



Effect of process medium on the synthesis of carbon coated lithium vanadium phosphate composite using rheological phase reaction method



Yue Wu^{a, b, *, 1}, Xiaoming Zhao^{a, b, 1}, Zhihao Song^{a, b}, Liping Lin^{a, b}, Chenqiang Du^{a, b}, Zhiyuan Tang^{a, b}

^a Department of Applied Chemistry, School of Chemical and Engineering, Tianjin University, Tianjin 300072, China

^b Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

HIGHLIGHTS

- $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ is synthesized by a modified rheological phase reaction method.
- The effects of process medium on rheological phase reaction route are investigated.
- The electrochemical properties of LVP samples using different media are compared.
- Ethylene glycol is favorable for the morphology and performance of LVP/C composite.
- LVP/C exhibits excellent rate and cycling performances in different voltage ranges.

ARTICLE INFO

Article history:

Received 3 September 2014

Received in revised form

13 October 2014

Accepted 15 October 2014

Available online 22 October 2014

Keywords:

Lithium vanadium phosphate

Rheological phase reaction

Process medium

Electrochemical performance

Lithium ion battery

ABSTRACT

$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites (LVP/C) are synthesized by rheological phase reaction (RPR) method using alginate acid (HALg) as the carbon source. Different process media are applied in the synthetic process to assess the possible effects on LVP/C composite. And the whole synthetic route is discussed in detail with qualitative and instrumental analysis, in terms of ball-milling process, rheology phase reaction process and thermogravimetric analysis of precursors. The much different morphological properties of as-prepared LVP/C composites demonstrate that process medium indeed has some effects on the synthetic process, especially on the refinement and dispersion of particles. According to these investigations, ethylene glycol (EG) is revealed more proper for preparing LVP/C using this method attributed to its moderate viscosity, surface activity and synergistic effects with HALg. The corresponding LVP/C composite shows nanoscaled particles with smooth surfaces and uniform size distribution. Besides, LVP-EG sample exhibits excellent electrochemical performances under different voltage windows as well. Between 3.0 and 4.3 V, when charge/discharge at 20/50 C, the composite exhibits relatively high capacity and stable cycling performance for 300 cycles. Within 3.0–4.8 V, it can cycle for 200 times at a high rate of 20 C without obvious capacity fading. The outstanding performances can be attributed to the enhanced electronic/ionic conductivities of LVP/C benefiting from the influences of EG and HALg via the RPR method.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The rapid development of cathode material greatly promotes the application of lithium ion battery in portable electronics, load-leveling applications and electric vehicles (EVs) [1,2]. Among lithium transition metal phosphates, olivine LiFePO_4 (LFP) has been commercially applied due to its low cost, environmental benignity,

cycling stability and high safety [3]. Compared with LFP, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) shows a higher discharge voltage and a larger theoretical capacity. Besides, LVP owns a three-dimensional framework which ensures much rapid and isotropic lithium ion transporting, in comparison with the one-dimensional channel-structured LFP [4]. However, the relatively low electrical conductivity resulted from the separated VO_6 octahedrons arrangement restricts its practical application [2,5,6]. Nowadays, carbon coating strategy is considered to be a much effective way to overcome this obstacle and has been universally applied in synthesizing LVP/C composite [7–10].

* Corresponding author. Tel.: +86 (0)769 8301 7180; fax: +86 (0)769 8319 5372.

E-mail address: tju_wuyue@163.com (Y. Wu).

¹ These authors contributed equally to this work.

So far, carbon coated LVP has been successfully prepared via various synthetic routes, such as hydrothermal synthesis (HTS), sol–gel method (SG) and solid–state reaction method (SSR) [8–10]. Conventionally, solid–state reaction method often results in relatively large particle size and the aggregation of materials, although the facile operation shows advantages in large-scale application [8,11]. Sol–gel method and hydrothermal method can realize more homogeneous mixing of raw ingredients in precursors and obtain relatively smaller particle sizes. Nevertheless, these two routes generally demand complicated operating procedures and high costs [9,10,12]. Recently, rheological phase reaction (RPR) method has been developed rapidly in the preparation of electrode materials. The RPR process is proved to be distinctive because that it not only owns a pretreatment as simple as SSR method, but also realizes a favorable two-phase exchange of matter and energy between solid particles and liquid substrate [13–19]. Further, it offers the opportunities to synthesize well-refined nanoparticles and to realize large-scale preparation of prospective materials.

As well known, ball-milling step and rheological phase reaction step are two main procedures in RPR method, during which the process medium may play a pretty important role [13–15]. The process medium as the ball-milling dispersant can influence the refinement extent and the dispersion state of raw materials, meanwhile it provides a reaction environment for the rheology phase and thus may affect the reaction process as well [16–19]. However, most studies are concerned about the comminuting conditions of ball-milling, i.e. the mass of grinding balls, rotation speed and the duration of ball-milling [20–22], while the effects of process medium on ball-milling effectiveness, reaction process and final product are rarely reported. When a solvent is added as the process medium, the obtained rheological phase system becomes much complicated which depends on many interrelated parameters, such as the characteristics of suspension, the nature of inter-particle forces, the properties of solvent and the viscosity of rheological phase system [22,23]. Hence, the possible roles of process medium during rheological phase process are multifaceted and much meaningful to be investigated.

In this work, an alginate assisted RPR method using different process media is applied to synthesize LVP/C composites. The intermediates after ball-milling process and the precursors after reaction process have been investigated to analyze the influences of process media on the synthetic route. The effects of these media on particle property and electrochemical performance of LVP/C composites have also been intensively studied with instrumental analysis. Besides, the final optimized LVP/C composite shows an excellent high-rate capability and cycling stability under both voltage windows of 3.0–4.3 V and 3.0–4.8 V.

2. Experimental

All the reagents used here were of analytical grade and were used directly without any purification. The cathode material LVP/C was prepared as follow.

2.1. Synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ cathode material

The LVP/C samples were fabricated via a modified RPR route using different process media. First of all, V_2O_5 , Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ with the molar ratio of $\text{Li}:\text{V}:\text{P} = 3:2:3$ were mixed with certain amounts of alginate. Then, the mixture was ball-milled for 12 h with an appropriate amount of solvent as the dispersant. There are five different solvents, deionized water (DIW), ethyl alcohol (EA), ethylene glycol (EG), glycerol (GI) and n-butyl alcohol (BA), used here as the dispersants and then as the reaction media for subsequent rheological phase reactions. Afterwards, the

obtained rheological phase was humidified at 80 °C for 5 h in a sealed container and then dried to obtain the LVP precursor. At last, the precursor was preheated at 350 °C for 4 h and subsequently calcined at 800 °C for another 8 h under N_2 atmosphere to yield the LVP/C composite. For convenience, the obtained LVP/C samples were denoted as LVP-DIW (or EA, EG, GI, BA) corresponding to different synthesis conditions. For comparison, the LVP/C sample without adding any liquid substrate was also prepared following the same synthesis route and denoted as LVP-Dry.

2.2. Sample characterization

The phase identifications of the as-prepared LVP/C composites were investigated by powder X-ray diffraction (XRD) (Rigaku D/max-III λ -ray Diffractometer with a $\text{Cu-K}\alpha$ radiation) in the angular range (2θ) from 10° to 80°. The particle morphologies of LVP/C samples were characterized with a scanning electron microscopy (SEM, S-4800). Crystal structure and carbon layer were observed using transmission electron microscopy (TEM, JEM-2010). The particle size distributions of the precursors were measured by Delsa Nano C particle analyzer with the testing range of 0.6 nm–30 μm (Beckman Coulter, USA). The thermal decomposition behavior of the precursors were examined by thermogravimetric (TG) method using the Netzsch STA 449 F thermal analyzer in N_2 atmosphere at a heating rate of 10 °C min^{-1} . Raman spectroscopy (Renisaw 2000) with 514.5 nm incident radiation was used to analyze the properties of residual carbon. The carbon contents of the obtained LVP/C composites were determined by the methodology previously reported [24], and the values of LVP-Dry, LVP-DIW, LVP-EA, LVP-EG, LVP-GI and LVP-BA samples are calculated to be 6.1%, 5.8%, 7.7%, 7.9%, 9.8% and 10.5% respectively.

2.3. Electrochemical performance characterization

The electrochemical performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ electrodes in half cells (vs. Li counter electrodes) was evaluated using CR2032 coin-type cells. The LVP electrodes were fabricated by mixing 80 wt.% active material with 10 wt.% super-P and 10 wt.% polyvinylidene difluoride (PVDF) in an appropriate amount of N-methyl-2-pyrrolidone to form slurry. Then the slurry was pasted onto the aluminum foils. Afterwards, the LVP electrodes were dried at 120 °C for 12 h under a vacuum atmosphere. The lithium metal foil was served as the counter and reference electrode, Celgard2300 as the separator, and 1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volumetric ratio of 1:1 as the electrolyte.

The galvanostatic charge–discharge measurements were conducted on a multi-channel battery test system (NEWARE BTS-610) in the voltage windows of 3.0–4.3 V (1 C = 133 mA g^{-1} vs. Li^+/Li) and 3.0–4.8 V (1 C = 197 mA g^{-1} vs. Li^+/Li). Cyclic voltammetry (CV) were carried out on an electrochemical working station (Gamry PCI4-750) in both potential ranges as well. The electrochemical impedance spectroscopy (EIS) curves were measured on the electrochemical working station (Gamry PCI4-750) at a frequency range of $10^{-2} - 10^5$ Hz.

3. Results and discussion

3.1. Effects of the process media on synthetic process

3.1.1. Effects of dispersants on ball-milling effectiveness

In this work, the modified RPR method used here combines the wet ball-milling strategy with the rheological phase reaction strategy. Namely, the solvents are used not only as the ball-milling dispersants, but also as the reaction media for the rheological

Download English Version:

<https://daneshyari.com/en/article/7735092>

Download Persian Version:

<https://daneshyari.com/article/7735092>

[Daneshyari.com](https://daneshyari.com)