed in 20 mL ethanol by magnetic stirring at 60 °C for 4 h. After ethanol completely evaporated, the mixture was milled and then calcined at 350 °C for 2 h. At last, a reddish brown 2LVP·LVO powder was obtained. Scheme 1 shows the schematic illustration of synthetic process of 2LVP·LVO composites, it briefly describes the whole synthesis process.

2.2. Material characterization

The phase composition of the as-synthesized powders was investigated by X-ray diffraction (XRD, Philips PC-APD with CuKα radiation). Thermogravimetric analysis (TG) of the composite was measured on a Pyris 1 TGA apparatus in the temperature range of 20–800 °C at a heating rate of 10 °C min^{-1} in air. The morphology

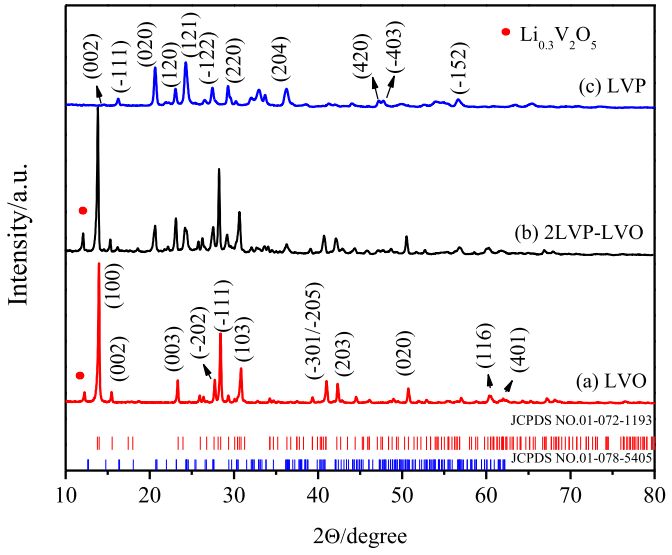

Fig. 1. XRD patterns of as-prepared powders: (a) LVO; (b) 2LVP·LVO and (c) LVP.

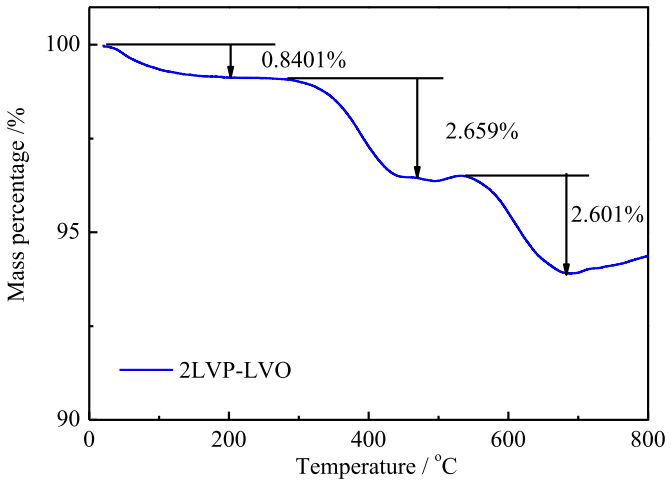

Fig. 2. TGA curve of 2LVP·LVO composite.