Electrochimica Acta 163 (2015) 132–139

Contents lists available at ScienceDirect

Electrochimica Acta

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

Two-dimensional nanocomposites based on tungsten oxide nanoplates and graphene nanosheets for high-performance lithium ion batteries

Da-Mi Kim [a], Si-Jin Kim [a], Young-Woo Lee [a], Da-Hee Kwak [a], Han-Chul Park [a], Min-Cheol Kim [a], Bo-Mi Hwang [a], Seul Lee [a], Jong-Ho Choi [b], Seongho Hong [a], Kyung-Won Park [a,*]

[a] *Department of Chemical Engineering, Soongsil University, Seoul 156743, Republic of Korea*
[b] *Department of New and Renewable Energy, Kyungil University, Gyeongsan 712701, Republic of Korea*

ARTICLE INFO

Article history:
Received 4 December 2014
Received in revised form 13 February 2015
Accepted 13 February 2015
Available online 17 February 2015

Keywords:
Composite
Tungsten oxide
Nanoplates
Graphene
Lithium ion batteries

ABSTRACT

Well-defined nanocomposite electrodes based on active materials and graphene have been known to hold improved lithium ion reaction properties such as the lithium ion insertion/desertion reaction, cycle life, and high rate performance. Here, we report two-dimensional nanocomposites consisting of WO_3 nanoplates and graphene nanosheets (GNS) using a hydrothermal method and heating process for use in high-performance lithium ion batteries. A compilation of the data from XRD, SEM, and TEM suggests that the nanocomposites consist of high crystalline WO_3 nanoplates and GNS. The capacity and high rate cycling performance of the nanocomposites as an anode for lithium ion batteries are evaluated using coin cells. The nanocomposite electrode with an optimized amount of GNS exhibits high reversible capacity, good capacity retention, and excellent high rate cycling performance.

1. Introduction

Lithium ion batteries (LIBs) have been considered as the most important energy storage devices for use in portable equipment such as cellular phones and lap-top computers as well as in high-capacity devices such as hybrid electrical vehicles. However, the rapidly advanced applications demand high capacity, fast charging/discharging rate, and improved cycle life [1–5]. For the advanced electrochemical characteristics in LIBs, both the composition and structure of negative and positive active materials for better LIBs characteristics have been investigated over the past few decades. In particular, electrode materials of LIBs require a high electrical conductivity specific surface area, low cost, and long-term electrochemical stability [6,7].

Typically, carbon-based materials have been used as a promising anode, even showing lower theoretical capacity in LIBs [8–12]. Furthermore, transition metal oxides have been investigated to replace graphite and have exhibited high reversible capacities, resulting from their unique electrochemical properties. However, most transition metal oxide suffers from poor rate performance leading to drastic capacity drop due to low electrical conductivity and large volume change during charge-discharge cycling [13–17]. Accordingly, many efforts have been made to overcome the critical problems using composite structures with carbon-based or other electrical conductive materials. Among the composites consisting of transition metal oxides and carbon-based materials, much interest has been given to two-dimensional structure composites containing graphene nanosheet (GNS), leading to higher specific capacity and better high-rate stability [18–27]. Graphene nanocomposites show good potential in LIBs due to their low energy barrier for Li-ion, large surface area, and excellent electrical conductivity. Tungsten oxide (WO_3) may be one of the powerful candidates in the transition metal oxides because of its environmental friendliness, and high theoretical capacity of 693 $mAh\,g^{-1}$ [28–36]. The charge-discharge mechanism of WO_3 is based on conversion reaction process, which requires the formation of a metal and lithium oxide, as follows:

$$WO_3\ (\text{crystalline}) + 6\,Li^+ + 6\,e^- \rightarrow W + 3\,Li_2O \qquad (1)$$

$$W + 3\,Li_2O \rightarrow WO_3\ (\text{crystalline}) + 6\,Li^+ + 6\,e^- \qquad (2)$$

Herein, we prepared the two-dimensional nanocomposites (WO_3/GNS) containing WO_3 nanoplates and GNS with varying amount of GNS synthesized using a hydrothermal method and heating process. The structure and morphology of the nanocomposites were characterized using XRD, SEM, and TEM analysis. The capacity, capacity retention, and high rate cycling performance

---

* Corresponding author. Tel.: +82 2 820 0613; fax: +82 2 812 5378.
E-mail address: kwpark@ssu.ac.kr (K.-W. Park).

http://dx.doi.org/10.1016/j.electacta.2015.02.121
0013-4686/

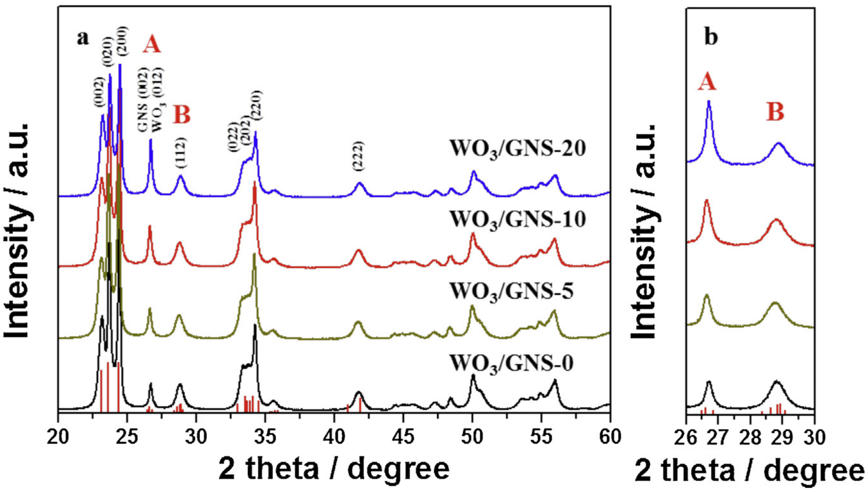

Fig. 1. (a) Wide scan and (b) small range (26°–30°) XRD patterns of the as-prepared WO_3/GNS-0, WO_3/GNS-5, WO_3/GNS-10, and WO_3/GNS-20. The red bars indicate XRD patterns of the bulk WO_3 (JCPDS No. 43-1035).

of the nanocomposites as an anode for lithium ion batteries were evaluated using coin cells.

2. Experimental Section

WO_3/GNS composite electrodes were synthesized using a hydrothermal method and heating process. To synthesize WO_3/GNS, the pre-oxidized GNS (ENanoTec 4 ~ 5 layer) powders with intended amounts of 5, 10, and 20 wt% were dispersed in 70 mL of 5 M hydrochloric acid solution (Samchun, 35–37%) with continuous sonication for 90 min at room temperature. With vigorous stirring, 1 g ammonium tungstate ($(NH_4)_{10}H_2(W_2O_7)_6$, Aldrich, 99.99%) was dissolved in the mixture solution. After sonication, the mixtures of tungsten salt and GNS powder in 5 M hydrochloric acid solution were heated 140 °C for 6 h. The resulting dispersion was cooled to room temperature, and the precipitates were then filtered and washed with di-water and ethanol several times. After drying at 50 °C in an oven, the temperature for the obtained powders was increased to 10 °C min^{-1} at 450 °C and kept in a box furnace at 450 °C for 2 h in an air atmosphere [37–40].

The size and morphology of the as-prepared samples were observed on a field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL Ltd.) and a field-emission transmission electron microscope (FE-TEM, Tecnai G2 F30 system operating at 300 kV). The crystal structure was studied using an X-ray diffractometer (XRD, D2 PHASER, Bruker AXS) with a Cu K_α ($\lambda = 0.15418$ nm) source with a nickel filter. The source was operated at 30 kV and 10 mA. The 2θ angular scan from 10° to 80° was explored at a scan rate of 0.5° min^{-1}. Thermogravimetric analysis (TGA) curves were obtained in a thermal analyzer (SDTA851, Mettler Toledo) in the range of 25–900 °C at a heating rate of 5 °C min^{-1} under an air flow of 60 cm^3 min^{-1}.

To assemble the coin cells (size 2032, Hohsen Corporation), the nanocomposite electrodes were used as a working electrode and evaluated with respect to a lithium foil (FMC Corporation) as a counter/reference electrode. The as-synthesized WO_3/G composite as an active material, Ketjen black as a conducting material (Alfa Aesar), and polyvinylidene difluoride (Alfa Aesar) as a binder with a weight ratio of 70:10:20 were mixed in 1-methyl-2-pyrrolidinone solvent (Aldrich, 99%). The well-mixed slurry was coated onto a Cu foil as a current collector using a doctor blade technique and then dried in an air atmosphere at 100 °C for 12 h. The average loading amount of active materials for all electrodes was 0.5 ~ 0.6 mg cm^{-2}. All of the WO_3/GNS electrodes were coated uniformly on 15 mm thick copper foil substrates and the thickness of the electrodes was 40 ~ 45 μm after pressing. The coin cells were assembled inside an argon-filled glove box (<5 ppm, H_2O and O_2). The electrodes of the cells were separated by a porous polypropylene membrane (Celgard 2400) and an electrolyte solution consisting of 1.1 M $LiPF_6$ in (ethylene carbonate:dimethyl carbonate) = (1:1) as a solvent mixture (Techno Semichem Co., Ltd). The charge–discharge cycling was performed within the voltage range of 0–3.0 V vs. Li/Li^+ on a battery test instrument (PEBC 50.2 PnE Solution Co., Ltd) under constant temperature of 25 °C. Electrochemical impedance spectroscopy measurements (EIS) were performed on the AUTOLAB electrochemical workstation by applying an AC voltage of 5 mV amplitude over the frequency range 100 kHz–0.01Hz at open circuit potential. All the measurements were performed at room temperature.

3. Results and discussion

The XRD patterns of the as-prepared WO_3/GNS nanocomposites (denoted as WO_3/GNS-0, WO_3/GNS-5, WO_3/GNS-10, and WO_3/GNS-20, respectively) with varying amounts of graphene (0, 5, 10, and 20 wt%, respectively) are shown in Fig. 1(a). The unit cell parameters of WO_3 for the as-prepared samples were determined to be a = 7.297 Å, b = 7.539 Å, and c = 7.688 Å in agreement with those of the bulk WO_3 material with a space

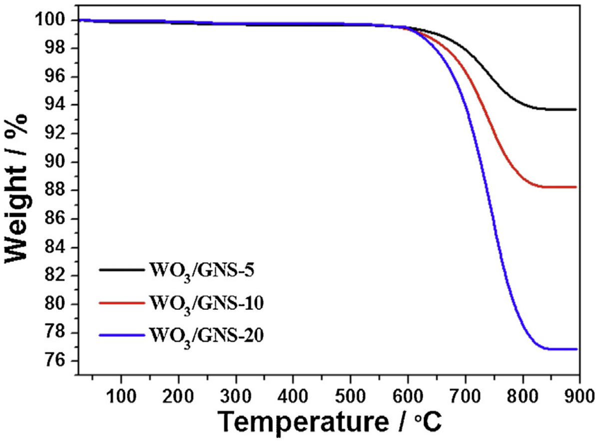

Fig. 2. TGA data of WO_3/GNS-5, WO_3/GNS-10, and WO_3/GNS-20.