Journal of Alloys and Compounds 613 (2014) 187–192

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Conductive surface modification of cauliflower-like WO_3 and its electrochemical properties for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 25 March 2014
Received in revised form 29 May 2014
Accepted 2 June 2014
Available online 14 June 2014

Keywords:
Lithium-ion batteries
Anode
Tungsten oxide
Hydrothermal reaction

ABSTRACT

Cauliflower-like WO_3 was synthesized by a hydrothermal reaction without a surfactant, followed by firing, and was investigated as an anode material for lithium-ion battery applications. The scanning electron microscope (SEM) and transmission electron microscope (TEM) characterization indicated that WO_3 nanorods had an aggregation framework and built a cauliflower morphology. With the objective of understanding the charge–discharge process within a voltage range of 0–3 V vs. Li^+/Li, in situ X-ray diffraction was used and a complex reaction of intercalation and conversion of WO_3 was revealed for the first time. The cauliflower-like WO_3 after being decorated with carbon provides a high gravimetric capacity of >635 mA h/g ($Li_{5.5}WO_3$) with good cycling and a high rate capability when used as an anode in lithium-ion batteries. Based on our studies, we attribute the high electrochemical performance to the nanoscopic WO_3 particles and a conductive carbon layer, which makes them a potential candidate for lithium-ion batteries.

1. Introduction

Metal oxides have been considered and investigated as alternative anodes for use in lithium ion batteries [1]. The research focus is on three different mechanism groups: intercalation–deintercalation reaction, alloying-dealloying reaction, and conversion (redox) reaction [2,3]. The intercalation–deintercalation mechanism (ex. TiO_2, $Li_4Ti_5O_{12}$, Nb_2O_5, KNb_5O_{13}, MoO_3, etc.) is that transition metal oxides and other compounds with a multi-dimensional layer structure can reversibly intercalate lithium ions into the lattice without destroying their crystal structure. Unfortunately, only a small number of lithium ions can be reversibly inserted into intercalation-type materials so that the specific capacity is limited [4–8]. The alloying-dealloying mechanism (ex. SnO_2, Sb_2O_3, ZnO_2, etc.) involving $MO_x + Li \rightarrow Li_yM + Li_2O$ is that metal (M) can form an alloy with lithium. The lithium alloying–dealloying reaction normally occurs at low potentials (below 1.0 V vs. Li^+/Li) and delivers high capacity values but fades extensively during the charge–discharge process [9,10]. The conversion mechanism (ex. NiO, CuO, Fe_2O_3, Fe_3O_4, Co_3O_4, etc.) usually produces metallic nanoparticles embedded in an insulating Li_2O matrix. Although the materials have generally much higher theoretical capacity than that of already-commercialized graphite, poor electrical conductivity and structural instability are the drawback [11–14].

Among the transition metal oxides, tungsten oxides (WO_2, WO_3, and $WO_3{\cdot}xH_2O$) as one of the important metal oxides with respect to physicochemical properties, have been extensively investigated for such applications as gas sensors, photocatalysis, electrochromic devices, electronic devices, dye-sensitized solar cells, supercapacitors, and lithium ion batteries [15,16]. The kinetics of the insertion reaction in metal oxides is often limited by the solid-state diffusion of the ions. The time constant in the process is determined by the chemical diffusion coefficient associated with the chemical structure and the pass length for ion transport connected with microstructure [17]. Interestingly, the tungsten oxides have better electronic conductivity ($10–10^{-6}$ S cm^{-1}) than some of the other oxides; in addition, they also rely on designing a nanostructured particle with a small radius and right crystalline phase for fast lithium-ion insertion and superior electrochemical performance [18,19].

From this point of view, a wide variety of approaches have been pursued over the years for the synthesis of tungsten oxides, such as nanoparticles, nanowires, nanorods, and nanoflowers using various approaches which include a hydrothermal reaction, combustion process, sol–gel process, solution-phase reaction, template directed method, mechanochemical activation, and hot-wire chemical vapor deposition (HWCVD) method [15,16,18,20–26]. However, most of

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http://dx.doi.org/10.1016/j.jallcom.2014.06.010
0925-8388/

the previous approaches led to the formation of monoclinic $W_{18}O_{49}$, hexagonal WO_3, and $WO_3{\cdot}xH_2O$ nanostructures. There have been very few studies on nanostructured monoclinic WO_3 (m-WO_3).

Here we report a facile hydrothermal process that obtains cauliflower-like carbon-coated WO_3 oxide with a high rate-capability and good cycling performance for lithium-ion batteries. The cauliflower-like carbon-coated WO_3 was characterized by X-ray diffraction (XRD), thermogravimetric-derivative thermal analysis (TGA/DTA), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), and electrochemical measurement. The motivation in this study was to explore the possibility of using m-WO_3 as an anode material for lithium-ion batteries and to elucidate its reaction mechanism with lithium during the charge–discharge process.

2. Experimental

The synthesis procedure is illustrated in Fig. 1. In a typical experiment, 25 mmol of sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, >99%, Aldrich) was dissolved in 100 ml deionized (DI) water with mild stirring. Oxalic acid ($H_2C_2O_4$, >99%, Aldrich) was added dropwise into the solution until the pH value reached 1.2 and tungstenic acid was precipitated thoroughly. Then the centrifuged precipitate was dissolved in 250 mL DI water, and 13 g of potassium sulfate (K_2SO_4, >99%, Aldrich) was added to the system. The prepared solution was transferred to a Teflon-lined autoclave and heated at 180 °C for 24 h with a heating/cooling rate of 2 °C/min. The resulting slurry was then filtered and washed with DI water before being dried in a vacuum oven. The powder was finally heated at 450 °C in air for 5 h. The cauliflower-like WO_3 (1 g) as synthesized above was dispersed in 20 mL of DI water and sonicated for a few minutes, followed by the addition of 1 g of D-glucose ($C_6H_{12}O_6$, >99.5%, Aldrich). The reaction mixtures were then transferred to a Teflon-lined autoclave and subjected to hydrothermal treatment at 180 °C for 12 h. The resulting slurry was then filtered and washed with DI water before being dried in a vacuum oven. The resulting material was isolated by centrifugation and further carbonized under Ar flow at 450 °C for 3 h.

The phase analysis of the synthesized samples was performed using a D8-Bruker X-ray diffractometer with Cu Kα radiation. To investigate any structural changes that may have occurred during electrochemical cycling, the in situ XRD was performed using a lab-made in situ cell. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a TA Instruments SDT 2960 in air at a heating/cooling rate of 10 °C/min. The morphology, microstructure, and composition of the synthesized samples were examined with a Hitachi S-4000 scanning electron microscope (SEM) and FEI Tecnai field emission transmission electron microscope (FE-TEM).

The electrodes for the electrochemical evaluation were prepared by mixing 70 wt.% active material powder, 15 wt.% carbon black (Super C65) as a conducting agent, and 15 wt.% polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidone (NMP) as a binder to form a slurry, followed by coating onto copper foil, pressing, and drying at 120 °C for 2 h in a vacuum. The CR2032 coin cells were assembled using polypropylene as a separator, lithium foil as the counter electrode, and 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) as the electrolyte. The charge–discharge experiments were performed galvanostatically at a constant current density of 50 mA/g of active material within the voltage range of 0–3 V vs. Li^+/Li. The electrochemical impedance spectroscopic analysis (EIS) was carried out with a Zahner zennium instrument by applying a 10 mV amplitude signal in a frequency range of 10 kHz to 0.01 Hz. For the EIS measurements, an active material content of ~3 mg served as the working electrode and lithium foil served as the counter and reference electrodes. The impedance response was measured after 20 cycles.

3. Results and discussion

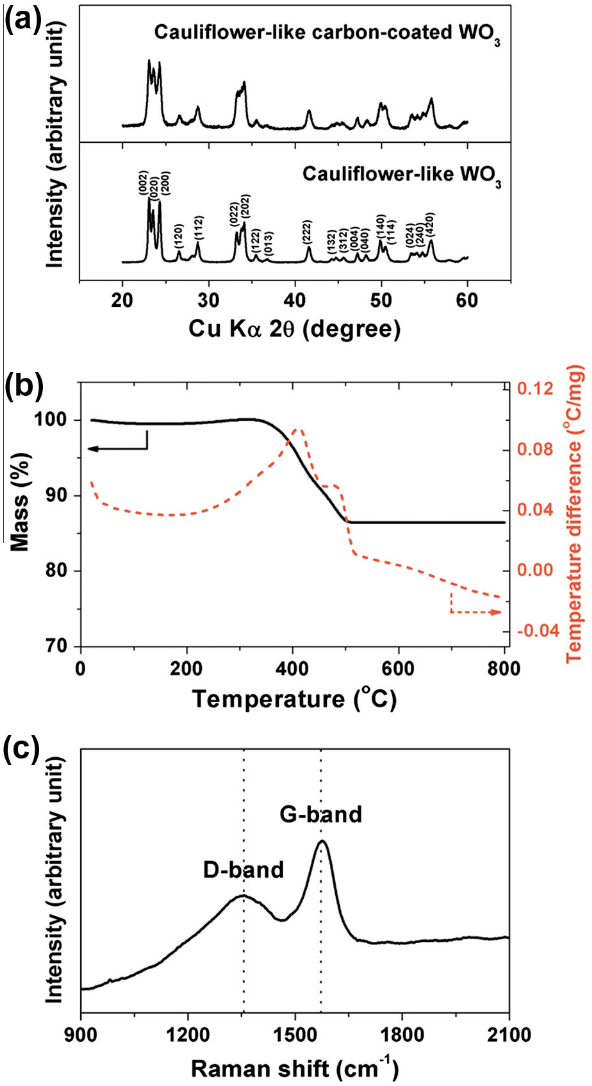

Fig. 2. (a) XRD patterns of cauliflower-like WO_3 and cauliflower-like carbon-coated WO_3 and (b) TGA/DTA plots of cauliflower-like carbon-coated WO_3.

The X-ray diffraction patterns of the cauliflower-like carbon-coated WO_3 and cauliflower-like WO_3 are shown in Fig. 2(a). All the reflections of samples before and after carbon coating could be indexed based on the m-WO_3 phase (JCPD No. 43-1035). No peaks corresponding to carbon in the cauliflower-like carbon-coated WO_3 are seen due to its amorphous nature. The carbon coating on the surface brought about a little weakening of the intensities of the XRD peaks. It also indicates that the carbon coating process did not destroy the structure of tungsten oxide. To obtain a better characterization of the carbon present in the cauliflower-like carbon-coated WO_3, a thermogravimetric-derivative thermal analysis (TGA/DTA) was performed as a function of temperature (Fig. 2(b)). Thermal studies were performed in air atmosphere at a heating rate of 5 °C/min. The as-prepared sample showed two exothermic DTA peaks below 500 °C, corresponding to

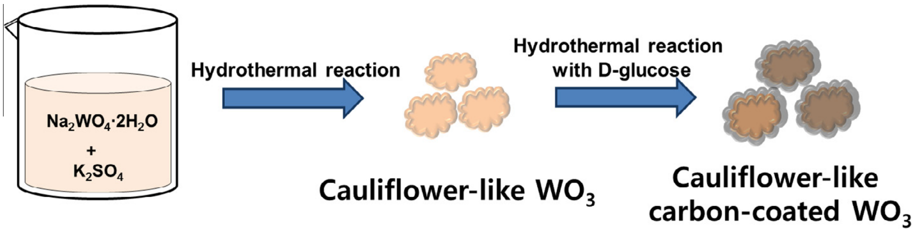

Fig. 1. Schematic illustration of the synthetic procedure for cauliflower-like carbon-coated WO_3.