



# Hydrothermal synthesis of sodium vanadate nanobelts as high-performance cathode materials for lithium batteries



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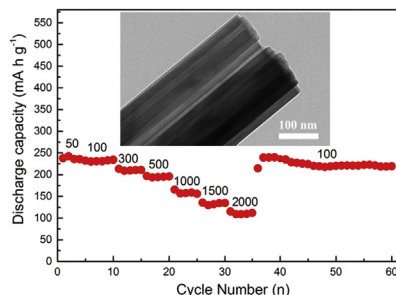
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## HIGHLIGHTS

- $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  nanobelts are prepared via a hydrothermal reaction followed by annealing.
- $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  exhibits high capacity, excellent cyclic stability and high-rate capability.
- High capacity of 248 and 214  $\text{mA h g}^{-1}$  are obtained at 300 and 500  $\text{mA g}^{-1}$ , respectively.
- The structural stability and charge-transfer resistance changes upon cycling are examined.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The sodium vanadate ( $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$ ) nanobelts have been successfully synthesized via a facile hydrothermal reaction followed by annealing. The ultra-long nanobelts have a length ranging from several micrometers to several dozens of micrometers. As cathode materials for lithium-ion batteries, the  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  nanobelts exhibit high discharge capacity, excellent cyclic stability and good rate capability. High discharge capacity of 248 and 214  $\text{mA h g}^{-1}$  can be obtained at the current density of 300 and 500  $\text{mA g}^{-1}$ , respectively. Meanwhile, it maintains a stable capacity of 113  $\text{mA h g}^{-1}$  after 200 cycles at a high current density of 2000  $\text{mA g}^{-1}$  with no capacity decay. The superior electrochemical performances may be attributed to the novel nanobelts structure and excellent structural stability of  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$ .

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## 1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used in portable electronic products and even electric vehicles (EVs) because of their high specific capacity, high power and energy density, long cycle life and environmental benignity [1–3]. The commercial cathode materials for LIBs are mainly  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiFePO}_4$ . However, these cathode materials suffer from low

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capacity that cannot completely meet the practical needs of large-scale and high-power applications [4–7]. From the perspective of improving the capacity,  $V_2O_5$ , with a high theoretical capacity of  $440 \text{ mA h g}^{-1}$  when 3  $\text{Li}^+$  ions are intercalated [8], has attracted much research attention [9–11]. However, the poor cyclic stability and high-rate capability of  $V_2O_5$  resulted from the low lithium ions diffusion coefficient and electronic conductivity have highly restricted their potential practical applications [12,13].

Recent studies imply that doping metal cations into  $V_2O_5$  layers is conducive to stable the whole structure [14], create more intercalation sites [15], or improve the intrinsic conductivity [16]. Considering these advantages, vanadate cathode materials have been intensively studied in the past few years [17–21]. As a typical silver vanadates,  $\text{Ag}_2\text{V}_4\text{O}_{11}$  with high theoretical capacity of  $315 \text{ mA h g}^{-1}$ , high-rate capability and long-term reliability has been commercially used as a cathode material in Li/SVO batteries [21]. Copper vanadates, such as  $\text{CuV}_2\text{O}_6$ , can deliver high initial discharge capacity ( $\text{CuV}_2\text{O}_6$  nanowires reported by Ma et al. exhibits a high specific discharge capacity of  $514 \text{ mA h g}^{-1}$  at  $20 \text{ mA g}^{-1}$ ) [17]. However, the cycling performances of silver and copper vanadates are unsatisfactory. To explore new vanadates as cathode for LIBs,  $\text{NiV}_3\text{O}_8$  and  $\text{ZnV}_2\text{O}_6$  also have been studied [20,22]. High initial capacity of  $347 \text{ mA h g}^{-1}$  can be achieved at  $30 \text{ mA g}^{-1}$ , and after 40 cycles,  $289 \text{ mA h g}^{-1}$  is maintained for  $\text{ZnV}_2\text{O}_6$  [20]. Potassium vanadates demonstrate good cycling performance at low current densities [19,23,24], but the rate performance need to be further improved.

Sodium vanadates are given great expectation as the cathode material for LIBs due to their high specific capacity, good reversibility, good rate capability and low cost [25–37]. Liu et al. have reported  $\text{NaV}_6\text{O}_{15}$  nanorods and investigated its electrochemical behavior as cathode material for LIBs [28]. R. Baddour-Hadjean et al. have found that  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  have three well-defined voltage plateaus and no phase transition occurs upon lithium intercalation process [30]. Wang et al. reported an ultrathin  $\text{Na}_{1.08}\text{V}_3\text{O}_8$  nanosheets with superior rate capability up to 50 C and good cycling performance as cathode material for LIBs [36]. In our previous work, the layer-by-layer stacked  $\text{Na}_{1.1}\text{V}_3\text{O}_{7.9}$  nanobelts [35],  $\text{Na}_{1.25}\text{V}_3\text{O}_8$  nanobelts [34], and mesoporous flake-like  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  [33], have been reported and their lithium intercalation properties are studied. Our previous work demonstrates the excellent structural stability and superior cyclic stability of sodium vanadates. Besides, sodium vanadates are also the ideal choice for sodium-ion battery cathodes [38–42]. Obviously, developing new sodium vanadates as cathode for lithium-ion or sodium-ion batteries is critical for the energy field.

In this work, we have introduced a facile hydrothermal reaction for the preparation of  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  nanobelts. The as-prepared  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  demonstrates the layer-by-layer stacked nanobelts structure. To the best of our knowledge,  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  material has not ever been reported as cathode for lithium-ion or sodium-ion batteries. Herein, for the first time, we evaluated the  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  nanobelts as cathode for LIBs, it exhibits superior performances including high specific capacity, excellent cyclic stability and high-rate capability, which is much better than those of many previous reported metal vanadium oxides. The superior performances may be attributed to the layer-by-layer stacked nanobelts structure and good structural stability upon cycling.

## 2. Experimental

### 2.1. Materials synthesis

All of the chemical reagents are of analytical grade and used without further purification. In a typical synthesis,  $0.5 \text{ g NH}_4\text{VO}_3$

was dispersed in 30 mL deionized water with magnetic stirring until form light yellow liquid at  $80 \text{ }^\circ\text{C}$ . Then  $0.722 \text{ g NaCl}$  and  $0.1781 \text{ g Sodium Dodecyl Sulfate}$  (abbreviated to SDS) were added under vigorous stirring. After continuous stirring for 30 min, the mixed solution was transferred to 50 mL Teflon-lined stainless autoclave and heated at  $200 \text{ }^\circ\text{C}$  for 12 h. After cooling down naturally, the precursors were collected by centrifugation and washed twice with pure ethanol, followed by drying at  $80 \text{ }^\circ\text{C}$  in vacuum for 12 h. Finally, the as-prepared precursors were annealed in air at  $400 \text{ }^\circ\text{C}$  for 4 h with a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ .

### 2.2. Structure characterization

The crystal phase identification of the as-synthesized powder was investigated by X-ray diffraction (XRD, Rigaku D/max 2500, XRD with  $\text{Cu K}\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ). Data for Rietveld structure refinement was obtained in the  $2\theta$  range of  $5\text{--}120^\circ$  with a  $0.02^\circ$  step interval and a 10 s step time. The chemical composition of samples was determined with an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The morphologies and structural characterization were conducted on a scanning electron microscopy (SEM, FEI Sirion200) and transmission electron microscopy (TEM, HEMe2100F/UHR).

### 2.3. Electrochemical measurements

The electrochemical performances were evaluated via stainless-steel coin cells (CR 2016).  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$ , acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 7:2:1 were mixed and dispersed in N-methyl-2-pyrrolidone (NMP) solution to make the slurry. The mixed slurry was coated on an aluminum foil and dried in a vacuum oven at  $100 \text{ }^\circ\text{C}$  for 12 h prior to coin-cell assembling. The cells were assembled in a glove box (Mbraun, Germany) filled with ultra-high purity argon, Li metal was used as counter electrode, polypropylene membrane as the separator, and 1 M  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 v/v) as the electrolyte. The cyclic voltammetry (CV) of Li/ $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  coin cell was tested using an electrochemical workstation (CHI660C, China) at a scan rate of  $0.1 \text{ mV s}^{-1}$  between 1.5 and 4 V. The galvanostatic charge/discharge experiments were performed in a potential range of 1.5–4 V at room temperature using a multichannel batteries testing system (Land CT2001A). The electrochemical impedance spectrometry (EIS) was tested by IM6ex (ZAHNER elektrik, Germany).

## 3. Results and discussion

The crystal structure of as-prepared  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  is confirmed by X-ray diffraction and Rietveld refinements. As shown in Fig. 1, the strong and sharp diffraction peaks indicate that the sample is well-crystallized. All the diffraction peaks can be well indexed to the monoclinic  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  phase [space group:  $C2/m$ , JCPDS card 75–1653] [43]. The lattice parameters via Rietveld refinements are  $a = 15.4045 \text{ \AA}$ ,  $b = 3.6101 \text{ \AA}$ , and  $c = 10.0740 \text{ \AA}$ , corresponding to a cell volume of  $V = 527.96 \text{ \AA}^3$ . No impurity phase is detected, illustrating the high purity of the as-prepared  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  nanobelts. The strongest peak is assigned to (200), suggesting that the  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  nanobelts exhibit preferential crystal orientation with a (200) facet. The chemical composition of sample was examined by ICP-OES measurement, shown in Table 1. The calculation result shows a molar ratio of Na: V = 0.755:6, which also confirm that the as-prepared sample consists of  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$ .

The morphology of as-prepared  $\text{Na}_{0.76}\text{V}_6\text{O}_{15}$  nanobelts is studied by SEM and TEM. As showed in Fig. 2a, the sample is composed of a large quantity of one-dimensional nanobelts with length ranging

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