Nano Energy 24 (2016) 32–44

Contents lists available at ScienceDirect

Nano Energy

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

Crumpled reduced graphene oxide conformally encapsulated hollow V_2O_5 nano/microsphere achieving brilliant lithium storage performance

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ARTICLE INFO

Article history:
Received 8 January 2016
Received in revised form
3 April 2016
Accepted 5 April 2016
Available online 8 April 2016

Keywords:
Crumpled reduced graphene oxide
Encapsulated materials
Vanadium pentoxide
Lithium ion batteries

ABSTRACT

It has remained a challenge to develop a facile and scalable approach to synthesize high-energy lithium-ion battery (LIB) electrode materials with excellent rate capabilities and prominent cycling stabilities for their applications in new generation energy storage devices. In this study, for the first time, we report a crumpled reduced graphene oxide (cG) encapsulated three-dimensional (3D) hollow vanadium pentoxide (V_2O_5) nano/microspheres fabricated by one-step solvothermal treatment followed by subsequent annealing. This rapid and effective synthesis method is environmental friendly and economically beneficial without involving costly organic vanadium sources, tedious operation, or sophisticated equipment. Remarkably, the desired cG-encapsulated V_2O_5 composite contains 5 wt% reduced graphene oxide (rGO), yet exhibits outstanding rate capacities and cycling stabilities. This product can deliver reversible capacities of 289 mA h g^{-1} at 100 mA g^{-1} and 163 mA h g^{-1} at 5000 mA g^{-1} (492 W h kg^{-1} and 9840 W kg^{-1}), as well as a capacity retention of about 94% after 200 cycles at 2000 mA g^{-1} in the potential range between 2.0 V and 4.0 V (*vs.* Li/Li^{+}). Furthermore, the unique structural feature and typical formation mechanism of the designed materials are clarified based on multiple experimental results. More commendably, a chain of solid powders had been successfully encapsulated using this scalable reaction system. It is expected that this versatile approach will facilitate the applications of cG, and provide a novel avenue to create more fascinating rGO-based functional materials.

1. Introduction

Lithium ion batteries (LIBs) have been regarded as one of the most promising candidates for applications in the coming era of electric and hybrid vehicles with the potential to lower fossil fuels consumption and reduce greenhouse gas emissions [1–4]. Nonetheless, to meet the constantly increasing demands of new generation energy storage devices such as portable electronic devices, electric vehicle propulsion, and grid-scale energy storage, high energy density rechargeable battery electrode materials with excellent rate capabilities and prominent cycling stabilities have attracted considerable research interests worldwide [5,6].

Being a well-known transition-metal oxide with multiple valence states, vanadium pentoxide (V_2O_5) has been extensively studied as one of the most promising LIB cathode materials due to its unique advantages such as its rich abundance, ease of synthesis, being relatively safer, and high specific capacity [7–11]. V_2O_5 consists of a layer structure stacked along the c-axis of the orthorhombic structure, as shown in the Supplementary Fig. S1a. Each layer is in turn made up of VO_5 square pyramids sharing edges and corners, and the layers are bonded together only by the interaction of weak van der Waals forces. Therefore, this structure easily undergoes multiple phase transitions, such as α, ε, δ, γ, and

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http://dx.doi.org/10.1016/j.nanoen.2016.04.002
2211-2855/

ω phases, relying on the depth of Li intercalation (x) [12]. The α-phase $Li_xV_2O_5$ ($x < 0.01$) and ε-phase $Li_xV_2O_5$ ($0.35 < x < 0.7$) have similar structure with the un-intercalated V_2O_5, but result in weak wrinkling of V_2O_5 layers [13]. With further Li intercalation, the δ-phase $Li_xV_2O_5$ ($0.7 < x < 1$) has more corrugated V_2O_5 layers. Meanwhile, the c parameter is doubled due to the shift of the V_2O_5 layers (see Supplementary Fig. S1b). When lithiated further, the irreversible structural variation to γ-phase $Li_xV_2O_5$ ($1 < x < 2$) appears. Fig. S1 clearly reveals the difference in crystal structures of δ-and γ-V_2O_5 phases. The layer wrinkling of γ-V_2O_5 becomes more evident than that in δ-phase [13]. A further deep discharge to $x > 2$ results in the irreversible formation of ω-$Li_xV_2O_5$ with a rock salt type structure, where the Li^+ migration will be very tardy [12]. As a result, the theoretical capacity and structural stability of V_2O_5 highly depends on the depth of the Li intercalation, *viz*., the potential window of charge/discharge measurement. Normally, when V_2O_5 is employed as a cathode material in the potential range of 2.0–4.0 V (*vs.* Li/Li^+), its theoretical capacity reaches about 294 mA h g^{-1} corresponding to the two Li intercalation/deintercalation mechanisms, much higher than those of conventional $LiMn_2O_4$ (148 mA h g^{-1}) [14], $LiCoO_2$ (140 mA h g^{-1}) [15], or $LiFePO_4$ (170 mA h g^{-1}) [16]. Nevertheless, the high specific capacity/energy has not been realized in practical LIB applications because of four drawbacks, as follows: (1) poor electrical conduction, (2) irreversible phase transitions upon deep discharge, (3) vanadium dissolution, and (4) fast increased charge transfer resistance upon cycling [12,17–21].

To mitigate the aforementioned intrinsic problems, decreasing their particle size to the nanoscale level is generally believed to be one of the most effective approaches due to the shorter transport lengths for both electrons and Li ions, larger electrode/electrolyte contact area, and higher electrochemical reaction activity and reversibility of the nanostructures for Li intercalation/deintercalation [22–25]. Along this direction, the nanostructured V_2O_5 with diverse morphologies including nanorods [20,21], nanofibers [22], nanobelts [23], nanosheets [24], and porous micro-spheres [11,25] has already been investigated to realize Li battery application. Furthermore, it is noteworthy that the introduction of electrically conductive materials, such as CNTs [26], conductive polymers [27], and reduced graphene oxide (rGO) [17,28,29], into these nanostructured V_2O_5 materials can further improve the battery properties. Among numerous conductive matrixes, rGO is preferable to replace other matrixes owing to its extraordinary properties including high electrical conductivity, unusual mechanical strength, and large specific surface area [30,31]. As a consequence, a number of rGO/V_2O_5 nanocomposites have been designed to idealize the electrochemical performance of the active materials, and have yielded a variety of notable results [17,28,29,32–36]. For example, Liu et al. have recently constructed V_2O_5 nanoribbons incorporated rGO sheets hybrid cathode materials that combined the effects of improving electronic conduction, Li-ion diffusion, and structural reversibility [29]. Despite the achieved high charge/discharge rates, these previous studies utilized costly organic vanadium source [32–34], tedious operation [28,29,35], or sophisticated equipment [17,36], in the synthesis process, which may be difficult to achieve large-scale applications. More importantly, the resulting V_2O_5 was only in a rough manner to combine with rGO, such as anchoring onto the rGO surface [17,29,32–34], sandwiching between rGO [28], and uneven hybrid or mixture with rGO [35]. There is still considerable room for improving the structure and properties of these composites for LIBs. Coincidentally, Zhao's group recently reported a cG-encapsulated 3D Ni_3S_2/Ni electrode with self-adaptive strain-relaxation via a multi-step process. The nanocomposites exhibited extraordinary electrochemical performance originating from the conformal wrapping of active materials by elastic rGO [37]. However, due to the lack of the appropriate synthetic methods, the cG-encapsulated electroactive materials were seldom previously reported to the best of our knowledge [37–39]. Therefore, there is still a great desire as well as challenge to develop an easy, effective, and extensible approach for the design and synthesis of this kind of material, allowing the facilitation of the applications of cG.

Herein, we present a facile and rapid approach to realize cG-encapsulated 3D porous V_2O_5 nano/microsphere for the first time. This high-efficiency synthetic method involves a one-step solvothermal synthesis subsequently followed by low-temperature annealing. The whole process is environmentally friendly and economically beneficial. Noticeably, when the obtained materials serve as a cathode material for LIBs, the resulting electrodes exhibit superior cycling stability and rate capacities, due to the simultaneous improvement of the above-mentioned four major drawbacks. Even more remarkable, a series of solid powder materials had been successfully encapsulated using this scalable reaction system, further highlighting the practicality of this versatile method. It is expected that such finding will open up the possibility of producing more novel rGO-based functional materials.

2. Experimental section

2.1. Materials preparation

Graphite oxide (GO) was fabricated by the modified Hummers method, as previously reported by our group [40]. The obtained GO was ground into fine powder. This purified powder was dispersed in ethylene glycol by ultrasonic cell disruption for 20 min to form a 2.0 mg mL^{-1} brown solution. Secondly, the commercial V_2O_5 (0.3 g) and $H_2C_2O_4 \cdot 2H_2O$ in a molar ratio of 1:3 was dissolved in 30 mL of deionized H_2O under vigorous stirring at 70 °C for 1 h until a clear dark blue VOC_2O_4 solution (0.11 M) was formed [41]. Then 3 mL of the prepared VOC_2O_4 solution and 5 mL of the prepared GO dispersion were added into a 50 mL Teflon container pre-filled with 30 mL of butanol [11]. After stirring for 30 min, the container was sealed in a steel autoclave and kept in an electrical oven at 200 °C for 8 h. After cooling down naturally, the precipitate was collected by vacuum filtration and washed with pure ethanol several times. Finally, the cG-encapsulated V_2O_5 was obtained by sintering the dried precipitate in air at 350 °C for 2 h with a heating rate of 5 °C min^{-1}. For comparison, the changed amounts (0 mL, 2 mL) of the prepared GO dispersion were used in the above-mentioned experimental system without adjusting other conditions to study their effect on the morphology, structure, and performance of the final V_2O_5.

2.2. Materials characterization

Field-emission scanning electron microscopy (FE-SEM) coupled with energy dispersive spectroscopy (EDS) images were taken using a Hitachi SU8010 field-emission scanning electron microscope. The microstructure and micro-area chemical composition of the samples were verified using a transmission electron microscopy (TEM, JEOL JEM-3000F) with an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) was performed on a Bruker AXS D8 advance X-ray diffractometer at the 2θ range of 10–70° using Cu Kα radiation ($\lambda = 1.5405$ Å). Traces software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files was employed to identify the material phases. The amount of graphene in the final product was estimated using a thermogravimetric analysis (TGA, Pyris Diamond6000 TG/DTA, PerkinElmer) from 25–500 °C at 5 °C min^{-1} under air atmosphere. Fourier transform infrared (FTIR) spectra were collected on a IRAffinity-1 FTIR spectrometer (SHIMADZU) by using pressed KBr pellets. Raman