Materials Research Bulletin 74 (2016) 90–95

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Microwave-assisted hydrothermal synthesis of V_2O_5 nanorods assemblies with an improved Li-ion batteries performance

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ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form 20 August 2015
Accepted 7 October 2015
Available online xxx

Keywords:
A. Nanostructures
A. Oxides
B. Chemical synthesis
D. Electrochemical properties
D. Energy storage

ABSTRACT

Vanadium pentoxide nanorods assemblies were synthesized by a microwave-assisted hydrothermal synthesis, combined with subsequently annealing treatment. The structure and morphology of the nanorods were characterized by XRD, FESEM and HRTEM, and the electrochemical properties of the electrodes made from the V_2O_5 nanorods were investigated. The V_2O_5 nanorods with an average diameter of 100 nm and lengths up to several micrometers are almost parallel distributed in the assemblies. The V_2O_5 nanorods assemblies exhibit an initial discharge capacity of 330 mAh g^{-1} at a current density of 50 mA g^{-1}, which is very higher than that of the separated V_2O_5 nanorods. The V_2O_5 nanorods assemblies also show a lower capacity fading rate in comparison with the separated V_2O_5 nanorods. A low polarization of the charge transfer reaction and a high diffusion rate of lithium ion inside the electrode composed of the paralleled nanorods are considered responsible for the enhanced capacity.

1. Introduction

One-dimensional (1D) nanostructured materials like nanowires, nanobelts and nanotubes have attracted much attention recently in lithium-ion batteries (LIBs) because of their short Li-ion insertion/extraction distance, facile strain relaxation upon electrochemical cycling and directional electron transport properties [1]. 1D nanostructures also can efficiently transport charge carriers and maintain an effective contact area with electrolyte in rechargeable battery because of the size confinement effect and large specific surface area. Great progress has been made over the last two decades in synthesizing different kinds of 1D nanostructures [2], a formidable challenge, however, is to assemble these nanoscale building blocks into an organized assemblies to achieve the desired properties. Different methods, such as dielectrophoretic assembly [3], microcontact printing [4], and lithographic strategies [5] have been explored to construct 1D nanostructure assemblies.

V_2O_5 possesses a multiple valence state and a layer structure that can facilitate the insertion of Li-ion between the layers, and thus has received particular interest as promising cathode material for LIB [6,7]. The intercalation of lithium ions into the V_2O_5 interlayers closely relates to the formation of $Li_xV_2O_5$ ($0 < x < 2$) [2], and the Li^+ can continue insert even at $2 < x < 3$, leading to a higher output voltage [8]. As a cathode material in LIBs, V_2O_5 can yield the maximum theoretic capacity of 440 mAh g^{-1} based on the intercalation of three lithium ions, which is nearly twice higher than that of $LiCoO_2$ (148 mAh g^{-1}) [9], and $LiFePO_4$ (170 mAh g^{-1}) [10]. Different methods have been proposed to prepare V_2O_5 hierarchical nanostructures, such as hydrothermal reaction [11,12] and ultrasonic spray pyrolysis [13]. Nevertheless, most of above-mentioned methods are time-consuming and require high temperature to achieve a higher crystallinity. The microwave irradiation has become increasingly popular because of a rapid volumetric heating to the required temperature with quick crystallization rate, a shorter reaction time, high reaction selectivity and energy saving compared with the conventional heating methods [14]. The study on the synthesis of V_2O_5 nanostructures by microwave irradiation is very few except for VO_2 nanocrystals [15–17]. In this paper, we report the microwave-assisted synthesis and electrochemical properties of V_2O_5 nanorods assemblies, and it was found that the assemblies show a higher and more stable electrochemical capacity in comparison with the separate V_2O_5 nanorods.

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http://dx.doi.org/10.1016/j.materresbull.2015.10.020
0025-5408/

2. Experimental

2.1. Materials and synthesis

All chemicals were analytical grade and used without further purification. In a typical preparation of V_2O_5 nanorods (sample A), a solution containing 2.75 mmol V_2O_5, 2.22 mmol oxalic acid and 30 ml H_2O was firstly mixed and stirred for 6 h, and then transferred to a Teflon-lined autoclave with a Teflon shell and put in the microwave-oven (MARS 6, CEM). The autoclave was heated at the rate of 10 K/min and kept at final temperature of 200 °C for 30 min. The reaction temperatures are measured by its pressure provided by the MARS 6 system. The obtained black product was washed with distilled water for several times to remove the unreacted amide and decomposition product, then dried at 70 °C for 24 h, and finally annealed at 300 °C in air for 1 h. For the synthesis of V_2O_5 nanorods assemblies (sample B), an additional 1 ml triethanolamine (TEA) was added slowly in the above mentioned solution and stirred for another 1 h. The following procedures are the same as preparing V_2O_5 nanorods.

2.2. Characterization

The structures of the samples were characterized by X-ray diffraction (XRD, X'Pert Pro MPD), field emission scanning electron microscopy (FESEM, Sirion 200) and high resolution electron microscopy (HRTEM, JEM 2010). Specific surface area was evaluated through measuring N_2 adsorption-desorption isotherms at 77 K with a Autosorb iQ Station.

2.3. Electrode and electrochemical characterization

To investigate the electrochemical properties, the mixture of the final products (80 wt%), acetylene black (10 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in *N*-methylpyrrolidone (NMP) solution was coated on Al foil current collector and dried under vacuum at 70 °C for 10 h. And then the coated Al foil was cut into disc electrodes with diameter of 14 mm by punch. The electrochemical properties of the electrodes were measured using CR2032 coin-type cells in an argon filled glove box using lithium foil as anode and 1 M solution of $LiPF_6$ in ethylene carbonate and diethyl carbonate (EC/DEC) as the electrolyte. Galvanostatic measurements of the cells were carried out under different current densities within 2–4 V using a Land 2001A battery testing system at room temperature. Cyclic voltammetry experiment was carried out with a VMP3 multichannel electrochemical workstation at a scanning rate of 0.2 mV s^{-1} in the range of 2–4 V vs. Li/Li^+.

3. Results and discussion

3.1. Synthesis of V_2O_5 nanorods

Fig. 1 shows XRD patterns of sample A before and after annealing treatment. One can see that all the diffraction peaks can be indexed to monoclinic VO_2 (B) (JCPDS Card no. 81-2392) after microwave irradiation without annealing treatment, see curve (1) in Fig. 1. After annealing treatment all the diffraction peaks can be indexed to orthorhombic α-V_2O_5 (JCPDS Card no. 041-1426), and no peaks of any other phases are detected, indicating the high purity of the V_2O_5 phase, see curve (2) in Fig. 1. The same results are obtained for sample B. These results indicate that a metastable VO_2 (B) phase is obtained after microwave treatment, and after subsequently annealing treatment the metastable VO_2 (B) phase completely transforms to α-V_2O_5 phase.

Fig. 2 shows typical FESEM images of samples A and B after annealing treatment. One can see that the sample A has a rod-like structure with an average diameter of about 100 nm and lengths between 500 nm and 2 μm. The V_2O_5 nanorods are all nearly

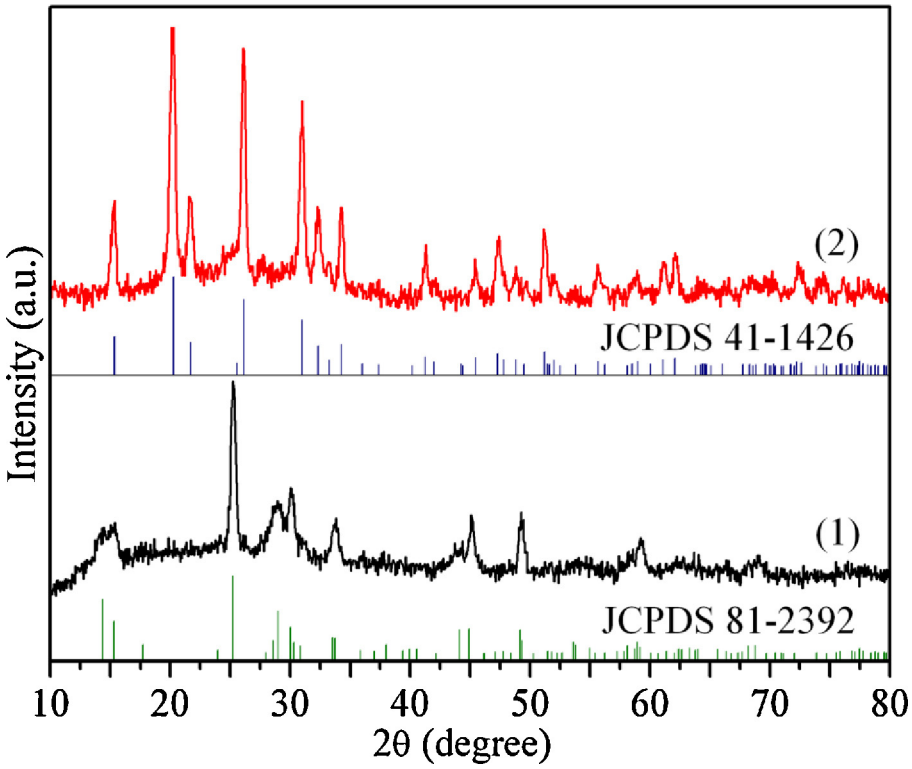

Fig. 1. XRD patterns of sample A before (curve (1)) and after (curve (2)) annealing treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)