



# Hierarchical vanadium pentoxide microflowers with excellent long-term cyclability at high rates for lithium ion batteries



Liang Chen<sup>a</sup>, Xin Gu<sup>a</sup>, Xiaolei Jiang<sup>a</sup>, Nana Wang<sup>a</sup>, Jie Yue<sup>a</sup>, Huayun Xu<sup>a</sup>, Jian Yang<sup>a,\*</sup>, Yitai Qian<sup>a,b,\*\*</sup>

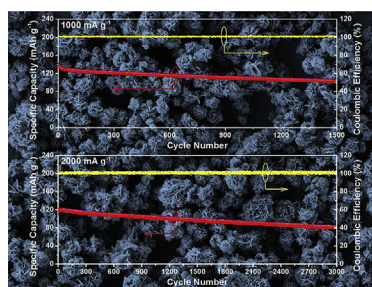
<sup>a</sup> Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, and School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, Shandong, PR China

<sup>b</sup> Hefei National Laboratory for Physical Science at Microscale, Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China

## HIGHLIGHTS

- V<sub>2</sub>O<sub>5</sub> microflowers composed of thin nanosheets are prepared by a two-step process.
- V<sub>2</sub>O<sub>5</sub> microflowers exhibit a capacity of 126 mAh g<sup>-1</sup> at 200 mA g<sup>-1</sup> over 150 cycles.
- The capacity could retain at 104 mAh g<sup>-1</sup> after 1500 cycles at 1 A g<sup>-1</sup>.
- The performance can be associated with their structure and capacitive contribution.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 24 June 2014

Received in revised form

2 September 2014

Accepted 5 September 2014

Available online 16 September 2014

### Keywords:

Vanadium oxide

Solvothermal synthesis

Hierarchical structure

Lithium ion batteries

## ABSTRACT

Hierarchical V<sub>2</sub>O<sub>5</sub> microflowers composed of thin nanosheets have been achieved by a solvothermal reaction first and then a low-temperature calcination. These micro-flowers are characterized by powder X-ray diffractometer (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). The nanoscale size and sheet-like structure of the building blocks in V<sub>2</sub>O<sub>5</sub> microflowers make them a promising cathode material for lithium ion batteries. After 1500 cycles at a current density of 1 A g<sup>-1</sup>, the reversible capacity of V<sub>2</sub>O<sub>5</sub> microflowers is kept at 104 mAh g<sup>-1</sup>. Even at a rate of 2 A g<sup>-1</sup>, the reversible capacity is still above 80 mAh g<sup>-1</sup> after 3000 cycles. The excellent electrochemical properties of V<sub>2</sub>O<sub>5</sub> microflowers are associated with their unique structure and capacitive feature.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

As a clean and reliable energy storage device, lithium-ion batteries (LIBs) have been widely applied in many portable electronics. But the

electrode materials in the commercial LIBs could not meet the needs for large energy density and high power density. Among the promising materials, vanadium oxides constructed by layered structures are very attractive for LIBs. Due to a variety of oxidation states of vanadium (+5, +4, +3, and +2), there is a rich chemistry associated with them [1]. In various vanadium oxides, V<sub>2</sub>O<sub>5</sub> has been demonstrated as one of the appealing candidates due to its low cost and high abundance as well as high theoretical capacity. However, V<sub>2</sub>O<sub>5</sub> suffers from its low ionic diffusivity (10<sup>-12</sup>–10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup>) [2,3] and its bad structure stability, leading to low capability and poor cyclability.

\* Corresponding author. Tel./fax: +86 531 88364489.

\*\* Corresponding author. Key Laboratory of Colloid and Interface Chemistry, Ministry of Education School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, Shandong, PR China. Tel.: +86 531 88366360.

E-mail addresses: [yangjian@sdu.edu.cn](mailto:yangjian@sdu.edu.cn) (J. Yang), [ytqian@ustc.edu.cn](mailto:ytqian@ustc.edu.cn) (Y. Qian).

In order to address these issues, many efforts have been devoted to the controls on the size, shape and structure of  $V_2O_5$ . As a result, various nanostructures of  $V_2O_5$ , such as nanoparticles [4–6], nanorods [7], nanotubes [8], nanowires [9,10], nanobelts [11,12] and nanosheets [13,14], have been synthesized and evaluated as electrode materials. Nanoscale size of these structures could increase the electroactive surface area, shorten the diffusion distance of  $Li^+$ , and alleviate the mechanical stress upon cycling, all of which promotes the rate capability and cycling stability. However, nanostructures always give rise to low volumetric energy density [15], which is against their applications in LIBs. Moreover, the expanded contact between electrolyte and nanostructures is also likely to enhance side reactions and reduce thermal stability [15]. In light of this, the assembly of nanostructures into hierarchical microparticles might be a good solution. Based on this concept, Lou et al. synthesized porous  $V_2O_5$  micro-spheres composed of uniform nanofibers as a cathode for LIBs, which exhibited a specific capacity of  $130 \text{ mAh g}^{-1}$  after 100 cycles at  $0.5C$  ( $\sim 75 \text{ mA g}^{-1}$ ) [15]. Wang and Su fabricated porous  $V_2O_5$  microspheres constructed of cross-linked nanobricks, which showed the reversible capacities of 100 and  $85 \text{ mAh g}^{-1}$  over 100 cycles at  $0.5C$  and  $1C$  ( $1C = 150 \text{ mA g}^{-1}$ ) [16]. Mai and his coworkers prepared porous  $V_2O_5$  microplates by the thermolysis of  $NH_4VO_3$  [17]. The microplates preserved the reversible capacities of 123 and  $108 \text{ mAh g}^{-1}$  after 100 cycles at  $1 \text{ A g}^{-1}$  and  $2 \text{ A g}^{-1}$ . The same group fabricated  $V_2O_5$  microflowers by a supercritical solvothermal reaction followed by a high-temperature calcination [18]. These microflowers kept a discharge capacity of  $108 \text{ mAh g}^{-1}$  after 200 cycles at  $10C$  ( $1C = 147 \text{ mAh g}^{-1}$ ). However, this preparation of  $V_2O_5$  microflowers is time-consuming, which needs at least 9 days. Recently, hollow microflowers composed of  $V_2O_5$  nanosheets were obtained by a similar but efficient procedure [19]. The hollow microflowers could deliver a discharge capacity of  $\sim 130 \text{ mAh g}^{-1}$  after 100 cycles at  $300 \text{ mAh g}^{-1}$ . But the hollow structures reduce the volumetric energy density.

Herein, hierarchical  $V_2O_5$  microflowers are synthesized by a time-efficient and facile process. These microflowers constructed by discrete and thin nanosheets, exhibit excellent electrochemical properties for lithium storage, particularly for the long-term cycling at high rates. They could preserve a reversible capacity of  $104 \text{ mAh g}^{-1}$  after 1500 cycles at a current density of  $1000 \text{ mA g}^{-1}$ . Even after 3000 cycles at  $2000 \text{ mA g}^{-1}$ , the specific capacity is still kept above  $80 \text{ mAh g}^{-1}$ . These  $V_2O_5$  microflowers not only present the longest cycle life to the best of our knowledge, and also the ultralow fading rate per cycle. The outstanding performances are associated with their structure and the capacitive component in the specific capacity.

## 2. Experiment section

### 2.1. Materials synthesis

In a typical procedure,  $NH_4VO_3$  (0.77 g) and oxalic acid (1.25 g) in a molar ratio of 2:3 were dissolved in 10 mL of deionized water, producing a dark green solution. Then, 2 mL of this solution was added into 35 mL of isopropanol. Due to the decreasing of the solvent polarity, some solutes precipitated from the solution. The suspension was centrifuged to obtain a clear solution. After that, the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 45 mL and kept at  $200 \text{ }^\circ\text{C}$  for 6 h. The resulting product was collected and washed with deionized water and absolute ethanol thoroughly. After dried at  $60 \text{ }^\circ\text{C}$  overnight in a vacuum oven, the product was calcined at  $350 \text{ }^\circ\text{C}$  for 2 h in air with a heating rate of  $1 \text{ }^\circ\text{C min}^{-1}$  to produce highly-crystallized  $V_2O_5$  microflowers.

### 2.2. Structure characterization

X-ray powder diffraction (XRD) patterns were achieved on a Bruker D8 advanced X-ray diffractometer with  $Cu \text{ K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The structure and morphology of the products were observed by a field emission scanning electron microscope (SEM, SUPRA<sup>TM</sup> 55), a transmission electron microscope (TEM, JEM-1011) with an accelerating voltage of 100 kV. Nitrogen sorption isotherm was examined on a Micromeritics ASAP-2020HD88 instrument at 77 K.

### 2.3. Electrochemical measurements

The electrochemical tests were examined by CR2032 coin cells. The working electrode was composed of 70 wt% active material ( $V_2O_5$ ), 20 wt% acetylene black as the conductive additive, and 10 wt% poly(vinylidene fluoride) (PVDF) as a binder. The slurry was coated on an aluminum foil and the coated foil was dried in vacuum at  $60 \text{ }^\circ\text{C}$ . The resulting films were pressed and punched into the discs with a diameter of 12 mm and used as a cathode. The typical disk electrode contained active material of  $\sim 1 \text{ mg cm}^{-2}$ . Then, it was assembled in an argon-filled glove box (Mikrouna, Super 1220/750/900) with a lithium foil as the counter and reference electrode, a mixture of 1 M  $LiPF_6$  in ethylene carbonate (EC)–ethyl methyl carbonate (EMC)–dimethyl carbonate (DMC) (1:1:1 by volume) as the electrolyte, and a Celgard 2300 micro-porous membrane as the separator. Galvanostatic discharge–charge cycles of cells were performed at room temperature using Land CT2001A battery cycler (Xinnuo, Wuhan China) in a voltage range of 2.5–4.0 V at different current densities. Cyclic voltammetry (CV) was measured by a LK2005A electrochemical workstation between 2.5 V and 4.0 V at various scan rates. Electrochemical impedance spectra (EIS) were acquired on an Autolab Potentiostat Galvanostat (PGSTAT204) over a frequency range of 100 kHz to 0.01 Hz.

## 3. Results and discussion

The product obtained by a solvothermal reaction between ammonium vanadate and oxalic acid, is characterized with a field-emission scanning electron microscope (FESEM). As shown in Fig. S1A, the product consists of uniform flower-like micro-spheres with an average size of around  $2 \text{ }\mu\text{m}$ . The magnified FESEM image (Fig. S1B) reveals that the microflowers are assembled by many thin nanosheets, which is also confirmed by transmission electron microscope (TEM) images in Fig. S1C and D. The powder X-ray diffraction (XRD) pattern (Fig. S2) reveal the poor crystallinity of these microflowers and could not be attributed to any known vanadates.

After calcination at  $350 \text{ }^\circ\text{C}$  for 2 h, these microflowers are converted to  $V_2O_5$  with the same morphology. Fig. 1A shows the XRD pattern of these  $V_2O_5$  microflowers (VFs). All the reflections can be indexed as orthorhombic-phase  $V_2O_5$  (JCPDS card No. 41-1426, space group:  $Pmmm$ ). It exhibits a unique layered structure in which the layers are constructed by square pyramids of  $[VO_5]$  via the edges and corners sharing (inset of Fig. 1A). This layered structure offers convenient pathways for lithium ions to diffuse in and out. The calculated lattice constants are  $11.502 \text{ \AA}$  for  $a$ ,  $3.56 \text{ \AA}$  for  $b$ ,  $4.36 \text{ \AA}$  for  $c$ , very close to the reported ones ( $a = 11.51 \text{ \AA}$ ,  $b = 3.565 \text{ \AA}$ ,  $c = 4.372 \text{ \AA}$ ). But the reflection intensity of  $\{110\}$  is extraordinarily high in comparison to the reported, suggesting the preferential growth of  $V_2O_5$ . This has been directly demonstrated by SEM and TEM images. As described in Fig. 1B, the product is predominant by a large number of rough microspheres with their sizes over  $2\text{--}4 \text{ }\mu\text{m}$ . A close-up view on the surface of a single microsphere (Fig. 1C and D) reveals that it is assembled by many

Download English Version:

<https://daneshyari.com/en/article/1284007>

Download Persian Version:

<https://daneshyari.com/article/1284007>

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