Journal of Power Sources 395 (2018) 158–162

Contents lists available at ScienceDirect

Journal of Power Sources

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

Short communication

One-step and short-time synthesis of 3D NaV_2O_5 mesocrystal as anode materials of Na-Ion batteries

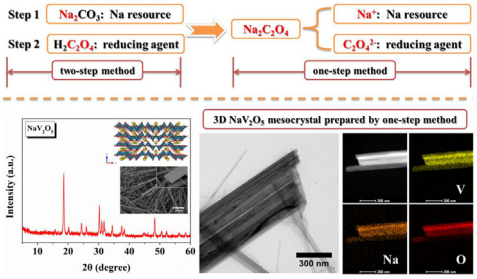
Pengcheng Liu[a], Kongjun Zhu[b,**], Kan Bian[a], Yuan Xu[b], Fan Zhang[a], Wei Zhang[b], Weiqing Huang[a], Jianhui Zhang[a,*]

[a] School of Mechanical and Electric Engineering, Guangzhou University, Guangzhou 510006, China
[b] State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

HIGHLIGHTS

- A fast synthesis of NaV_2O_5 mesocrystal is realized by a one-step hydrothermal.
- $Na_2C_2O_4$ is tactfully designed as simultaneously reducing reagent and Na resource.
- The synthesis time is greatly shortened more than 5 times.
- The crystal growth mechanism of NaV_2O_5 mesocrystal is also revealed.
- As-obtained NaV_2O_5 mesocrystal exhibits the improved electrochemical performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Na-ion battery
NaV_2O_5
Anode material
Hydrothermal method
One-step synthesis

ABSTRACT

NaV_2O_5, possessing robust, open and large-space layered crystal structure, was recently found as one novel promising intercalation-type high-capacity anode material for Na-ion batteries. To address its difficult issue of morphology control for conventional solid-state method, our group proposed previously a two-step hydrothermal method to controllably synthesize a well-crystallized NaV_2O_5 mesocrystal. However, this two-step method was still time-costing and a bit complex. In order to further promote its further research development and industrial application, it remains a huge and attractive challenge to explore a simple and time-saving method to synthesize promising NaV_2O_5. Herein, we propose a facile one-step hydrothermal strategy to realize the short-time synthesis of 3D bundle-like NaV_2O_5 mesocrystal. In this simple one-step method, sodium oxalate ($Na_2C_2O_4$) is tactfully designed as simultaneously reducing reagent and Na resource, so that its synthesis time is greatly shortened more than 5 times. Furthermore, the crystal growth mechanism of NaV_2O_5 mesocrystal is also revealed. Amazingly, the ex-situ XRD measurement reveals that the electrochemical intercalation/deintercalations are reversible and the crystal structure of NaV_2O_5 is stable. So, NaV_2O_5 mesocrystal prepared by one-step method exhibit the promising electrochemical performance, and its reversible capacity is up to 360 mAh/g.

1. Introduction

It has become a continuous hot issue in 21th contrary to develop and utilize the green and clean energy, such as solar and wind power [1,2]. To better realize the availability of these intermittent and unstable clean energies, large-scale energy storage system (ESS) has

* Corresponding author.
** Corresponding author.
E-mail addresses: kjzhu@nuaa.edu.cn (K. Zhu), zhangjh@nuaa.edu.cn (J. Zhang).

https://doi.org/10.1016/j.jpowsour.2018.05.067
Received 20 January 2018; Received in revised form 23 April 2018; Accepted 20 May 2018
0378-7753/

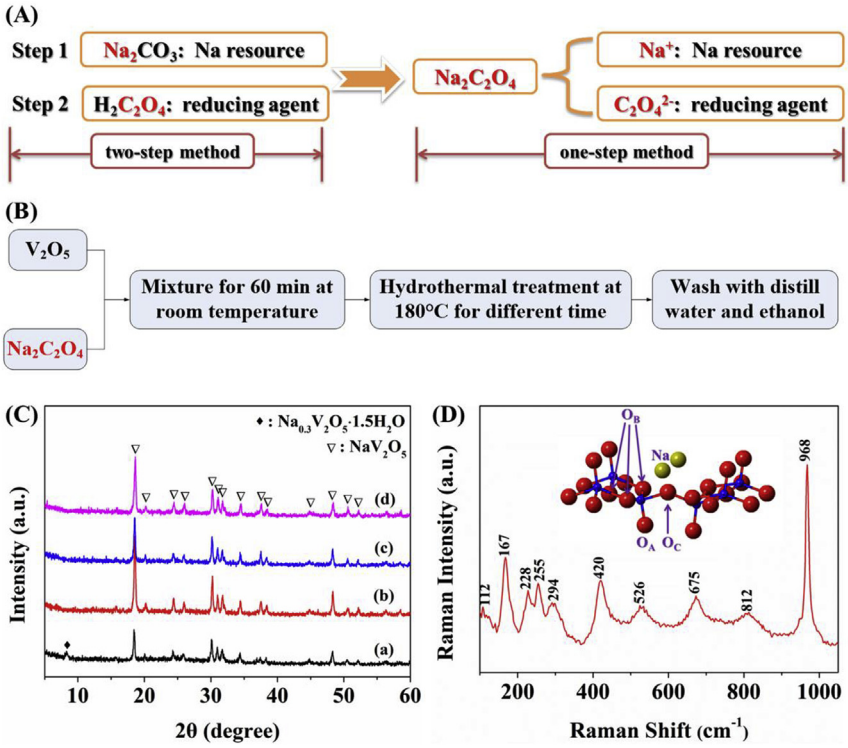


Fig. 1. One-step hydrothermal method for NaV_2O_5. (A) Idea origin process of one-step hydrothermal method; (B) flow chart of one-step hydrothermal method; (C) XRD pattern of products synthesized by one-step hydrothermal method for different time: (a) 12 h, (b) 18 h, (c) 36 h, (d) 48 h; (D) Raman spectrum of product synthesized by one-step hydrothermal method for 18 h.

attracted huge attention and interests [3–5]. Owing to the abundance and low cost of Na resource, Na-ion batteries (NIBs) are considered as one of the most promising candidates for the application of large-scale ESS [6,7]. However, unfortunately, graphite, the most successful anode material of Li-ion batteries, cannot be used as anode material of NIBs due to the exhibited low capability caused by the larger radius of Na ion than that of Li ion [6,8]. So, it is quite urgent to develop the novel and promising anode materials for NIBs.

Some potential anode materials for NIBs have been proposed to address the above issues, including the alloy-type (such as SnO_2, Si, and so on) [9,10] and intercalation-type (such as $Na_{0.66}$ $[Li_{0.22}Ti_{0.78}]O_2$, $Li_4Ti_5O_{12}$, and so on) [11–13] anode materials. The alloy-type anode materials can usually deliver large specific capacity, but they simultaneously suffer from huge volume change during charging-discharging, which results in a poor cycling life [9]. On the contrary, the intercalation-type anode materials, such as "zero-strain" $Na_{0.66}$ $[Li_{0.22}Ti_{0.78}]O_2$, can often exhibit better cycling performance due to their strong structural stability, but their theoretical specific capacities (such as 116 mAh/g for $Na_{0.66}$ $[Li_{0.22}Ti_{0.78}]O_2$) are still insufficient [11]. Therefore, it becomes a very attractive and interesting issue if the new intercalation-type anode materials with larger specific capacity and similar structural stability can be found.

Recently, we found that NaV_2O_5, possessing robust, open and large-space layered crystal structure, was a novel intercalation-type anode material for NIBs with a high reversible capacity (362 mAh/g) through Density Functional Theory (DFT) calculation and electrochemical testing [7,14]. Moreover, we proposed for the first time a hydrothermal strategy to address the difficult issue of morphology control of NaV_2O_5 for conventional solid-state method [15–17], and controllably synthesized a well-crystallized NaV_2O_5 mesocrystal. However, this hydrothermal strategy is a two-step method, and thereby it is still time-costing and a bit complex, which is disadvantageous to the further research and development of NaV_2O_5 in the aspects of electrochemistry mechanism, performance improvement, practical commercialized applications and so on. So, it remains a huge and attractive challenge to explore a simple and time-saving method to synthesize promising NaV_2O_5.

Herein, we propose a facile one-step hydrothermal strategy to realize the short-time synthesis of 3D bundle-like NaV_2O_5 mesocrystal. In this simple one-step method, sodium oxalate ($Na_2C_2O_4$) is tactfully designed as simultaneously reducing reagent and Na resource, so that its synthesis time is greatly shortened more than 5 times. Furthermore, the crystal growth mechanism of NaV_2O_5 mesocrystal is also revealed. Excitingly, NaV_2O_5 mesocrystal prepared by one-step method exhibits the better electrochemical performance compared with the one prepared by two-step method.

2. Results and discussion

To synthesize NaV_2O_5, the raw materials should include V resource, Na resource and reducing reagent. Previously, we proposed a two-step hydrothermal method to successfully synthesize the NaV_2O_5 mesocrystal for a reaction time of 96 h by taking V_2O_5, Na_2CO_3 and oxalic acid ($H_2C_2O_4$) as V resource, Na resource and reducing reagent respectively, as shown in Fig. S1 [14]. In the first step, V_2O_5 and Na_2CO_3 were hydrolyzed as V and Na ions, and a homogeneous sol formed. When $H_2C_2O_4$ was added in the second step, hydrolyzed Na ions were intercalated into V-O layers, and nucleation and crystal growth also occurred. Although the crystal growth behavior of NaV_2O_5 can be well revealed through the slow two-step reaction process, the two-step method is still time-costing and a little complex. The reason is that the hydrolysis process of V_2O_5 and Na_2CO_3 in the first step as well as the intercalation process of Na ions in the second step are both quite slow, which is disadvantageous to the industrial application and further development of novel and promising NaV_2O_5 anode materials for NIBs. So, it remains an urgent and hot issue to explore a simple and time-saving method to synthesize NaV_2O_5.

Based on the detailed analysis of reaction and crystal growth mechanism for the previous two-step method, we find that the Na ion in Na_2CO_3 is the actual Na resource, and the $C_2O_4^{2-}$ in $H_2C_2O_4$ is the actual reducing reagent, as shown in the left part of Fig. 1A. So, an attractive and interesting method come into our mind whether a compound containing simultaneously Na^+ and $C_2O_4^{2-}$ can be found. Finally, we find the promising $Na_2C_2O_4$. Importantly, $Na_2C_2O_4$ can