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Micro-sized cadmium tungstate as a high-performance anode material for lithium-ion batteries

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ABSTRACT

The application of cadmium tungstate ($CdWO_4$) to a lithium-ion battery anode was firstly reported in this paper. It was prepared by a facile precipitation reaction process. The $CdWO_4$ sample was characterized using X-ray diffraction and scanning electron microscopy. The electrochemical properties of $CdWO_4$ anode were investigated. The $CdWO_4$ delivered a high initial discharge capacity of 2042.4 mA h g^{-1}. The $CdWO_4$/C composite showed an improved electrochemical performance with an initial discharge capacity of 2304.1 mA h g^{-1} and achieved a discharge capacity of 305.1 mA h g^{-1} after 19 cycles. Electrochemical reaction mechanism of $CdWO_4$ with Li was also studied by cyclic voltammetry. It is suggested that $CdWO_4$ can be a promising high-capacity anode material for lithium-ion batteries.

1. Introduction

With the emergence and rapid development of lithium-ion batteries, anode materials play a crucial role in the lithium-ion storage. Among available anode materials, graphite has been commercialized due to its excellent cycling behavior and promotes rechargeable Li-ion cell's wide application to the portable, entertainment, computing and telecommunication equipment [1]. However, graphite has the limitations of the low theoretical capacity of 372 mA h g^{-1}, which can not satisfy the request of energy density for EV and HEV [2,3]. Furthermore, commercial lithium-ion batteries have a certain amount of carbon footprint about 70 kg CO_2 per kW h [4], which should be reduced to a low level given the global warming. Therefore, one of recent research focuses of Li-ion batteries is on seeking alternatives to commercial graphite.

In recent years, high-performance nanocomposite anode materials become one of the hottest research topics of lithium-ion batteries. Various nanocomposites such as Fe_3O_4/C, Co_3O_4/graphene, SnO_2/graphene, and mesoporous C–TiO_2–SnO_2 nanocomposites [5–8], which consist of transition metal oxides and carbon materials, have been widely studied to improve the energy density of Li-ion batteries. For example, CoO/graphene nanohybrids prepared by an ultrasonic method show a high reversible capacity of 650 mA h g^{-1} after 50 cycles, high coulombic efficiency (over 95%) and excellent cycling stability [9]. However, nanocomposites with an excellent electrochemical performance have the disadvantages of low initial specific capacity [10–13] and complex fabrication technique process [14,15]. Moreover, high cost and low output make nanocomposites can not satisfy commercial demand on account of high purity and homogeneous dimension requirement of nano-sized raw materials. Therefore, the novel and promising anode materials with excellent electrochemical performance, low cost and high output should be sought and studied.

Cadmium tungstate ($CdWO_4$) has attracted increasing attention due to its low radiation damage, high average refractive, high X-ray absorption coefficient and photo-catalytic function. It shows wide application prospect ranging from nuclear instrument detection, gamma camera, X-ray computed tomography to photocatalyst [16–19]. Nevertheless, to the best of our knowledge, the electrochemical performance of $CdWO_4$ has not yet been reported so far, although $ZnWO_4$ and $MnWO_4$ with the same structure as $CdWO_4$ have been studied as the novel anode materials for lithium-ion batteries [21–23]. $CdWO_4$ belongs to the monoclinic $P_{2/c}$ space group and its structure can be described as consisting of Cd and W atoms each being in a nearly octahedral coordination surrounded by six nearest neighbor oxygen atom sites (Fig. 1) [20,21]. Accordingly, cadmium tungstate, which has the high oxidation state W^{6+} and the open framework structure, may function in the lithium extraction/insertion reaction as an anode material. In this work, we report a facile and effective fabrication method to obtain $CdWO_4$ particles via the precipitation reaction route. The $CdWO_4$/C composite was prepared by using ball milling. The electrochemical properties of $CdWO_4$ as an anode material were investigated.

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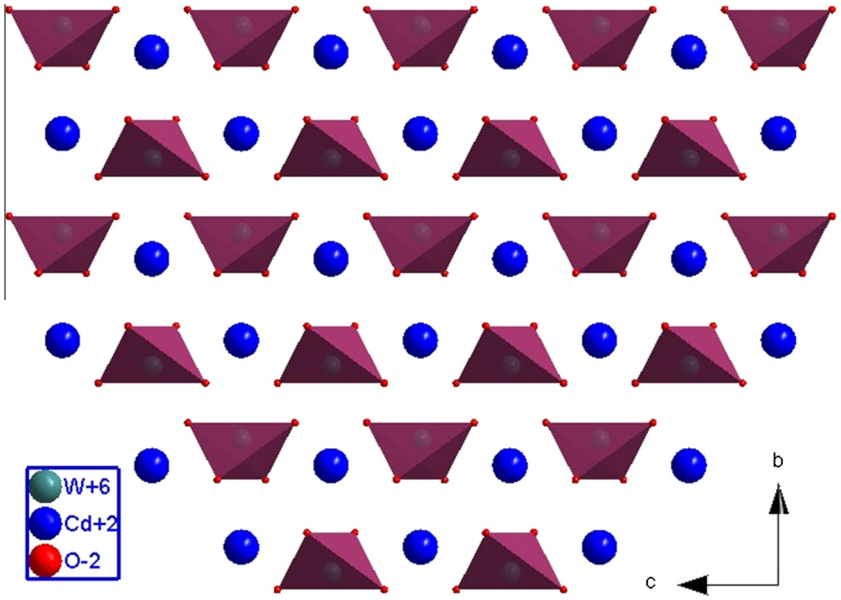

Fig. 1. Crystal structure of cadmium tungstate.

2. Experimental

2.1. Material preparation

Cadmium tungstate was prepared by using H_2WO_4, NH_4OH and $CdNO_3{\cdot}4H_2O$ as starting materials. Ammonium tungstate solution was firstly formed through dissolving tungstic acid into concentrated ammonium hydroxide. The color of stirred and heated mixture changed from a yellow suspension to a transparent solution. Then, equimolar $Cd(NO_3)_2$ solution was added to $(NH_4)_2WO_4$ solution slowly and dropwise. The pH of $(NH_4)_2WO_4$ solution was controlled in the range from 8.5 to 9.0 using $NH_3{\cdot}H_2O$. The precipitate was filtered and washed using distilled water and anhydrous alcohol, and then dried at 100 °C. Finally, the obtained sample was calcined at 1000 °C for 4 h. The as-prepared $CdWO_4$ were mixed with carbon black by using high energy ball milling with alcohol in a zirconia container for 10 h in an appropriate weight ratio of 2:1.

2.2. Characterization of samples

The structure characterization was carried out using powder X-ray diffraction (XRD, Bruker D8 Focus diffraction with nickel-filtered Cu Kα radiation). The scanning electron microscopy (SEM, Hitachi TM-3000) was conducted to probe the morphologies of $CdWO_4$ powder and $CdWO_4$/C composite.

Electrochemical properties of cadmium tungstate anode were investigated after assembling the coin cells in an Ar-filled glove-box. The anode was prepared by spreading a mixture of active material (60 wt.%), carbon black (30 wt.%), and poly(vinylidene fluride) binder (10 wt.%) dissolved in N-methyl pyrrolidone onto a copper foil current collector. The electrode was pressed and cut into a circular shape with a diameter of 15 mm. The metal lithium foil and glass fiber were used as a current electrode and separator, respectively. The electrolyte used was 1 mol L^{-1} $LiPF_6$ in mixed solvent of dimethyl carbonate and ethylene carbonate (EC: DMC = 1:1, v/v). All the galvanostatic charge/discharge tests were carried out by multichannel Land battery test system at a constant current density of 50 mA g^{-1} between 0 and 3.0 V. The cyclic voltammogram (CV) curves were obtained at a scan rate of 0.1 mV s^{-1} between 0 and 3.0 V by CHI 1000B electrochemical workstation.

3. Results and discussion

X-ray diffraction patterns of $CdWO_4$ (CWO) and ball-milled $CdWO_4$/C composite are shown in Fig. 2. It is obvious that all the reflection peaks of $CdWO_4$ are well indexed as monoclinic wolframite tungstate structure (space group $P_{2/c}$), and no other impurity is detected. The crystal lattice parameters calculated by the XRD data are a = 5.026 Å, b = 5.861 Å, c = 5.074 Å, which are very close to the standard data (a = 5.029 Å, b = 5.860 Å, c = 5.071 Å). After mixed with carbon, all the refection peaks of $CdWO_4$/C composite are agreed well with the pure sample, but become much

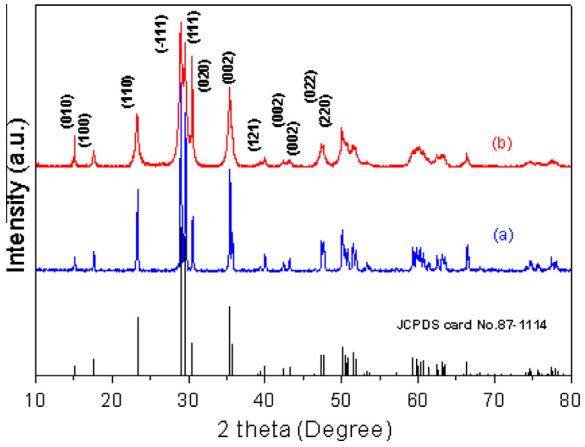

Fig. 2. X-ray diffraction patterns of (a) $CdWO_4$; (b) $CdWO_4$/C composite.

broad due to the carbon black. On the other hand, the morphologies of $CdWO_4$ particles and $CdWO_4$/C composite were observed by scanning election micrographs (SEM), as shown in Fig. 3. The $CdWO_4$ particles are irregular block with the particle size of about 1–9 μm. For the $CdWO_4$/C composite, the surface of particles is completely covered by carbon black, which could build an electro-conductive network.

Cyclic voltammetry was performed to verify the conversion reaction of $CdWO_4$ during charge and discharge processes. Fig. 4 shows the CV curves of the $CdWO_4$ anode cycled between 0 and 3.0 V. As shown in Fig. 4, the first discharge cycle differs from the subsequent charge–discharge cycles, which could be attributed to the irreversible structural destruction of $CdWO_4$ [24,25]. Obviously, two reduction peaks are observed at around 0.7 and 1.5 V in the first cathodic scan, which possibly correspond to the reduction of $CdWO_4$ to Cd^0 and W^0 and the formation of amorphous Li_2O [26–28]. However, these peaks decreased in subsequent cycles, indicating that semi-reversibly reaction occurred between $CdWO_4$ and Li. For the charge process, the anodic peaks at around 0.4, 1.0, 2.5 and 3.0 V are observed. These peaks disappear in subsequent cycles, which results from an irreversible process. The changes of position and intensity of redox peaks should be attributed to the