



Advanced and safer lithium-ion battery based on sustainable electrodes

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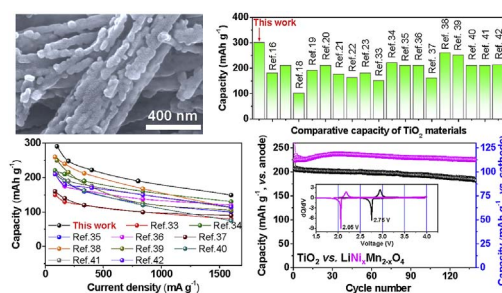
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HIGHLIGHTS

- A new porous structured anatase TiO₂ nanobundles (PTNBs) is synthesized.
- The synthetic strategy is green and the formation mechanism is discussed.
- The PTNBs exhibits high lithium storage capacity and better rate capability.
- Sustainable and safer Li-ion full battery of PTNBs/LiNi_xMn_{2-x}O₄ are presented.

GRAPHICAL ABSTRACT



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ABSTRACT

Seeking advanced and safer lithium-ion battery with sustainable characteristic is significant for the development of electronic devices and electric vehicles. Herein, a new porous TiO₂ nanobundles (PTNBs) is synthesized through a scalable and green hydrothermal strategy from the TiO₂ powders without using any high-cost and harmful organic titanium-based compounds. The PTNBs exhibits an extremely high lithium storage capacity of 296 mAh g⁻¹ at 100 mA g⁻¹, where the capacity can maintain over 146 mAh g⁻¹ even after 500 cycles at 1000 mA g⁻¹. To pursue more reliable Li-ion batteries, full batteries of PTNBs/LiNi_xMn_{1-x}O₄ (x = 0, 0.5) using spinel structured cathode are constructed. The batteries have the features of sustainability and deliver high capacities of 112 mAh g_{cathode}⁻¹ and 102 mAh g_{cathode}⁻¹ with stable capacity retentions of 99% and 90% over 140 cycles. Note that the energy densities can achieve as high as 267 and 270 Wh kg_{cathode}⁻¹ (535 and 540 Wh kg_{anode}⁻¹) respectively, which is feasible to satisfy diverse requirements for energy storage products. We believe that the universal synthetic strategy, appealing structure and intriguing properties of PTNBs is applicable for wider applications, while the concept of sustainable strategy seeking reliable and safer Li-ion battery can attract broad interest.

1. Introduction

The safety issue and sustainability of lithium-ion batteries (LIBs) has attracted more attention because it has become one bottle-neck in the

dramatically increased demand of grid energy storage system, electronic devices and electric vehicles [1–3]. To guarantee the durability of LIBs, the strategies of controlling inner thermal effect [4], adding stabilizer in electrolyte [5,6], modifying battery configuration [7,8],

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and developing solid-state batteries [9] are being widely investigated. All these researches greatly improve the safety factors; however, more technologies and knowledges are still quested towards more reliable battery system particularly satisfying for the sustainable development [10]. Based on the model of current LIBs (*i.e.*, graphite vs. lithium layered metal oxide), several aspects can be further explored. For example, replace of graphite anode, because its low voltage for the lithium-ions intercalation may lead the formation of lithium dendrites, which can impale the separator and cause the short circuit [11]. Besides, the flammable properties of carbon anode and lithiated carbon (*i.e.*, Li_xC_6) [12], together with the side reactions of electrode and electrolyte beyond a high cut-off voltage (*e.g.*, $> 4.0\text{ V}$) [13,14], always lead to an unsatisfactory safety, low Coulomb Efficiency (CE) and severe capacity decay. Thus herein, we choose sustainable TiO_2 as anodic material considering its non-flammable characteristic and the moderate voltage platform (*i.e.*, $\sim 1.7\text{ V}$) for the storage of lithium. Distinct from the previous researches preparing the TiO_2 -based composites *via* conductive compositions modification [15–17], metal/non-metal elements-doping [18–20], and/or surface coating/nitridation/hydration [21–23], a scalable, green and convenient strategy was developed to synthesize a novel structured TiO_2 nanobundles (PTNBs), which demonstrates extremely high and even better performances in lithium (ion) battery.

To design the safer and sustainable LIBs, the cobalt-free, cost-effective and spinel structured $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0, 0.5$) cathode is chosen instead of lithium layered metal oxide considering its higher stability [24]. It is well known that the oxygen evolution reaction of lithium layered metal oxide as cycling remains challenging in current LIBs [25]. Stimulated by the high capacity of PTNBs (*e.g.*, 280 mAh g^{-1} at 100 mA g^{-1}) available in industrial production, two kinds full batteries of PTNBs/ $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ with high CE and stability have been introduced. The constructed battery is reliable and has the advantages of improved safety, stability and sustainability, where the features can satisfy diverse requirements in sustainable energy storage products.

2. Experimental

2.1. Synthesis of PTNBs

Typically, 1.0 g industrial-grade TiO_2 powders were dispersed into 70 mL 10.0 M NaOH solution and stirred for 4 h. The solution was transferred into Teflon lined stainless steel autoclave and thermally treated at $180\text{ }^\circ\text{C}$ for 24 h in oven. After cooling down to the room temperature, the powders were collected by filtration and then washed by HCl ($\text{pH} = 1$) and water to neutral. The powders were re-dispersed into 70 mL 1.0 M acetic acid solution and kept stirring for 30 min; subsequently the solution was thermally treated at $180\text{ }^\circ\text{C}$ for 4 h in the Teflon lined stainless steel autoclave. Finally, calcination of the powders at $500\text{ }^\circ\text{C}$ for 4 h under a steady air gives rise to the product of PTNBs.

2.2. Electrode preparation

The active materials of PTNBs, conductive carbon of Super P, and binders of polyacrylic acid/carboxymethyl cellulose (PAA-CMC) [26] with the mass ratio of 7.5:1.5:0.5:0.5 were homogeneously mixed in water to form a slurry, which was then casted on the copper foil by doctor blade. After vacuum drying at $80\text{ }^\circ\text{C}$ overnight, the foil was punched into circular electrode with a diameter of 14 mm (alternatively $\text{Ø}16$ for full battery). The mass density of active materials is about 2 mg cm^{-2} with the thickness around at 40–50 μm . Note that a rough comparative lithium storage capability of TiO_2 is listed and discussed as one of the reference considering the mass density and thickness of TiO_2 is different or lack in different literature. For the preparation of cathodic electrode, the cathodic powders of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0, 0.5$) were synthesized first by the sol-gel method [27]. And then, the

ingredients of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ cathode, Super P, graphite and polyvinylidene difluoride (PVDF) binder with the mass ratio of 8.5:0.5:0.5:0.5 was mixed to form a slurry in the *N*-Methyl-2-pyrrolidone (NMP). The slurry was casted on the aluminium foil and then dried at $120\text{ }^\circ\text{C}$ for 12 h before punch. The mass density of LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were controlled around at 4 mg cm^{-2} .

2.3. Characterizations and measurements

The crystal information was acquired by X-ray powder diffraction (XRD) using a X'Pert-ProMPD (Holand) D/max- γ A X-ray diffractometer with Cu K α radiation ($\lambda = 0.154178\text{ nm}$). The morphology of PTNBs was characterized by the scanning electron microscopy (SEM) on a FEI-quanta 200 F scanning electron microscope with acceleration voltage of 30 kV. The distribution and crystalline structure of PTNBs was analysed by the transmission electron micrograph (TEM) with using the FEI-Tecna F20 (200 kV) transmission electron microscope (FEI). Nitrogen adsorption-desorption isotherms were measured by the instrument of ASAP2050 (Micromeritics Instrument Corporation) surface area & porosity Analyzer at 77 K. The electrochemical tests were carried out using the 2032-type coin cell and they were assembled in the glove box filled with pure argon, in which the moisture and oxygen were strictly controlled below 0.1 ppm. The half-cell has the configuration of Li metal (–) | Microporous polypropylene separator | electrode (+) filled with the electrolyte of 1.0 M LiPF_6 , 1 wt% vinylene carbonate (VC) additive in the mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) (w/w, 1/1). In the full battery, the electrodes of LiMn_2O_4 or $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were applied as cathode versus the anode of pre-lithiated PTNBs. The principle of designing full battery was followed by the description in recent literature [28]. Before assembling the full battery, the PTNBs electrode is prelithiated first to compensate the irreversibility. The prelithiation process is similar as the that in recent literature [28], in which the PTNBs electrode contacts with the electrolyte-wetted lithium foil and reacts for a certain time. The amount of lithium in anode after the prelithiation can be controlled by the reaction time and calculated by the discharged capacity differences in the first cycle comparing to that of the pristine one. Generally, the prelithiation procedure is needed to get a good battery performance; otherwise the large irreversibility of anode (*i.e.*, PTNBs) would consume a large part of lithium ions from cathode, leading to a low coulombic efficiency and inferior cycle ability. Galvanostatic charge-discharge was conducted by the TOSCAT-3100 at different current densities, and the cyclic voltammetry was collected by the instrument of Biologic VMP3 under the scan rate of 0.1 mV s^{-1} .

3. Results and discussion

3.1. Features of PTNBs

The PTNBs has a high crystallization belonging to the anatase TiO_2 (JCPDS Card No. 89-4921) (Fig. 1a). The features of PTNBs including the morphology of uniform nanobundles, high length/diameter ratio (*e.g.*, average length of 1–5 μm with the diameter of 200 nm) and rich porosity were demonstrated in SEM and TEM images (Fig. 1b–c). The nanobundle consists of connected nanocrystals, where numerous pores and crystalline boundaries were constructed, giving rise to a rough surface. The building block of nanocrystals has the lattice fringe with a spacing of 0.35 nm as observed under HRTEM (Fig. 1d), which is consistency with and correspond to the (001) planes of crystalline TiO_2 . The porosity and external structure were measured by BET analysis (Fig. 1e–f), where the N_2 adsorption-desorption isotherm can be categorized as type III isotherm considering the absence of the typical distinct hysteresis loop [29]. The result is in accordance with the structural observations. The pore volume of PTNBs is moderate around $0.057\text{ cm}^3\text{ g}^{-1}$ because of the ultrathin thickness (Fig. 1b). The specific structure of PTNBs could be ascribed to the formation mechanism,

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