



Reduced graphene oxide enwrapped vanadium pentoxide nanorods as cathode materials for lithium-ion batteries



Dezhi Chen ^{a,*}, Hongying Quan ^b, Shenglian Luo ^{a,*}, Xubiao Luo ^a, Fang Deng ^a, Hualin Jiang ^a

^a Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, School of Environmental and Chemical Engineering, Nanchang Hangkong University, No. 696, Fenghe Nan Avenue, Nanchang 330063, China

^b School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang 330063, China

HIGHLIGHTS

- rGO enwrapped V₂O₅ nanorods composites were prepared for the first time.
- The electrochemical properties were studied as cathode materials.
- rGO/V₂O₅ composites show excellent electrochemical lithium storage activity.
- The structure-component-property relationships were discussed.

ARTICLE INFO

Article history:

Received 10 August 2013

Received in revised form

19 September 2013

Accepted 23 September 2013

Available online 1 October 2013

Keywords:

Reduced graphene oxide

Vanadium pentoxide

Cathode

Lithium-ion battery

Nanocomposite

ABSTRACT

Novel reduced graphene oxide/vanadium pentoxide (rGO/V₂O₅) nanocomposites were fabricated by coassembly between negatively charged graphene oxide and positively charged oxide nanorods. A series of characterization including X-ray diffraction, Raman spectrum, scanning electron microscopy and transmission electron microscopy indicated that the V₂O₅ nanorods with the width of about 50 nm and the length from a few hundred nanometers to several micrometers were enwrapped by rGO layers to form core-shell nanostructures. Compared with the pristine V₂O₅ nanorods, the as-prepared rGO/V₂O₅ nanocomposites with 13 wt% rGO showed a significantly enhanced electrochemical performance with high reversible capacities, good cycling stabilities and excellent rate capabilities as a cathode material for lithium batteries. The rGO/V₂O₅ nanocomposites electrodes delivered a stable discharge capacity around 140 mA h g^{−1} at a current density of 150 mA g^{−1} for 100 cycles in the voltage range of 2.5–4.0 V. Furthermore, the nanocomposites electrodes delivered discharge capacities of 287 mA h g^{−1} and 207 mA h g^{−1} during the first and 50th cycles in the voltage range of 2.0–4.0 V at a current density of 100 mA g^{−1}, respectively. The as-synthesized nanocomposites are promising candidates for electrical energy storage applications.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries (LIBs) have been considered as the most effective technologies for electrochemical energy storage over the last two decades [1]. Electrode materials play dominant roles in the performance of LIBs. To meet the ever-growing demand for portable power sources, especially for high-energy and high-power applications such as electrical vehicles (EVs) and hybrid electrical vehicles (HEVs), numerous efforts have been devoted to develop cost-effective and high-performance electrode materials [2–6]. As a kind of promising cathode material, vanadium pentoxide (V₂O₅) with a layered structure has attracted much

attention due to its high capacity, high output voltage, and low cost [7]. However, the practical application of V₂O₅ is limited by its intrinsic low-diffusion coefficient of lithium ions ($\sim 10^{-12}$ cm² s^{−1}) and moderate electronic conductivity (10^{-2} – 10^{-3} S cm^{−1}) [8,9]. One generally accepted strategy to overcome these obstacles is to reduce the size of oxides to nanoscale and load onto conductive carbonaceous matrices [1,4,10]. For a given electrode material, the decrease in size can effectively shorten the diffusion time of lithium ions within the material. Meanwhile, the introduction of conductive carbonaceous materials can obviously improve the electronic conductivity and electrochemical stability of the whole electrode.

Recently, a new carbon nanomaterial, graphene has received considerable attention for its unique properties such as superior electrical conductivity, excellent mechanical flexibility, large surface area and high thermal stability [11]. Furthermore, low cost

* Corresponding authors. Tel.: +86 791 83953373.

E-mail addresses: cdz1030@126.com (D. Chen), sluo@hnu.edu.cn (S. Luo).

graphene can be produced in bulk, efficiently through chemical oxidation of graphite to hydrophilic graphite oxide, which can then be exfoliated as individual graphene oxide (GO) sheets by ultrasonication [12]. The GO is then converted to conducting graphene by the chemical reduction process. Generally, these graphene sheets obtained by the chemical reduction method are also known as reduced graphene oxide (rGO). Consequently, rGO/V₂O₅ nanocomposites have been fabricated as cathode materials for LIBs by different synthesis routes [13–16]. Compared with pristine V₂O₅ nanostructures, these as-prepared nanocomposites exhibited significantly enhanced reversible capacities and cycling stabilities as well as excellent rate performance. However, the high quality percentage content (> 20 wt%) of rGO in these nanocomposites decreased the specific reversible capacity of the whole cathode. Although lower rGO (4.5 wt%) can also enhance the electrochemical performance of the as-prepared nanocomposites for lithium ion storage [17], these V₂O₅ nanomaterials are still prone to strong aggregation during the cycle processes because of nonintimate contact between rGO layers and V₂O₅. This leads to a decrease in capacity of nanocomposites by 20–50% of their first reversible capacity after 30 cycles. One of the most promising approaches to resolve these problems is to prepare monodisperse V₂O₅ nanocrystals wrapped by ultrathin and high electrical performance rGO layers. Recently, some groups have synthesized rGO-wrapped metal oxides nanocomposites through electrostatic interactions between negatively charged GO sheets and positively charged metal oxide nanocrystals modified by surface grafting [18–20]. The GO is then converted to conducting rGO by the chemical reduction process. The novel strategy is not only simple, but also able to pre-select nanostructures with desired functionalities and morphology.

Herein, we prepared rGO-encapsulated V₂O₅ nanocomposites by coassembly between negatively charged GO and positively charged oxide nanorods. The process is driven by the mutual electrostatic interactions of the two species, and is followed by thermal reduction. The as-synthesized nanocomposites possess flexible and ultrathin rGO shells that effectively enwrap the oxide nanorods. As a cathode material for LIBs, the nanocomposites with 13 wt% rGO show high reversible capacities, good cycling stabilities and excellent rate capabilities.

2. Material and methods

2.1. Preparation of V₂O₅ nanorods

In a typical synthesis, 0.3 g of ammonium metavanadate (Tianjing Jinghua) and 0.50 g of triblock copolymer P123 (EO₂₀PO₇₀EO₂₀, EO=ethylene oxide, PO=propylene oxide; Sigma) were dissolved in 30 mL of DI water containing 1.5 mL of 2 M HCl. This mixture was stirred at room temperature for 7 h and then transferred to an autoclave and heated to 120 °C for 24 h. The resulting precipitate was vacuum-filtered and rinsed with DI water. This as-prepared precipitate was calcined at 500 °C for 2 h to obtain V₂O₅ nanorods (Fig. S1).

2.2. Preparation of rGO/V₂O₅ nanocomposites

V₂O₅ nanorods (0.4 g) were first dispersed in 200 mL ethanol by sonication for 30 min. Then, aminopropyltrimethoxysilane (APTS, 1 mL) was added, and refluxed for 4 h to obtain APTS-modified V₂O₅ nanorods. A certain amount of negatively charged GO suspension (0.2 mg/mL, obtained by the modified Hummers method [21]), as shown in Fig. S2, was added into positively charged amine-functionalized V₂O₅ nanorods dispersion under vigorous stirring at pH 6 to fabricate GO-enwrapped V₂O₅ nanorods (GO/V₂O₅). After

mixing for 1 h, the mixture was centrifuged and washed with deionized water. Finally, the as-prepared product was calcined at 300 °C for 30 min to obtain rGO-enwrapped V₂O₅ nanorods (rGO/V₂O₅) nanocomposites.

2.3. Characterization

X-ray diffraction (XRD) analyses were carried out on an X-ray diffractometer (XRD-6000, Shimadzu Scientific Instruments). The XRD patterns with Cu K α radiation ($\lambda=1.5406$ Å) at 40 kV and 40 mA were recorded in the range of $2\theta=10$ – 60° . The XRD specimens were prepared by means of flattening the powder on the small slides. Scanning electron microscope (SEM) images were achieved by an FEI Quanta 250 field-emission gun environmental scanning electron microscope at 10 kV with the samples obtained from the thick suspension dropping on the silicon slice. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F transmission electron microscope (JEOL Ltd., Japan) operated at 200 kV. Energy dispersive spectrometry (EDS) was obtained from an Apollo-300 field-emission gun scanning electron microscope. Raman spectra were recorded from 1100 to 1800 cm⁻¹ on a LabRAM HR800 Laser Raman spectroscope (HORIBA Jobin Yvon Co. Ltd., France) using a 632.5 nm argon ion laser. All samples were deposited on silicon wafers in powder form without using any solvent. Thermogravimetric (TG) analysis was performed in air using a Pyris Diamond TG analyzer (PerkinElmer Inc., USA). The samples were heated from 50 °C to 550 °C at 5 °C/min.

2.4. Electrochemical measurements

The electrochemical properties of the rGO/V₂O₅ nanocomposites and pristine V₂O₅ nanorods as cathode materials in lithium ion cells were evaluated by a galvanostatic charge/discharge technique. The test electrodes were prepared by mixing active materials (nanocomposites 80% or pristine V₂O₅ 70%) with carbon black (nanocomposites 10% or pristine V₂O₅ 20%) and 10% polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone to form a slurry; CR2032 type coin cells were finally assembled in a highly-pure argon-filled glovebox using the test electrodes and the metallic lithium counter/reference electrode, a polypropylene separator (Celgard 2400) and an electrolyte of 1 mol/L LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DMC) (EC/DMC, 1/1 vol). Charge–discharge measurements were carried out galvanostatically using a battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics. Ltd., China). The electrochemical impedance measurements were performed on a CHI660D electrochemical workstation (Shanghai Chenhua Co. Ltd., China) at an AC voltage of 5 mV amplitude in the range of 100 kHz–0.01 Hz.

3. Results and discussion

The overall synthesis procedure for the rGO-enwrapped V₂O₅ nanorods composites (rGO/V₂O₅) is illustrated in Fig. 1. First, V₂O₅ nanorods were modified by surface grafting of APTS to render the V₂O₅ surface positively charged. The modified V₂O₅ nanorods were then assembled with negatively charged GO by electrostatic interactions. Finally, the aggregates were thermally reduced to prepare rGO/V₂O₅ nanocomposites. Fig. 2 shows digital photographs of pristine V₂O₅ nanorods, GO/V₂O₅ and rGO/V₂O₅. As presented in Fig. 2a, pure V₂O₅ is orange, and then turns to brown (Fig. 2b) for GO layers. Finally, after the thermal treatment, the product becomes black (Fig. 2c).

Fig. 3a shows the XRD patterns of pristine V₂O₅ nanorods, GO/V₂O₅ and rGO/V₂O₅. All diffraction peaks can be attributed to

Download English Version:

<https://daneshyari.com/en/article/1544588>

Download Persian Version:

<https://daneshyari.com/article/1544588>

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