Electrochimica Acta 188 (2016) 625–635

Contents lists available at ScienceDirect

Electrochimica Acta

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

Synthesis and characterization of novel hierarchical starfish-like vanadium oxide and their electrochemical performance

Xing Liang, Guohua Gao*, Guangming Wu*, Huiyu Yang

Shanghai Key Laboratory of Special Artificial Microstructure materials and technology, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China

ARTICLE INFO

Article history:
Received 15 October 2015
Received in revised form 18 November 2015
Accepted 7 December 2015
Available online 9 December 2015

Keywords:
vanadium oxide
hierarchical starfish-like structure
cathode material
lithium ion batteries

ABSTRACT

A novel hierarchical starfish-like vanadium oxide is synthesized by a simple and direct hydrothermal method using a functional V_2O_5 sol as a vanadium source. The formation mechanism of hierarchical starfish-like structure is discussed. Results demonstrate that the functional V_2O_5 sol plays a crucial role in the formation of a hierarchical starfish-like structure. Starfish-like vanadium oxide is composed of single crystals of a metastable VO_2 (B) phase that grow along the (1 1 0) plane and four oblique sheets growing on the flanks of the (1 1 0) plane. The starfish-like structure can be preserved and undergoes phase transition to the orthorhombic V_2O_5 phase when calcined at 350 °C. Hierarchical starfish-like V_2O_5 displays higher electrochemical performance than pristine V_2O_5 powder as a cathode material for LIBs. This improved performance could be attributed to the shortened diffusion path of lithium ions in the former; a large electrode/electrolyte contact area resulting from the unique hierarchical starfish-like structure composed of nanosheets also offers better electrolyte wetting and alleviates the structural degradation upon cycling. The hierarchical starfish-like V_2O_5 can deliver a discharge capacity of approximately 163 mA h g^{-1} at a high current density of 1000 mA g^{-1} (5C) even after 50 cycles.

1. Introduction

Lithium-ion batteries (LIBs) have attracted significant research attention because of their extensive applications in portable electronic devices [1]. However, the applications of these batteries in electrical vehicles (EVs) and hybrid electrical vehicles (HEVs) are limited because of the low energy and power density of current commercial LIBs [2]. Therefore, developing high-performance cathode materials is necessary to meet the demands for use in EVs and HEVs. Vanadium pentoxide (V_2O_5), a potential cathode materials, is a unique intercalation compound that has attracted great interest because of its low cost and high theoretical capacity of 442 mA h g^{-1} when intercalated with three lithium ions [3]. This feature is a significant advantage compared with other cathode materials, such as $LiCoO_2$ (140 mA h g^{-1}), $LiMn_2O_4$ (148 mA h g^{-1}) and $LiFePO_4$ (170 mA h g^{-1}) [4–8]. However, V_2O_5 suffers from poor rate capacity and cycling stability because of its several intrinsic flaws, including a low ion diffusion coefficient ($\sim 10^{-12}$ cm^2 s^{-1}), poor electronic conductivity ($10^{-2} \sim 10^{-3}$ S cm^{-1}), and irreversible structural changes during cycling [9–11].

To overcome these drawbacks and improve the diffusion capacity of lithium ions in vanadium oxides, various nanostructures, such as nanowires [12,13], nanotubes [14,15], nanofibers [16,17], nanosheets [18,19], nanospheres [20,21], and nanoflowers [22,23], have been synthesized. Among these nanostructured materials, two-dimensional (2D) nanosheets show excellent electrochemical properties, which are attributed to their fast charge transfer and short diffusion path [24–26]. Compared with one-dimensional (1D) and two-dimensional (2D) structures, three-dimensional (3D) hierarchical structures with nanoscale building blocks can realize efficient electron/ion transport and a stable structure during cycling process. Consequently, these 3D hierarchical structure materials may potentially exhibit excellent rate capabilities and long-term cycling stability when used as cathode materials of LIBs [23,27–30]. A some common explanation for the excellent electrochemical performance of 3D hierarchical structures is that these materials can not only enlarge the contact area between the electrode and electrolyte, shorten the pathway of electrons/ions transport, effectively facilitate ionic diffusion, but also accommodate the volume changes upon cycling and maintain the hierarchical network structure cycling stability [31–33]. Therefore, the synthesis of hierarchical structures composed of nanosheets is desirable. Hierarchical structures would inherit the superior characteristics of their nanoscalar building blocks, and

* Corresponding authors.
E-mail addresses: gao@tongji.edu.cn (G. Gao), wugm@tongji.edu.cn (G. Wu).

http://dx.doi.org/10.1016/j.electacta.2015.12.057
0013-4686/

gain additional benefits from the unique secondary structures produced.

In our previous work, we prepared a functional V_2O_5 sol via a sol-gel method and studied the hydrolysis growth process of this sol [34,35]. Based on our research results, we report a simple hydrothermal method to synthesize a novel vanadium-based nanostructure that uses this sol as a vanadium source. The resulting nanostructure, which resembles a hierarchical starfish composed of nanosheets, presents good electrolyte penetration and a shortened lithium ion diffusion path. While star-shaped vanadium oxide has been reported in the previous literatures, the electrochemical performance of this material has not been extensively studied [36,37]. The V_2O_5 hierarchical starfish was subsequently used as a cathode material for LIBs, and good specific capacity and remarkable rate capability compared with those of pristine V_2O_5 powder were obtained; such qualities may be attributed to the unique hierarchical starfish structure composed of nanosheets.

2. Experimental

2.1. Synthesis of V_2O_5 sol

V_2O_5 sol was prepared from commercial V_2O_5 powder via heating reflux. Briefly, raw V_2O_5 powder was immersed in benzyl alcohol and isopropanol (molar ratio of 1:4:40), and then the suspension was heated at 110 °C under a water-cooled distilling flask for 4 h to form the vanadium oxide (VO_x) oligomers. After filtration, unreacted V_2O_5 was removed through distillation and centrifugation to obtain the light yellow V_2O_5 sol; the V_2O_5 content of this sol is ~55 mg ml^{-1}. In this reaction, benzyl alcohol functioned as a reducing agent and isopropanol functioned as a solvent. The as-prepared V_2O_5 sol is highly sensitive to water, and hydrolysis can rapidly occur even in air [35].

2.2. Preparation of hierarchical starfish-like structure

Exactly 2 ml of absolute ethanol was added to 15 ml of the as-prepared V_2O_5 sol under vigorous stirring. After approximately 10 min, 30 ml of deionized water was added to the mixture under rapid stirring to obtain a red-brown viscous slurry. The final slurry was transferred into a 50 ml Teflon-lined autoclave with a stainless steel shell. The autoclave was kept at 180 °C in a constant temperature oven for 7 days. Finally, the precipitate was filtered before washing with absolute ethanol and deionized water. Samples were calcined at 350 °C for 1 h at a heating rate of 3 °C min^{-1} in air.

2.3. Material characterizations

The morphology and structure of the samples were observed by field emission scanning electron microscopy (FESEM, Philips-XL-30FEG) and transmission electron microscopy (TEM, JEOL-1230). X-ray powder diffraction (XRD) patterns were obtained by using a RigakuD/Max-C diffractometer with Cu Kα radiation source (λ = 1.5406 Å). Nitrogen adsorption isotherms for calculating the Brunauer-Emmett-Teller (BET) surface area were measured using an Autosorb-1 (Quantachorme) analyzer.

2.4. Electrochemical measurements

The working electrodes (cathode) were prepared by mixing 70 wt% active materials, 20 wt% carbon black as a conducting agent and 10 wt% poly (vinylidene fluoride) (PVDF) as a binder. N-

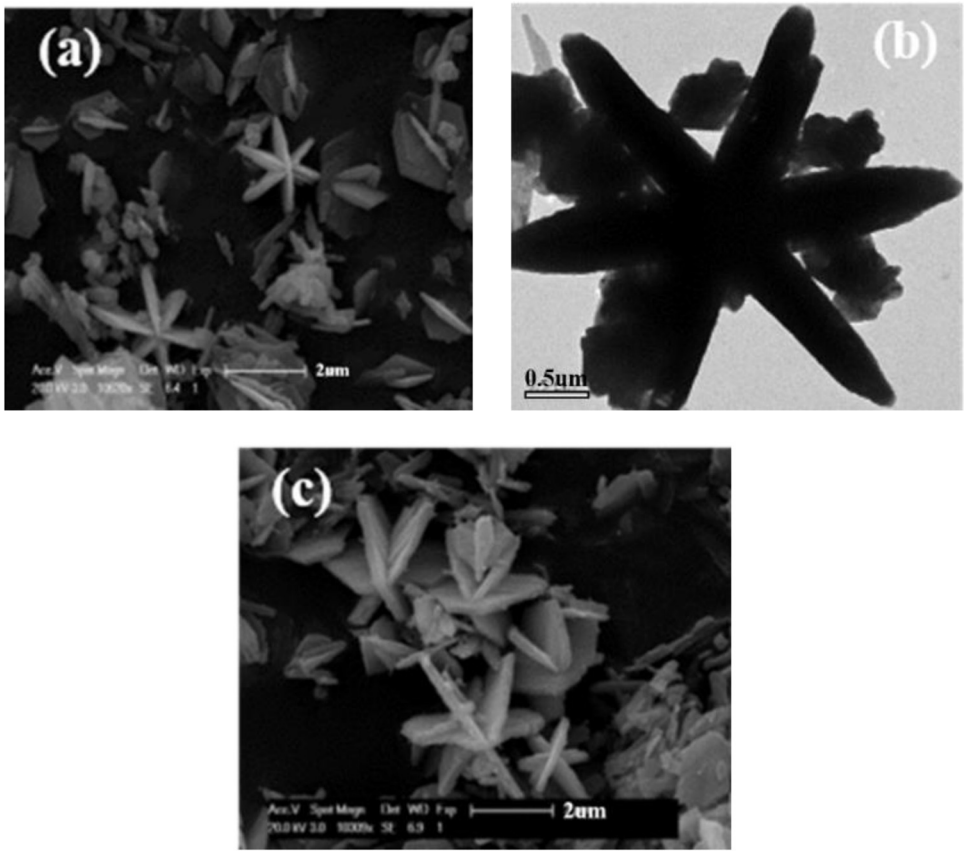

Fig. 1. characterization of the prepared vanadium oxide. (a and b) FESEM and TEM images of as-prepared samples, respectively. (c) FE-SEM image of calcined samples.