



# One-pot hydrothermal synthesis of $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$ nanocomposite as a sodium-ion battery cathode for improved reversible capacity and rate performance



Jingjie Feng<sup>a</sup>, Zhenming Xiong<sup>b</sup>, Long Zhao<sup>a</sup>, Chunmao Huang<sup>a</sup>, Huatao Liu<sup>b</sup>, Siyuan Chen<sup>a</sup>, Zhen Wang<sup>a</sup>, Quan Kuang<sup>a</sup>, Youzhong Dong<sup>a</sup>, Qinghua Fan<sup>a</sup>, Yanming Zhao<sup>b,c,\*</sup>

<sup>a</sup> School of Physics, South China University of Technology, Guangzhou, 510640, PR China

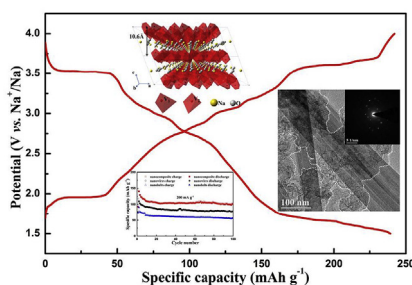
<sup>b</sup> School of Material Science and Engineering, South China University of Technology, Guangzhou, 510640, PR China

<sup>c</sup> Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, South China University of Technology, Guangzhou, 510640, PR China

## HIGHLIGHTS

- $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  is investigated as cathode for sodium batteries.
- $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  exhibits high specific capacity and superior cycling performance.
- A interlayer gap of 10.0 Å was observed in well crystallized  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  nanowires.
- $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  exhibits a remarkable energy density of  $597 \text{ Wh kg}^{-1}$ .

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Sodium-ion batteries  
Nanostucture  
Bilayer  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$   
Ketjen black  
Hydrothermal method

## ABSTRACT

Na-containing bilayer vanadium oxides offer outstanding storage capabilities for lithium and sodium batteries, but a multistep process for chemical pre-intercalation of Na-ion exposes a limitation for the application. Herein, we propose a facile one-pot hydrothermal approach to synthesize well crystallized bilayer  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  with ketjen black as conductive dense-network. As a cathode in sodium-ion batteries, the resultant  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  nanocomposite exhibits a high specific capacity of  $239 \text{ mA h g}^{-1}$  at a current density of  $20 \text{ mA g}^{-1}$  as well as an enhanced rate performance at high current rates up to  $640 \text{ mA g}^{-1}$ . *Ex situ* XRD and XPS analysis are conducted to demonstrate the high specific capacity and investigate the changes in structure. Moreover, it is noticeable that two pronounced voltage plateaus reflect the high electrochemical activity of  $\text{V}^{4+}/\text{V}^{5+}$ , contributing to a remarkable energy density of  $597 \text{ Wh kg}^{-1}$ , which is one of the highest records for cathode of sodium-ion batteries ever reported.

## 1. Introduction

Although lithium-ion batteries (LIBs) have been widely used in portable equipment and electric vehicles, the application in large-scale energy storage system is still limited by the high cost and scarce natural

resources of lithium as well as its reliability and stability [1–7]. As an alternative to lithium-ion batteries, sodium-ion batteries (SIBs) provide a solution to meet the requirement of large-scale energy storage system due to the low cost, improved safety characteristics, abundant sodium resources, and the similar electrochemical mechanism with lithium-ion

\* Corresponding author. School of Physics, South China University of Technology, Guangzhou, 510640, PR China.  
E-mail address: [zhaoym@scut.edu.cn](mailto:zhaoym@scut.edu.cn) (Y. Zhao).

batteries based on intercalation chemistry [8–13]. However, the difference of ionic radius ( $\text{Li}^+$ : 0.76 Å and  $\text{Na}^+$ : 1.02 Å) in the six-fold coordination environment [14] results in a smaller diffusion coefficient and more sensitive structural distortion during Na ions intercalation/deintercalation. Thus, it is imperative to develop suitable cathode materials with high reversible capacity, sufficient energy density and satisfying rate performance.

Metal oxides have wide applications in energy conversion and storage technologies [15–19]. Benefited from the unique structure, vanadium-based oxides with layered structure have been intensively researched as the cathode materials for sodium-ion batteries due to the great potential to reach high specific capacities. However, the narrow interlayer spacing of orthorhombic  $\text{V}_2\text{O}_5$  leads to low sodium ion diffusion efficiency, limiting the improvement in electrochemical performance [20,21]. Bilayer  $\text{V}_2\text{O}_5$  with a large interlayer spacing was proved to have high specific capacities due to the enlarged space which can accommodate more Na ions and facilitate the diffusion of Na ions [20]. Moreover, pre-intercalation of alkali metal ions into the bilayer vanadium oxide can enhance the specific capacity and cycling stability for the cathode material [22–25]. On the one hand, the pre-intercalation ions fixed between layers can act as pillar cations to stabilize the unique bilayer structure, leading to improved cycling performance [9]. On the other hand, mixed valences of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  account for improved electronic conductivity and more active redox sites during sodium insertion/de-insertion process [26]. C.Y. Lee et al. [23] reported that, synthesized by aging sodium vanadium oxide gels with an ion exchange resin,  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  ( $0.12 < x < 0.32$ ) with the bilayer structure achieved a discharge capacity of  $300 \text{ mA h g}^{-1}$  in the first cycle as a cathode for lithium-ion battery. M. Clites et al. successfully synthesized chemically pre-intercalated Na–V–O nanowires via sol–gel process followed by aging for 4 days and hydrothermal treatment, where an initial discharge capacity of  $365 \text{ mA h g}^{-1}$  for Na-ion battery cathode could be received in the voltage range of 1.0–4.0 V ( $\sim 220 \text{ mA h g}^{-1}$  in the voltage range of 1.5–4.0 V) [22]. Inspired by these work, pre-intercalated vanadium oxide with a unique bilayer structure may be developed to a promising cathode material for SIBs.

Although a high capacity is obtained, bilayer vanadium-based oxides are still difficult to overcome the disadvantages of fast capacity fading and poor rate performance. For bilayer  $\text{Na}_x\text{V}_2\text{O}_5$  as cathode of sodium batteries, only 48.8% of capacity remained after 30 cycles at a current density of  $20 \text{ mA g}^{-1}$ . This phenomenon may be caused by instability of the microstructure commonly appeared in vanadates. In addition, multistep synthesis and lengthy pre-intercalated processing might introduce extra safety issues and hardly fulfills the requirement of practical applications [27]. Therefore, a simple approach to achieve ion pre-intercalation for bilayer vanadium-based oxides with a stable crystal structure is desirable to enhance the cycling and rate performances. Moreover, coating conductive agent and downsizing the particles are effective ways to increase the conductivity of active materials and shorten electron and Na-ion transport path [28–31]. Herein, we employed a facile hydrothermal method to in-situ synthesize bilayer  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  nanocomposite with high specific capacity and superior cycling stability.

Furthermore, to the best of our knowledge, in-situ synthesized bilayer  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  nanocomposite has not been investigated as cathode for sodium batteries. In this work,  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  nanobelts and nanowires were synthesized via a one-pot hydrothermal method. Ketjen black (denoted by KB) was introduced to the synthesized process accompanied with chemical pre-intercalation, which could enhance electronic conductivity of as-prepared bilayer vanadium oxide. At the presence of reducing agent, the pre-intercalated process was conducted rapidly and well-defined nanowires were formed with an outstanding crystallinity, which is expected to possess a superior structural stability. Well distributed ketjen black has good contact with the  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  nanowires and prevents them from aggregation, forming a conductive dense-network. As expected,  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  nanocomposite

exhibits an excellent electrochemical performance for cathode of SIBs. A high specific capacity of  $239 \text{ mA h g}^{-1}$  was delivered at a current density of  $20 \text{ mA g}^{-1}$  and 91% discharge capacity can be retained after 90 cycles at a current density of  $200 \text{ mA g}^{-1}$ . Interestingly, two pronounced voltage plateaus reflected the high electrochemical activity of  $\text{V}^{4+}/\text{V}^{5+}$ , contributing to a remarkable energy density of  $597 \text{ Wh kg}^{-1}$ , which is one of the highest records for cathode of NIBs ever reported.

## 2. Experimental section

### 2.1. Materials synthesis

Nanostructural  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  was prepared via a one-pot hydrothermal approach. In a typical synthesis,  $\text{V}_2\text{O}_5$  (0.91 g), NaOH (0.2 g for  $\text{NaOH}:\text{V}_2\text{O}_5 = 1:1$  and 0.36 g for  $\text{NaOH}:\text{V}_2\text{O}_5 = 1.8:1$  respectively) powders were mixed with 70 mL distilled water followed by vigorous stirring at  $70^\circ\text{C}$  until a homogeneous solution was formed. Then, 2.5 mL anhydrous ethanol was added to the solution drop by drop with continuously stirring. Next, the solution was transferred into a 100 mL Teflon-lined autoclave and the total volume of the solution was about 70 mL. The autoclave was sealed and then hydrothermally treated at  $180^\circ\text{C}$  for 24 h and naturally cooled to room temperature. The precipitates were collected and washed by deionized water and ethanol repeatedly. Finally, the products were dried at  $80^\circ\text{C}$  in an oven to obtain pure  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  samples.  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  nanocomposite was synthesized by the same way as the  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  nanowires except that ketjen black suspension was added dropwise to the solution followed by vigorous ultrasonic treatment until it is well-dispersed.

### 2.2. Materials characterization

The XRD patterns were collected by a D/Max-2400 (Rigaku) diffractometer with Cu K $\alpha$  radiation. X-ray powder diffraction data (XRD) for Rietveld refinement analysis were collected by a X'Pert PRO (PANalytical, the Netherlands) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The Rietveld refinement of the data for  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  was performed by GSAS program (Larson & Von Dreele, 2000). Morphological studies were carried using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images were recorded by a JEOL 2010 microscope. Thermogravimetry analysis (TGA) curves were obtained by a STA-449-F3 Thermal Analyzer (NETZSCH, the Germany) with a heating rate of  $5^\circ\text{C}/\text{min}$  in the temperature range from  $50^\circ\text{C}$  to  $700^\circ\text{C}$  under a flowing air atmosphere. X-ray photoelectron spectroscopy (XPS) was carried out using an ESCALAB 250Xi spectrometer. The electrode sample in a fully discharged state for *ex situ* XPS and different discharged/charge states for *ex situ* XRD measurement was prepared by collecting and washing the active material by DMC (Dimethyl carbonate) in a glove box filled with ultra-high argon.

### 2.3. Electrochemical testing

The electrochemical performances of these nanostructural materials were measured with two-electrode electrochemical cells by an automatic battery tester system (Land, China). The  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  nanocomposite cathodes were fabricated by grinding the  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}/\text{KB}$  nanocomposite with polyvinylidene fluoride (PVDF) binder at a weight ratio of 90:10 in N-methyl-2-pyrrolidone (NMP) while the  $\text{Na}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  nanobelts and nanowires cathodes were fabricated by grinding the one-dimensional nanomaterials with ketjen black particles and polyvinylidene fluoride (PVDF) binder at a weight ratio of 82:8:10. The obtained slurry was evenly coated on Al foil and the weight of active material loaded on the electrodes was about 2 mg. Two-electrode electrochemical cells were assembled using a Mikrouna glove box filled with ultra-high argon. Sodium metal foils were used as counter

Download English Version:

<https://daneshyari.com/en/article/7724802>

Download Persian Version:

<https://daneshyari.com/article/7724802>

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