



Vanadyl phosphate/reduced graphene oxide nanosheet hybrid material and its capacitance



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ABSTRACT

The layered structure stability of bulk vanadyl phosphate dihydrate (VOPO₄·2H₂O) is investigated by using a deintercalation-intercalation reaction process involving short-range swelling, its basal spacing can be reversibility controlled and the layered structure can be maintained to above 400 °C. By using delaminated vanadyl phosphate (VOPO₄) nanosheets in 2-propanol, VOPO₄/reduced graphene oxide (RGO) hybrid electrode materials for supercapacitor with different mass ratios of VOPO₄ nanosheets to graphene oxide (GO) nanosheets have been prepared based on a nanosheet reassembling reaction between the exfoliated VOPO₄ nanosheets and GO nanosheets and followed by calcinating in a tubular furnace at 400 °C for 3 h under N₂ atmosphere, and their electrochemical properties are systematically investigated by cyclic voltammetry and galvanostatic charge-discharge in 0.5 M K₂SO₄ electrolyte. The VOPO₄/RGO hybrid electrode with a mass ratio of VOPO₄/RGO = 1 exhibits a high specific capacitance of 378 F g⁻¹ at a scan rate of 5 mV s⁻¹ with a good rate capability. This method broadens the application field of VOPO₄ nanosheets, and also supplies promising electrode candidate candidates for supercapacitor.

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1. Introduction

Supercapacitors (SCs), also known as electrochemical capacitors, have attracted considerable attention as energy storage devices due to their high power density, long life cycle, good reversibility, environmental friendliness, and safety [1–3]. However, SCs have a relatively low energy density in contrast to batteries, which has limited their use in many applications [4,5]. According to E (energy density) = $1/2CV^2$, the energy density of a supercapacitor is dependent on the cell potential (V) and capacitance (C) [6], and a high capacitance and wide operating cell voltage are required to increase the energy density of SCs while retaining their intrinsic high specific power. In general, the cell potential can be widened by assembling asymmetric capacitor or by using ionic liquid as electrolytes, while the capacitance can be improved by preparation new electrode materials with novel structure and morphology [7–10]. Therefore, new electrode materials with novel structure and morphology can be used as

an important way to improve the performance of SCs [11,12]. Because faradic pseudocapacitance is carried out by fast redox reactions or phase changes on the surface or subsurface of electrodes offering much higher energy densities than electrical double-layer capacitor [13], the new and environmentally friendly metal oxide-based or polymer-based hybrid electrode materials in pseudocapacitors will increase their specific capacitance due to their high ideal capacitance [14–17]. Up to now, many research works focus on the design, characterization and preparation of the multicomponent electrode materials combining energy storage of electrostatic attraction and faradic reaction, in which active materials such as metal oxides or conducting polymers can enhance the capacitance remarkably, while the carbon-based material as a support, not only increases the effective utilization of active materials, but also improves the electrical conductivity and mechanical strength of the composite electrodes [18–21].

The research results also indicate that the two-dimensional nanostructures not only have large specific surface area, but also facilitate the charge transfer during an electrochemical process, and they seem to be the most practical option for improving the electrochemical performances [22,23]. Therefore, the electrode materials with novel two-dimensional nanostructures and multi-component hybrid behaviors are expected to be developed. VOPO₄·2H₂O are linked together through corner-sharing VO₆

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octahedra and PO₄ tetrahedra to form V–P–O layered structure [24], it can provide the higher potential and active center to generate pseudocapacitance [25], and it also should be one of the most promising electrode materials with peculiar layered structure [26]. Up to now, VOPO₄ · 2H₂O is mainly used as the positive electrode materials for lithium batteries [27–29], while their pseudocapacitance is little given to attention. Xie group has reported that the flexible ultrathin-film pseudocapacitor based on hybrid structure of a newly found VOPO₄ ultrathin nanosheets and graphene sheets exhibits extremely high specific capacitance (up to 8360.5 mF cm⁻²), high redox voltage (up to 1 V), long cycle life (more than 2000 cycles) and excellent flexibility, leading to an ultrahigh energy density of 1.7 mWh cm⁻² and a power density of 5.2 mW cm⁻² [30]. Liu group has studied the pseudocapacitance of VOPO₄ · 2H₂O as an electrode material synthesized by reflux and hydrothermal methods, and found its specific capacitance is about 202 F g⁻¹ at 2 mV s⁻¹ [31]. Whether VOPO₄ · 2H₂O do a battery or capacitor electrode material, the lower capacities than the theoretical values and poor cyclability unfortunately prevent it from being used in large-scale applications [32]. To overcome these problems, it may be a good treatment method to hybrid electronically conductive materials, such as carbon-based materials with VOPO₄ nanosheets.

In the present work, the VOPO₄/GO layered hybrid material was firstly prepared by a controllable nanosheet reassemble technology between VOPO₄ nanosheets and GO nanosheets at room temperature on the basis of the investigation of VOPO₄ nanosheet structural stability, then it was calcinated in a tubular furnace at 400 °C for 3 h under N₂ atmosphere, GO was successfully converted into RGO while VOPO₄ · 2H₂O into VOPO₄, and VOPO₄/RGO layered hybrid material was obtained. Also the electrocapacitive property of VOPO₄/RGO layered hybrid material was investigated by CV and galvanostatic charge-discharge tests.

2. Experimental Section

2.1. Materials preparation

All chemicals (analytical grade) were used as received without further treatment.

The preparation of VOPO₄ and GO ultrathin nanosheets. The bulk VOPO₄ · 2H₂O was prepared using a reflux method according to the reference [33]. Briefly, a mixture of V₂O₅ (2.4 g), H₃PO₄ (85%, 13.3 mL) and H₂O (67.7 mL) was refluxed at 110 °C for 16 h and then the system was permitted cool down to room temperature. The resulting precipitate was collected by filtration, washed several times with deionized water and acetone, and dried in vacuum oven at 60 °C for 8 h, VOPO₄ · 2H₂O yellow powder was obtained. Then VOPO₄ · 2H₂O yellow powder (200 mg) was dispersed in 200 mL 2-propanol, and the obtained suspension was ultrasonicated in iced water for about 2 hours, bulk VOPO₄ · 2H₂O was exfoliated into their ultrathin nanosheets, and the concentration of VOPO₄ · 2H₂O nanosheet suspension was about 1 mg mL⁻¹ [30]. Graphite oxide (GO) was fabricated from crude flake graphite by a modified Hummer's method [34]. The as-prepared GO was then treated by ultrasonication treatment using a KQ-600kDE Digital Ultrasonic cleaning device (600 W, 80% amplitude) in water bath for 4 hours, and GO nanosheet homogeneous dispersion (1 mg mL⁻¹) was obtained after removing the unexfoliated substances by the centrifugal treatment.

The preparation of VOPO₄/RGO hybrid electrode materials. VOPO₄/GO hybrid electrode material with a mass ratio of VOPO₄/GO = 1 was firstly prepared by a controllable nanosheet reassemble technology between VOPO₄ nanosheets and GO nanosheets at room temperature. The GO nanosheet suspension (1 mg mL⁻¹, 50 mL) was slowly added into the colloidal suspension of VOPO₄

nanosheets (1 mg mL⁻¹, 50 mL) with constant stirring for 30 minutes at room temperature. Subsequently, the mixture suspension was frozen by liquid nitrogen and then dried by a cryodesiccation process to removal the residual water and 2-propanol, the VOPO₄/GO layered hybrid material was obtained, which are abbreviated as VGO-1. The VGO-1 layered hybrid material was calcinated in a tubular furnace at 400 °C for 3 h under N₂ atmosphere, GO in VGO-1 hybrid material was reduced into RGO, and the VOPO₄/RGO layered hybrid material was finally prepared, which is abbreviated as VRGO-1-400.

By changing the mass ratio of VOPO₄ nanosheets to GO nanosheets, VRGO-X-M hybrid materials with different VOPO₄ amounts could be prepared by the similar process, in which X is the mass ratio of VOPO₄ to GO and M is the calcination temperature in N₂ for 3 h. For comparison, GO and VOPO₄ · 2H₂O were also calcinated in furnace at 400 °C for 3 h under N₂ atmosphere, respectively.

2.2. Materials characterization

The X-ray diffraction (XRD) patterns were carried out using a D/Max-3c X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å), scanning from 5° to 80° and using an operating voltage and current of 40 kV and 20 mA, respectively. The morphology of the products was examined with the TM3000 scanning electron microscopy (SEM) and the SU8020 Field emission gun scanning electron microscopy (FE-SEM). Transmission electron microscope (TEM) images were collected by using a JEM-2100 microscope. Samples for TEM observation were prepared by dispersing the materials in alcohol by an ultrasonic treatment for several minutes. X-ray photoelectron spectroscopy (XPS) investigation was performed with the AXIS ULTRA (Kratos Analytical Ltd.) using Al Kα radiation (1486.6 eV) as an excitation source. To ensure the accuracy of the data measured, all the binding energies were calibrated relative to the C 1s peak (284.6 eV) from hydrocarbons adsorbed on the surface of the samples [35].

2.3. Electrochemical measurements

All electrochemical measurements were carried out with a CHI660 electrochemical workstation (CH Instruments Inc. China) in a conventional three-electrode cell which contains the working electrode, counter electrode (Pt foil) and reference electrode (Ag/AgCl electrode). The working electrode was prepared by mixing VRGO (80 wt%) as the active material with acetylene black (15 wt%) and polyvinylidene fluoride (5 wt%) (The purities of acetylene black and polyvinylidene fluoride were battery-grade). The first two constituents were first mixed together to obtain a homogeneous black powder. Polyvinylidene fluoride (PVDF) solution (1 mg mL⁻¹, in deionized water) was added to the homogeneous black powder, giving a rubber-like paste. The paste was then brush-coated onto a Ni foam current collector with a definite of 2.0 cm². The foam was dried at 110 °C in a vacuum oven for 12 h to remove the solvent and then uniaxially pressed to make the electrode material adhere to the current collector more completely. The mass loading for each electrode was about 2–3 mg, and the electrolyte was 0.5 M K₂SO₄ solution.

The cyclic voltammetry (CV) and galvanostatic charge-discharge tests were conducted in above work system. CV tests were performed at a potential window of -0.5~0.3 V with different scan rates, and the specific capacitance C (F g⁻¹) was calculated from CV results using the following formula:

$$C = \int i dV / m v (\Delta V)$$

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