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Carbon-coated lithium titanium phosphate nanoporous microplates with superior electrochemical performance

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HIGHLIGHTS

- $LiTi_2(PO_4)_3$/C nanoporous microplates were prepared by a solvothermal method.
- $LiTi_2(PO_4)_3$/C nanoporous microplates show superior electrochemical performance.
- The superior electrochemical performance is attributed to the unique structure.
- Uniform coating of carbon layer enhances the electrochemical performance.

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ABSTRACT

In this study, we report a facile method to synthesize carbon-coated $LiTi_2(PO_4)_3$ nanoporous microplates (LTP/C MPs) using ethylenediamine as the chelating agent and carbon source. The as-prepared LTP/C MPs with thickness of 0.4 μm consist of interconnected nanosized particles embedded in nano-thickness carbon layer and well-dispersed nanopores. The carbon layer significantly improves the electrochemical performance of $LiTi_2(PO_4)_3$ microplates. LTP/C MPs deliver a reversible capacity of 121 mAh g^{-1} at 0.2C (1C = 138 mAh g^{-1}) and show a remarkable capacity retention of 94.2% over 100 cycles when matched with Li metal counter electrode. It also presents excellent electrochemical properties as anode material for aqueous rechargeable lithium batteries (ARLBs). LTP/C MPs//$LiMn_2O_4$ ARLB shows a high discharge capacity of 76 mAh g^{-1} at 20 mA g^{-1} and superior rate capability. The results suggest a practical stratagem to develop a novel composite in which the carbon is coated with $LiTi_2(PO_4)_3$ nanoporous microplates, which can become one of the promising electrode materials for both non-aqueous and aqueous lithium ion batteries.

1. Introduction

In recent years, the NASICON-type lithium titanium phosphate ($LiTi_2(PO_4)_3$) has been demonstrated as an interesting cathode electrode material for polymer lithium batteries [1], and it is also a promising anode electrode material in aqueous rechargeable lithium batteries [2–4]. $LiTi_2(PO_4)_3$ has a rhombohedral (space group: R3c) structure with an open three-dimensional framework that consists of formula $Ti_2P_3O_{12}$. The framework is built of PO_4 tetrahedron linked by corners to TiO_6 octahedron. Conversely, TiO_6 units are connected with six PO_4 groups. The interstitial voids generated within the network consist of two types known as M_1 and M_2 sites. The M_1 site is coordinated by a trigonal antiprism of oxygen and the M_2 site has a distorted eight-fold coordination. The charge-compensating alkaline ions are located in these two positions. Initially, it was believed that Li ions occupy the M_2 sites during insertion to form $Li_3Ti_2(PO_4)_3$ [1]. The conduction channels are generated along the c-axis direction, in which Li ions occupy the interstitial sites. Consequently, the Li ions can move easily along the conduction channels [2].

As a matter of fact, $LiTi_2(PO_4)_3$ has recently attracted attention for the electrode of choice in both nonaqueous lithium ion battery and aqueous rechargeable lithium battery. However, pristine $LiTi_2(PO_4)_3$ generally shows extremely poor capacity performance [5–7]. The poor electronic conductivity of the low intrinsic three-dimensional phosphates limits the wide use of $LiTi_2(PO_4)_3$ in large-scale applications [8–10]. Therefore, much efforts have been

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made to overcome the drawbacks. The electrochemical behaviors of $LiTi_2(PO_4)_3$ in organic electrolyte have been previously studied [1,9–12]. Patoux et al. [1] prepared $LiTi_2(PO_4)_3$ by using traditional solid-state method and subsequently ball-milled with 16.7 *wt.%* carbon forming $LiTi_2(PO_4)_3/C$ nanocomposite. The cell presented discharge capacities of 120 and 95 mAh g^{-1} for the first and the 40th, respectively, between 2.0 and 3.4 V at 1C. In our previous work, we also successfully synthesized $LiTi_2(PO_4)_3/C$ composites by the polyvinyl alcohol assisted sol–gel method and ball-milling method. A reversible discharge capacity of 129.5 mAh g^{-1} could be obtained at 0.1C between the voltage of 1.5 and 3.5 V. The electrochemical performance of $LiTi_2(PO_4)_3/C$ composites is much better than pure $LiTi_2(PO_4)_3$ [9,10]. Pechini-type methods, including a combined process of metal complex formation and in situ polymerization of organics, were also used to synthesize $LiTi_2(PO_4)_3$ [11]. Wessels et al. [12] used Pechini-type method to synthesize $LiTi_2(PO_4)_3/C$ with a carbon content of 4 *wt.%*, the obtained materials delivered an initial discharge capacity of 115 mAh g^{-1} with 70% capacity retention after 160 cycles at the current density of 15 mA g^{-1} between 2.0 and 3.0 V. All those reported $LiTi_2(PO_4)_3/C$ nanocomposites in organic electrolyte showed better rate capability and cycle performance than pristine $LiTi_2(PO_4)_3$, indicating that forming $LiTi_2(PO_4)_3/C$ composites is one of the most effective ways to improve its electrochemical performance. Besides, $LiTi_2(PO_4)_3$ was also proposed to be used as suitable negative electrode of lithium ion battery with aqueous electrolyte [2–4,12]. $LiTi_2(PO_4)_3//LiMn_2O_4$ electrodes tested in 5 M $LiNO_3$ aqueous solution delivered capacity approximately 45 mAh g^{-1} at average voltage of 1.50 V [4]. $LiTi_2(PO_4)_3$ was synthesized using a Pechini method and tested in pH-neutral Li_2SO_4 delivered an initial discharge capacity of 118 mAh g^{-1} at 0.2C [12]. Similarly, $LiTi_2(PO_4)_3$ anode in aqueous lithium battery still remains to improve the electrochemical performance. Furthermore, it is worth noting that most of the above methods to synthesize $LiTi_2(PO_4)_3/C$ nanocomposites include at least two-steps, i,e., the synthesis of $LiTi_2(PO_4)_3$ and carbon coating. In the above, the products suffer from the problems of disordered morphology and inhomogeneous particle sizes. Even the chemical vapor deposition (CVD) method for preparing $LiTi_2(PO_4)_3/C$ [2] and the facile microwave-assisted solvothermal process for synthesizing $LiTi_2(PO_4)_3$/reduced graphene oxide (rGO) nanocomposite [13] still suffer the same problems. Hence, it is still a great challenge to develop facile methods which can realize the control of morphology and the improvement of electronic conductivity.

Solvothermal/hydrothermal method, as a widely-used strategy to prepare various nanospheres, nanoplates and hollow materials, has the advantages of fast reaction kinetics and reasonable control of morphology [14–18]. On the other hand, the solvothermal/hydrothermal method used to synthesize regular $LiTi_2(PO_4)_3$ has never been reported. Therefore, we firstly synthesize the $LiTi_2(PO_4)_3/C$ nanoporous microplates (LTP/C MPs) by a one-step solvethermal method in this context. Benefitting from the porous plate structure, electrolyte can penetrate into the synthesized electrode material flexibly. Besides, LTP/C MPs demonstrate much better electrochemical performance than bare $LiTi_2(PO_4)_3$ nanoporous microplates (LTP MPs) due to the uniform carbon layer. Ultimately, the LTP/C MPs show excellent electrochemical performance as electrode materials for non-aqueous lithium ion batteries and aqueous rechargeable lithium batteries.

2. Experimental

2.1. Material synthesis

The materials were synthesized by a solvothermal route. 3.4 mL tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) was first dissolved into the ethanol and acetone mixture solution. Then, 45 mL distilled water was added into the above solution drop by drop and stirred for half an hour, yielding an ivory suspension. A stoichiometric amounts of lithium acetate hydrate ($CH_3COOLi\cdot 2H_2O$) and ammonium dehydrogen phosphate ($NH_4H_2PO_4$) were introduced into the above suspension liquid under magnetic stirred for 3 h. After that, 3.0 mL anhydrous ethylenediamine (EDA) was added to the solution and stirred for 30 min. The resulting suspension was transferred into a sealed Teflon-lined container, and kept at 180 °C for 10 h. After reaction, the precipitate was collected by filtration and washed with deionized water and ethanol for several times to remove the impurities. The obtained precipitate was dried at 80 °C in an oven to form white precursor. Finally, the precursor was calcined at 850 °C for 10 h in argon (Ar) atmosphere to get the black $LiTi_2(PO_4)_3/C$ nanoporous microplates (LTP/C MPs). For comparison, bare $LiTi_2(PO_4)_3$ nanoporous microplates (LTP MPs) were also obtained under the same condition, besides the annealing process under Air atmosphere.

2.2. Structure characterization

The LTP/C MPs were analyzed by thermogravimetry (TG) using a Thermogravimetric-differential Thermal analyzer (Standard Type High temp. Type, Rigaku) in air atmosphere.

The structures of synthesized samples were characterized by X-ray diffraction spectroscopy (XRD). X-ray powder diffraction data were obtained by using a Rigaku D/MAX-2500 powder diffractometer with a graphite monochromatic and Cu-Kα radiation ($\lambda = 0.15418$ nm) in the 2θ range of 10–80°.

Scanning electron microscope (SEM) images of the samples were collected by using JEOL JSM-6610LV scanning electron microscope. Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) measurements were carried out by using a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV.

2.3. Electrochemical measurements

The lithium titanium phosphate electrodes were fabricated by mixing the powder mixture of the sample, acetylene black (AB), and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10 and pasted onto pure aluminium film. The lithium half-cells (CR2025-type) were assembled with the lithium titanium phosphate electrodes thus fabricated, metallic lithium counter electrode, celgard 2300 film separator, and 1 M $LiPF_6$ in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) as the electrolyte. The assembly of the testing cells was carried out in an argon-filled glove box, where the concentrations of water and oxygen were kept less than 5 ppm. The discharge–charge cycle tests were run at different current densities of 0.2, 0.5, 1, 2, 5 and 10C ($1C = 138$ mAh g^{-1}) between 1.5 and 3.5 V. The electronic conductivity was tested via the four-point probe method using a RTS-8 Digital instrument on the samples that were pressed at 5 MPs into disks with a usual diameter of 8 mm and a thickness of 1.6 mm. All the tests were performed at room temperature.

The $LiMn_2O_4$ electrode was fabricated by mixing commercial $LiMn_2O_4$ (provided by the Haixing Battery Co., Ltd., China), AB, and PVDF binder in a weight ratio of 80:10:10. A three-electrode electrochemical cell was employed for the measurement of cyclic voltammetry (CV) of LTP/C MPs composites and $LiMn_2O_4$ electrode in saturated $LiNO_3$ aqueous electrolytes. The as-prepared electrode, a saturated calomel electrode (SCE), and a stainless steel mesh were used as the work, the reference, and the counter electrode, respectively.