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Enhanced lithium storage of mesoporous vanadium dioxide(B) nanorods by reduced graphene oxide support

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ABSTRACT

A facile synthesis of vanadium oxide with reduced graphene oxide (rGO) is developed and used as cathode material for lithium ion batteries. VO_2(B) nanorods and VO_2(B)-rGO composite were prepared by a hydrothermal method using $NaVO_3$ precursor and sodium oxalate as a reducing agent. The monoclinic phase and nanorod like morphology of synthesized materials were confirmed by XRD, SEM, and TEM respectively. The electrochemical properties of samples were investigated at 1.5–4.0 V, and 0.1 C rate, and the VO_2(B) nanorods exhibit reversible capacity of about 159 mAh g^{-1}, whereas VO_2(B)-rGO exhibits 274 mAh g^{-1}. The reasonable discharge capacities were obtained at high rates. The enhanced performance in electrical energy storage system reveals the effectiveness of rGO in the composite, as it enhances the conductive electron pathway to overcome the intrinsic limits of single phase VO_2(B).

1. Introduction

Lithium ion batteries (LIBs) are of great importance for electrical and electronic vehicles as a power source device because of the environmental benignity, high capacity, long cycle life, and less self-discharge, etc. [1]. The transition-metal oxides have attracted extensive attention as cathode materials for lithium ion battery [2–6]. Among these, vanadium oxide has been considered as one of the most promising cathodes, because of its layered structure and variable oxidation (from +2 to +5) states [7,8]. In VO_x based materials in which the atoms link each other by covalent bonds to form two dimensional layers that are stacked together through the weak Vander Waals interaction. This allows introduction of the foreign ion or molecule into the interlayer and providing good diffusion channel for Li-ion [9–11] and vanadium oxides VO_x (V_2O_5, VO_2, V_2O_4, V_2O_3, V_6O_{13}) [12] are also interesting electrode materials for lithium-ion batteries because of its various oxidation states and good reactivity. Among these, VO_2(B) with metastable monoclinic structure is a promising cathode material for LIB, because of its tunnel structure, through which lithium ions can easily intercalate and deintercalate [13–15], and its high theoretical capacity of 320 mAh g^{-1} [13].

Many researchers have been constructing composite structures of the electrode material with graphene [16,17], carbon nanotubes [18–22], etc. Graphene and rGO are composed of sheet-like structure with very high surface area (2680 m^2 g^{-1}) and electronic conductivity [23]. sp^2 hybridized carbon atoms possess network structure with excellent chemical stability. Inorganic nano-scaled structures will increase surface area of the electrode, shorten the diffusion distance for lithium ions and improve the accessibility of the active surface. Anchoring of nanoparticles on graphene can effectively reduce the degree of restacking of graphene sheets and increase the lithium storage capacity and cycling performance. Graphene can also effectively prevent the volume expansion/contraction and aggregation of NPs during Li-ion charge/discharge process [24–26]. Graphene layer acts as a highly conductive matrix for enabling good contact between them and also provides a support for anchoring well-dispersed NPs [27–30]. Composition of the VO_2(B) nanomaterial with graphene exhibits the high performance and capacity retention ratios [16,17,22]. Porosity in the materials helps the electrolyte ions to keep in and provides complete access to the electrode materials toward intercalation/deintercalation during charge–discharge processes. This leads to enhancement in rate performance as the contact area of the electro-active surface is improved [31].

Among various methods available to prepare VO_x based metal oxide nanomaterials, we have opted hydrothermal method to prepare mesoporous VO_2(B) and its rGO composite because of its various advantages. The benefits of this method are controllable morphology, size distribution, environmentally benign reaction conditions and low temperature. Because of low synthesis temperature, hydrothermal reaction will not break weak interactions

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(Vander Waals, hydrophilic-hydrophobic interaction, etc.). These interactions favor the self-assembly of molecular precursors and can play an important role during the formation of the oxide network.

Fan et al. have reported the preparation of VO_2(B)/graphene nano ribbon hybrid and used it as a cathode material for LIB. It exhibits the discharge capacity of 172 mAh g^{-1} and capacity retention rate of 37% after 30 cycles at a current density of 40 mA g^{-1} in a potential window of 1.5–4.0 V [32]. Zhao et al. has prepared the VO_2-carbon nanobelts by hydrothermal method and used them as cathode materials for LIB. It exhibited the discharge capacity of 153 mAh g^{-1} after 100 cycles at a current density of 50 mA g^{-1} in 1.5–4.0 V [33]. Rui et al. have prepared the VO_2(B)@C nanobelts by hydrothermal method and observed the electrochemical performances of 128 mAh g^{-1} after 50 cycles at a current density of 100 mA g^{-1} for 2.0–4.0 V [34]. Balogum et al. have prepared the VO_2-carbon quantum dots by hydrothermal method and used for LIB application. It exhibited 125 mAh g^{-1} after 100 cycles at a current density of 100 mA g^{-1} for 1.5–3.5 V [35]. Mahadi et al. have prepared the VO_2(B)-rGO by hydrothermal method and used it as the cathode material to examine the battery performances. They observed the discharge capacity of 250 mAh g^{-1} after 50 cycles at a current density of 50 mA g^{-1} in 2.0–4.1 V [36]. Yang et al. have reported the synthesis of VO_2(B)-flake graphite by hydrothermal method and used it as the anode material to examine battery performances. It exhibited first discharge capacity of 900 mAh g^{-1} and retained 357 mAh g^{-1} even after 26 cycles at a current density of 50 mA g^{-1} [37].

In the current research work, VO_2(B) NRs and VO_2(B)-rGO composite were synthesized by hydrothermal method using sodium oxalate. We have opted sodium oxalate as a reducing agent because, in addition to its good reducing property, it is low-cost, easily available and completely soluble in water. It completely reduces sodium vanadate [(Na)VO_3—V^{+5}) to Vanadium dioxide [VO_2—V^{+4}] in acidic medium. As prepared materials were used as cathode materials for LIB, the results show the enhanced specific discharge capacity for VO_2(B)-rGO composite (274 mAh g^{-1}) compared to VO_2(B) (159 mAh g^{-1}) at 0.1 C rate in typical potential range of 1.5–4.0 V.

2. Experimental

2.1. Preparation of VO_2(B) nanorods

VO_2(B) nanorods (NRs) were prepared by a hydrothermal method using sodium vanadate and sodium oxalate as a reducing agent. In a typical synthesis, 0.1 M $NaVO_3$ and 0.1 M $Na_2C_2O_4$ were separately prepared in 30 mL deionized water. These two solutions were mixed under vigorous magnetic stirring. In order to improve the solubility, the solution was heated to about 45 °C. 2 M HCl was used to maintain the pH = 1 of the solution. The solution was transferred to a Teflon tube and maintained for at 200 °C about 48 h. Then the sample was washed with distilled water and methanol for three times to remove the impurities. The collected sample was dried in an oven at 60 °C for 1 h.

2.2. Preparation of VO_2(B)-rGO composite

The above as-prepared VO_2(B) was mixed with reduced graphene oxide (30 mg) and grounded using ethanol as a solvent. The obtained composite was kept for dry at room temperature about 1 h.

Under these reaction conditions, it is been found that sodium oxalate rapidly and quantitatively reduced the acid solutions of sodium metavanadate to VO_2(B) NRs. The reaction may be represented by the following equation.

$$2NaVO_3 + Na_2C_2O_4 + 4HCl \rightarrow 2VO_2 + 4NaCl + 2H_2O + 2CO_2$$

2.3. Sample characterization

X-ray diffraction (XRD) data of samples were collected with a Rigaku-smart lab XRD-6000 diffractometer, using CuKα radiation ($\lambda = 0.15418$ nm) at 40 kV, 30 mA. The Fourier transform infrared spectra (FTIR) of the samples were collected using Bruker Alpha spectrometer. Raman spectra were recorded at different spots in backscattering geometry using 514.5 nm Ar^+ laser in HORIBA LabRam HR800 spectrometer. The size and morphology of synthesized samples were determined using scanning electron microscopy (SEM VEGA3 TESCAN) operated at 30 kV and transmission electron microscopy (TEM, Hitachi H7650B) operating at 200 kV. The Energy Dispersive X-ray Spectroscopy (EDAX) was measured on eZAF smart quant. Surface area and pore characteristics were analyzed under liquid nitrogen temperature by Quanta Chrome Nova-1000 surface analyzer instrument. Adsorption desorption isotherm measurements were carried out for the evolution of porosity and textural properties. BET, BJH (Barrett–Joyner–Halenda) methods were used to evaluate surface area, pore diameter and pore volume. TG-DTA results were obtained using Perkin Elmer Diamond instrument with air flow rate of 60 mL min^{-1} and the heating rate was 10 °C min^{-1}.

2.4. Electrochemical measurements

The cathode was composed of active materials (VO_2(B) or VO_2-rGO composite), conductive carbon black (acetylene black) and a polymer binder (polyvinylidene fluoride, PVDF) respectively in the weight ratio of 80:10:10. The above materials were taken in a mortar and ground well with a few drops of *N*-methyl pyrrolidone added to obtain slurry. This slurry was coated on pre-heated aluminum collector, and then the electrodes were dried in vacuum for 24 h. Celgard porous polypropylene membrane (2400) was used as a separator, lithium metal was used as a reference electrode/counter electrode and 2:1:2 volume ratio of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) in 1 M $LiPF_6$ was used as an electrolyte. The mass of the active materials of VO_2(B) and VO_2(B)-rGO composite was coated on current collector is 2.12 mg and 1.87 mg. The cells were assembled in an Argon-filled glove box (MBraun model Unilab). Electrochemical measurements were measured using standard CR2032 coin type cell. The biologic science battery tester BCS-805 was used to examine the electrochemical performance of prepared electrodes. Cyclic voltammetry (CV) was measured between 1.5 and 4.0 V at the scan rate of 0.1 mV s^{-1}, the galvanostatic charge–discharge capacities were measured at 0.1 C rate and, 1.5–4.0 V, and the electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 0.01 Hz to 10 kHz with an amplitude of 5 mV.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the typical XRD pattern of the VO_2(B) NRs and VO_2(B)-rGO composite. All the diffraction peaks of the VO_2(B) sample are in good agreement with the monoclinic phase (space group C2/m) with the lattice constants of $a = 12.03$ Å, $b = 30.69$ Å, $c = 6.42$ Å, and $\beta = 106.6$ Å (JCPDS 65-7960). The broadening peak from 22° to 27° indicated the presence of rGO in VO_2(B) material. The calculated crystallite sizes of the VO_2(B) NRs and VO_2(B)-rGO

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