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The electrochemical performance of lithium vanadate/natural graphite composite material as anode for lithium ion batteries

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ABSTRACT

Li_3VO_4 nanoparticles with mean size about 100 nm are uniformly deposited on the surface of natural graphite via a quasi sol gel method. The electrochemical performance of the Li_3VO_4/natural graphite composite as anode for lithium ion batteries is studied via galvanostatic battery testing, which shows excellent cycle stability and rate capability. At a specific current of 156 mA g^{-1}, it delivers discharge and charge capacity of 579 and 427 mAh g^{-1} in the initial cycle, which maintain of 469 and 468 mAh g^{-1} after 100 cycles. After 60 cycles at various specific currents from 234 to 11,719 mA g^{-1}, the discharge capacity can restore to 450 mAh g^{-1} when reverting the discharge/charge current to 234 mA g^{-1}. It is demonstrated that natural graphite has important effect on the electrochemcial performance of the composite electrode, and an appropriate amount of natural graphite is beneficial to reduce the charge transfer resistance and maintain stable charge transfer process in cycling.

1. Introduction

Lithium ion batteries have been not only widely used in today's portable electronic devices such as laptop computer, mobile phone and digital camera, but also are considered as the possible power sources of electric vehicles and field communication. The exploration and design of new advanced materials with high capacity and good electrochemcial performance has become one of the key issues in the development of lithium ion batteries.

As a new kind of anode, lithium vanadate (Li_3VO_4) shows higher volumetric capacity than graphite and lower voltage plateau and higher specific capacity than $Li_4Ti_5O_{12}$ [1], which suggests it as an ideal anode candidate for lithium ion batteries. Kim et al. fabricated Li_3VO_4 micro-particles by solid state reaction and solution-based methods, and the Li_3VO_4 prepared by solution-based method can deliver discharge capacity of 190 mAh g^{-1} after 100 cycles [2]. Li et al. reported the preparation of Li_3VO_4 micro-particles by a solid state method, which shows reversible capacity of 323 mAh g^{-1} as anode for lithium ion battery [1]. Shi et al. reported the fabrication of Li_3VO_4 microbox via a hydrothermal method, which shows reversible capacity higher than 330 mAh g^{-1}, without obvious capacity attenuation over 50 cycles [3]. In our previous study, we found Li_3VO_4 microparticles that prepared via hydrothermal pretreatment and subsequent annealing can deliver discharge capacity of 398 mAh g^{-1} after 100 cycles [4], and Li_3VO_4 deposited on Ni foam shows improved reaction kinetics and structure stability in cycling [5].

Meanwhile, it is demonstrated that combing Li_3VO_4 with graphene and coating Li_3VO_4 with carbon can effectively improve its electrochemical performance [3,6], which endows Li_3VO_4/C composite with great potential as anode for lithium ion batteries. However, graphene shows disadvantages over other carbon materials in terms of high cost, complicated fabrication method and easy to aggregate, which are not beneficial for large-scale fabrication. In contrast, natural graphite has the advantages over other carbon materials in terms of abundance in nature, low cost, high electronic conductivity and good structure stability, which has become an ideal carbon component in composite electrode materials [7].

Here in this paper, we report a facile way to deposite Li_3VO_4 nanoparticles on natural graphite, which shows excellent electrochemical performance as anode for lithium ion batteries. The facility, low cost and high efficiency of the preparation way is beneficial for the large-scale fabrication of Li_3VO_4/natural graphite composite and the practical application of Li_3VO_4/natural graphite in lithium ion batteries.

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2. Experimental

2.1. Fabrication procedure

The chemicals were analytical grade and purchased from Shanghai Chemical Reagents. Natural graphite was provided by Yichang Hengda graphite company (99.9%). In a typical procedure, 1 mmol V_2O_5, 3 mmol Li_2CO_3 and 5 mmol hexamethylenetetramine were dissolved in 30 ml distilled water. After stirring for 20 minutes, the homogeneous yellowy suspension was transferred into a 50 ml teflonlined autoclave, distilled water was subsequently added to 80% of its capacity. The autoclave was at last sealed and placed in an oven, heated at 120 °C for 24 h. After the reaction, the final viscous solution was transferred in a beaker, an appropriate amount of natural graphite (0.045, 0.09 and 0.18 g) was added into the solution and stirred for 1 h. Finally the suspension was dried and annealed in N_2 atmosphere at 500 °C for 5 h.

2.2. Structure and morphology characterization

The structure and morphology of the resulting products were characterized by X-Ray powder diffraction (Rigaku Ultima IV Cu Kα radiation λ = 1.5406 Å) and field-emission scanning electron microscopy (FE-SEM JSM 7500 F, JEOL).

2.3. Electrochemical characterization

For fabricating lithium ion battery, coin-type cells (2025) of Li/1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, 1:1:1 v/v/v)/Li_3VO_4/natural graphite electrode were assembled in an argon-filled dry box (MIKROUNA, Super 1220/750, $H_2O < 1.0$ ppm, $O_2 < 1.0$ ppm). Celgard 2400 microporous polypropylene was used as the separator membrane. Galvanostatic charge/discharge test was characterized on a multichannel battery test system (LAND CT2001A) in the voltage region between 0.02 and 3 V. The cyclic voltammetry (CV) measurement of the electrodes was carried out on a CHI660C electrochemical workstation at a scan rate of 0.2 mV s^{-1} between 0 and 3 V. Electrochemical impedance spectroscopy (EIS) measurement was performed on a CHI660C electrochemical workstation under open circuit conditions over a frequency region from 0.01 Hz to 100 kHz by applying an AC signal of 5 mV in amplitude throughout the test.

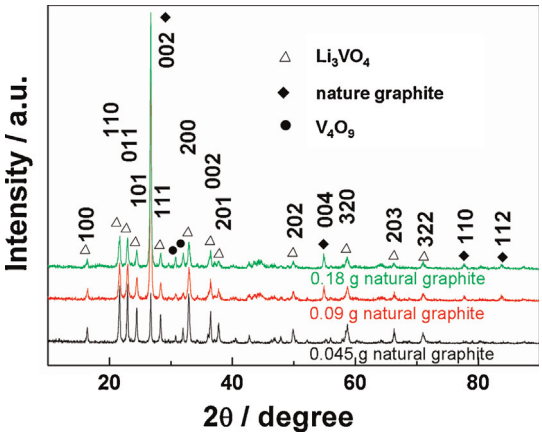

Fig. 1. XRD patterns of the obtained samples with different amount of natural graphite.

3. Results and discussion

XRD patterns of the as-prepared composites are shown in Fig. 1. As seen, the diffraction peaks located at 16.3°, 21.6°, 22.9°, 24.4°, 28.2°, 32.8°, 36.3°, 37.6°, 49.8°, 58.7°, 66.2° and 70.9° can be attributed to the (100), (110), (011), (101), (111), (200), (002), (201), (202), (320), (203) and (322) crystal faces of orthorhombic Li_3VO_4 with lattice constants a = 6.319 Å, b = 5.448 Å and c = 4.940 Å, which is in good agreement with the JCPDS, no. 38–1247. Strong and sharp diffraction peaks suggest that the obtained Li_3VO_4 is well crystallized. Two small diffraction peaks located at 30.4° and 31.6° (marked by*) can be indexed as the (311) and (112) crystal faces of orthorhombic V_4O_9 (JCPDS, no. 24–1391). Meanwhile, the diffraction peaks located at 26.4°, 54.6°, 77.3° and 83.3° are attributed to the (002), (004), (110) and (112) faces of hexagonal

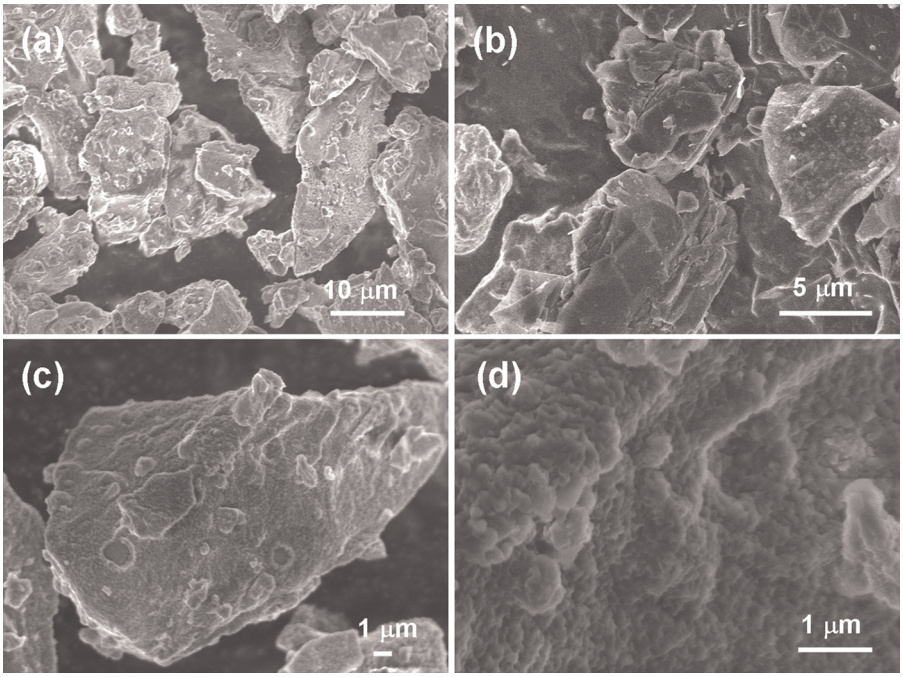

Fig. 2. Low magnification SEM images of Li_3VO_4/natural graphite composite with 0.09 g natural graphite (a) and natural graphite (b). SEM image (c) and magnified SEM image (d) of a single particle.