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The lithium storage properties of potassium octatitanate as anode materials for lithium-ion batteries

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ABSTRACT

Herein, potassium octatitanate ($K_2Ti_8O_{17}$, denoted as KTO), with a novel leaf-like morphology and a nanoscale size of less than 50 nm, was synthesized by a facile hydrothermal method and evaluated as anode materials for lithium-ion batteries. It was found that this material can reversibly intercalate lithium. As a result, the KTO shows impressive electrochemical performance, in terms of high lithium storage, good cycle performance and ultra-long life. This work may open up a broader vision into developing anode materials for lithium-ion batteries.

1. Introduction

Due to the fast development of electrical vehicle and hybrid electric vehicles and, at the same time, the currently commercial graphite anode can not meet the demand of next generation lithium-ion batteries (LIBs), the desire for next generation electrode materials with good safety, higher capacity, better cyclic and rate performance have been becoming more and more urgent [1]. Titanium is the ninth most abundant element on earth, as well as the synthetic methods of titanium dioxide and titanate are easy. No surprise, the research on titanium (Ti)-based materials (such as TiO_2, $Li_4Ti_5O_{12}$, $Na_2Li_2Ti_6O_{14}$ and so on) as anode materials for LIBs has attracted extensive attention due to their merits of higher work potential and superior structural stability [2,3]. But, the low capacity and poor power hinder the practical use of Ti-based materials in LIBs. Thus, the research focus on Ti-based materials is improving capacity and power performance. The main strategy is fabrication or development of proper nanostructures or new Ti- based materials [4].

Recently, lots of nanostructural TiO_2-based materials, such as nanowires, nanofibers, nanotubes, nanoribbons and nanosheets, had been prepared and displayed improved electrochemical performance as anode for LIBs, in terms of higher capacities and better rate capabilities [5–10]. Besides, new materials based on layered sodium titanate, such as $NaTi_3O_6(OH)\cdot 2H_2O$ and novel urchin-like nano/micro structure of $H_2Ti_2O_5$, have been researched and exhibited improved capacities and rate capabilities [11,12]. It was accepted that the electrochemical performance of Ti-based anode materials strongly dependent on their sizes, morphologies, structures and components which would provide electrodes with large specific surface area, good structure stability, more lithium intercalation, and fast mass and electron transport kinetics.

Herein, inspired by the above introduction, we synthesized a novel leaf-like $K_2Ti_8O_{17}$ (denoted as KTO) with a nanoscale size of less than 50 nm by a facile hydrothermal method and further evaluated its lithium storage performance as anode materials for LIBs. As a result, the KTO exhibits impressive electrochemical performance. This work may provide a new way for developing anode materials for LIBs.

2. Experiment

2.1. Preparation of KTO

In a typical synthesis, 1.5 mL of tetrabutyl titanate (TBT) was slowly dropped into 60 mL of 0.2 M KOH aqueous solution containing 0.05 wt% of H_2O_2 in advance. After stirring for 0.5 h, the obtained solution was transferred into a Teflon-lined stainless steel autoclave, and then placed in an oven at 180 °C for 24 h. After cooled down to room temperature, the white precipitation ($K_2Ti_8O_{17}$) was collected through centrifugation, washed with deionized water and ethanol thoroughly, and dried in an oven at 70 °C under vacuum for 12 h.

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2.2. Materials characterization

The characterizations of KTO were carried out by transmission electron microscopy (TEM, JEOL JEM-2010), X-ray diffraction measurement (XRD, Rigaku, D/max-Rbusing Cu K radiation) and X-ray photoelectron spectroscopy measurement (XPS, AXIS ULTRA DLD instrument with using aluminum K X-ray radiation). The specific surface area was examined by nitrogen (N_2) adsorption/desorption isotherms (Micromeritics ASAP 2010 instrument).

2.3. Electrochemical measurements

Electrochemical performances of KTO were studied using 2016-type coin cells assembled in an argon-filled glove box (German, M. Braun Co., $[O_2] < 1$ ppm, $[H_2O] < 1$ ppm). The working electrodes were consisted of the active material KTO, conductive material (acetylene black, AB), and binder (sodium carboxymethyl cellulose (CMC)) in a weight ratio of 70:20:10 and then pasted on Cu foil. After that, the electrodes were dried in a vacuum oven at 110 °C for overnight. The pure lithium and glass fiber (GF/A) purchased from Whatman was respectively used as the counter electrode and separator. The electrolyte is composed of a solution of $LiPF_6$ (1 M) in EC and DMC (1:1 by volume). The galvanostatic discharge/charge cycle tests were carried out on a CT2001a cell test instrument (LAND Electronic Co.) at room temperature. Cyclic voltammetry (CV) test was conducted on a CHI660D electrochemical workstation.

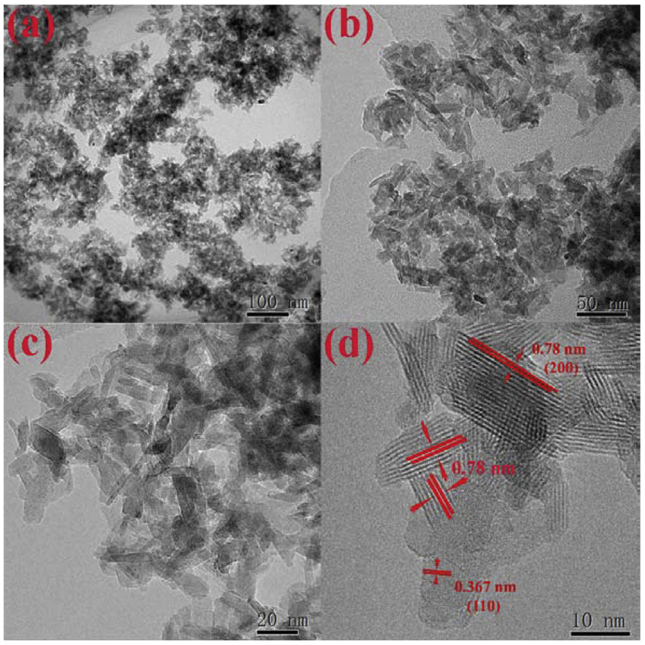

Fig. 1. TEM images with different magnifications (a–c) and HRTEM image (d) of KTO.

3. Results and discussion

Fig. 1(a–c) shows the TEM images of KTO with different magnifications, it can be clearly seen that the KTO is composed of novel leaf-like nanorods with average sizes of less than 50 nm. The HRTEM image, given in Figs. 1d and S1, syllabify shows two sets of lattice fringes with a spacing of 0.78 and 0.367 nm assigned to the d200-spacing and d110-spacing of monoclinic $K_2Ti_8O_{17}$, respectively, suggesting the as-synthesized KTO has a highly crystalline structure [13].

Fig. 2a gives the XRD patterns of KTO, the all diffraction peaks can be well indexed into monoclinic structured $K_2Ti_8O_{17}$ (JCPDS No. 41-1100) with a space group of C2/m [14]. The peaks show broad nature which can be attributed to the small crystal size of KTO. Fig. 2b displays the N_2 adsorption/desorption isotherms of KTO, a large specific surface area of 181.5 $m^2\ g^{-1}$ is recorded, which also demonstrates the small crystal size nature of KTO. The larger specific surface area and small size would be promoted the transferring dynamics of ions and electrons by providing the electrode with larger contact interface with electrolyte and shortening the diffusion distance of ions and electrons.

Finally, the lithium storage properties of as-prepared KTO are evaluated as anode materials for LIBs, as displayed in Fig. 3a. It exhibits an impressive performance, delivering a high reversible capacity of 317.7 mA h g^{-1} after 460 cycles at 50 mA g^{-1}. The coulombic efficiency is 44.5% at first cycle but quickly increases to above 94% after 3 cycles and then stabilizes at above 99%, demonstrating good cycling stability. The initial capacity loss may be mainly ascribed to the nanostructured characteristic and trace water adsorbed on the large specific surface area of KTO, and the formation of SEI film. Fig. 3b shows the representative galvanostatic charge/discharge profiles of KTO at a current density of 50 mA g^{-1} within a cut-off voltage window between 0.01 and 3 V. The discharge and charge capacities at 1st, 2nd, 30th, 50th, and 100th are 683 and 304, 306.5 and 263.1, 227.2 and 225.3, 227.3 and 224.9, and 219 and 218.7 mA h g^{-1}, respectively. It can be distinctly observed that, after second cycle the coulombic efficiency increases to above 99% and then stabilizes throughout the entire cycle tests, implying the formed SEI film retained intact and good reversibility of electrochemical reactions. In order to more intuitive to observe the electrochemical behavior of KTO, the cyclic voltammograms curves (CV curves) are conducted at a scan rate of 0.3 mV s^{-1} between 0.0 and 3.0 V, as presented in Fig. 3c. During

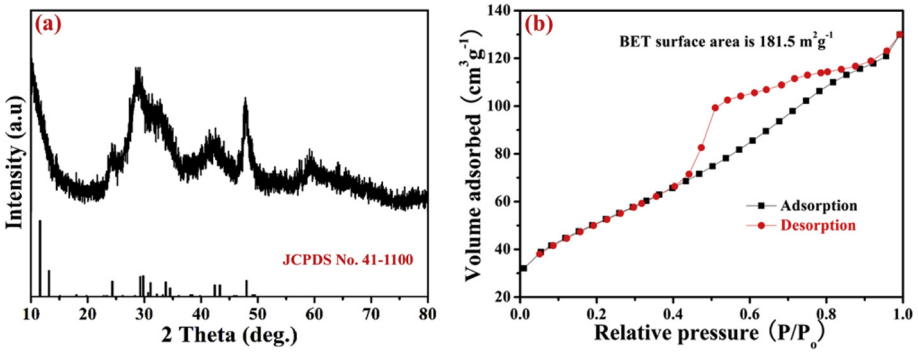

Fig. 2. XRD patterns (a) and N_2 adsorption/desorption isotherms (b) of KTO.