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Metal–organic framework derived titanium-based anode materials for lithium ion batteries

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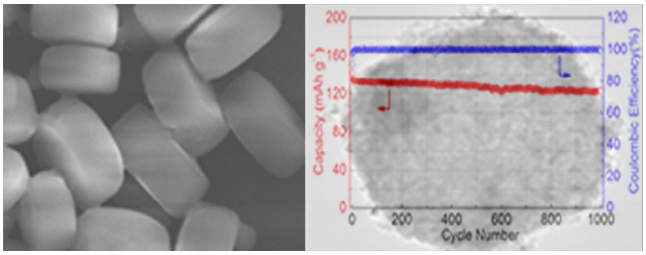
HIGHLIGHTS

- Porous TiO_2 and $Li_4Ti_5O_{12}$ were prepared using a titanium-based MOF as template.
- High porosity avails the penetration of electrolyte and tranfer of Li^+/electrons.
- Nanosized porous TiO_2 and $Li_4Ti_5O_{12}$ display excellent electrochemical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Here, we report a facile and scalable strategy to prepare porous anatase TiO_2 tablet consisted of nanoparticles, which is evolved from titanium-based metal–organic framework (MOF) template. After subsequent wet-chemical lithiation and post-annealing, porous $Li_4Ti_5O_{12}$ nano-tablet is also obtained. When tested as anode materials for lithium ion batteries, both of them exhibit outstanding electrochemical performances. The capacity of the anatase TiO_2 reaches up to 228 mAh g^{-1} at 0.1 A g^{-1}. At the same time, $Li_4Ti_5O_{12}$ delivers a high reversible capacity of 158 mAh g^{-1} at 0.1 A g^{-1}, and excellent cycling stability of maintaining a capacity of 122 mAh g^{-1} after 1000 cycles at 1 A g^{-1} between 1.0 V and 2.5 V. The excellent electrochemical properties are attributed to their unique porous structure, which increases active sites to accommodate lithium ions and improve ionic diffusion.

1. Introduction

Recently, rechargeable lithium ion batteries possess the merits of large electrical energy storage and continuous power output capabilities in portable electronics, electric vehicles and hybrid electric vehicles [1–4]. Traditional graphitic carbons anode used for lithium ion batteries display poor rate property, which results from their low lithium ion diffusion coefficient. Because of the low lithium ions intercalation voltage (approximately 0.1 V *vs.* Li^+/Li), solid electrolyte interface (SEI) film and lithium dendritic crystals are easily formed on the surface of graphitic carbons anode, which would exist safety threat and poor cycle life [5–8]. To meet the demands of long cycle life, good rate capability and high safety, titanium-based anode materials have been extensively studied for lithium ion batteries due to several inherent advantages [9–16].

As for TiO_2 polymorphs, the insertion and extraction reactions of lithium ions occur in the voltage range of 1.4–1.8 V *vs.* Li^+/Li [5,17]. Low packing density of anatase TiO_2 (density, ρ = 3.89 g cm^{-3}) and TiO_2-B (ρ = 3.73 g cm^{-3}) exhibit higher lithium storage capacity compared to densely packing of brookite (ρ = 4.13 g cm^{-3}) and rutile (ρ = 4.25 g cm^{-3}) [5,18]. Anatase TiO_2 is known as an electrochemical active material. The chemical diffusivity of lithium ions in anatase TiO_2 mostly depends on the electronic conductivity of TiO_2 and the diffusion distance of lithium

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ions in the bulk of TiO_2. Reducing anatase TiO_2 particle size is significant to improve the diffusion of lithium ions due to shortening Li^+ diffusion pathways [19,20].

Additionally, $Li_4Ti_5O_{12}$ is regarded as one of the most promising anode materials for lithium-ion batteries, and it is crucial for nanostructured $Li_4Ti_5O_{12}$ to achieve high electrochemical properties. Spinel $Li_4Ti_5O_{12}$ possesses a high intercalation/deintercalation potential voltage of 1.55 V *vs.* Li^+/Li, which can effectively avoid the formation of solid electrolyte interphase (SEI) layer and dendritic lithium [21–23], thus exhibiting high safety [24]. Besides, $Li_4Ti_5O_{12}$ is a kind of "zero-strain" materials with merely 0.2% volume change during charge/discharge process [25,26]. The lattice parameter of $Li_4Ti_5O_{12}$ (8.3595 Å) and the discharged product of $Li_7Ti_5O_{12}$ (8.3538 Å) are quite close [27–29]. Meanwhile, $Li_4Ti_5O_{12}$ is low cost and environmental benignity. The capacity of lithium storage is mainly achieved through the reversible transition reaction between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$. Introducing porous structure can effectively relieve the issue of the intrinsically poor electronic conductivity of spinel $Li_4Ti_5O_{12}$ (energy gap 3.8 eV), and improve its electrochemical property due to large specific surface area and short diffusion length [30,31].

In recent years, metal–organic frameworks (MOFs) have attracted more and more attention due to their large specific surface area and high porosity. The incorporation between inorganic metal clusters and organic linkers results to a diversity of three-dimensional structures [32–34]. One of the most significant features of MOFs is their interaction with small organic molecules to form micro-mesoporous hybrid materials, having been applied in a variety of fields [35]. For example, the Ti-based MOF $Ti_8O_8(OH)_4(bdc)_6$(MIL-125(Ti)) (bdc = benzene-1,4-dicarboxylate) had been reported, which was used as photocatalyst for the reduction of CO_2 [35,36]. This kind of MOF material can be of a great many immobilized titanium sites within porous MOFs, and it can also result to isostructural MOFs [35]. Wang et al. [37] reported a rutile TiO_2-C nanocomposite as a kind of lithium ion battery anode materials by two-step pyrolyzation of the MIL-125(Ti) with high electrochemical performance.

Here, we design a facile method to synthesize titanium-based anode materials. Firstly, we prepared nano-tablet-like TiO_2 by pyrolyzing Ti-based MOF (MIL-125(Ti)) at high temperature under air atmosphere. By introducing wet-chemical lithiation and calcination, porous $Li_4Ti_5O_{12}$ nano-tablet was obtained. This novel nanostructure could effectively facilitate the fast transfer of lithium ions and electrons. The MOF route for synthetizing tablet-morphology TiO_2 and $Li_4Ti_5O_{12}$ is much different from other traditional methods, and it is easy to form separated nanoparticles in homogeneous reaction conditions. Meanwhile, it shortens the diffusion channel of lithium ions and electrons through small nanoparticles. Due to the facile preparation method and superior electrochemical performance, nano-tablet-like TiO_2 and $Li_4Ti_5O_{12}$ will become the promising anode materials for next generation lithium ion batteries.

2. Experimental

2.1. Materials preparation

2.1.1. Preparation of MIL-125(Ti) precursor

MIL-125(Ti) or $Ti_8O_8(OH)_4(bdc)_6$ was prepared by the following procedure reported elsewhere [35]. Typically, a mixed solution of containing 3.0 g of 1, 4-benzenedicarboxylic acid, 6 mL of anhydrous methanol, 54 mL of anhydrous N,N-dimethylmethanamide (DMF) and 1.56 mL of tetrabutyl titanate (TBT) was stirred until the solution becomes clear, and then introduced into a 100 mL Teflon lined autoclave and heated at 150 °C for 72 h. After cooling down to room temperature, the resultant white suspension was filtered and washed with methanol for several times, and then dried the obtained white powder under vacuum at room temperature.

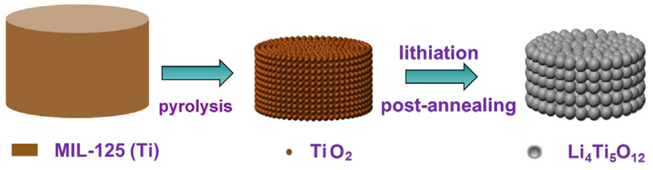

Fig. 1. Schematic illustration of the synthetic process of porous TiO_2 and $Li_4Ti_5O_{12}$.

2.1.2. Preparations of porous TiO_2 and $Li_4Ti_5O_{12}$

The prepared of MIL-125(Ti) was heated to 400 °C at a speed of 1 °C min^{-1} and kept at that temperature for 2 h under air atmosphere to receive TiO_2 product, then the obtained powder was immersed in 30 mL of LiOH solution (2 M) at 60 °C for 10 h. The resulting precipitation was washed with DI water for several times and dried at 60 °C for 12 h, followed by calcination at 550 °C for 2 h under air atmosphere to obtain $Li_4Ti_5O_{12}$.

2.2. Material characterization

The microstructural properties of the resultant samples were obtained by using a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6308LV) and transmission electron microscope (TEM, Philips CM100). The crystal structure was characterized by X-ray diffraction (XRD, Bruker D8 with Cu Kα radiation). The porous structure was tested by the nitrogen adsorption–desorption technique by an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics BK122T-Banalyzer).

2.3. Electrochemical test

Electrochemical tests were carried out in standard CR2032-type coin cells. The working electrodes were prepared by mixing the active materials, acetylene black and poly (vinylidene fluoride) (PVDF) with a weight ratio of 70: 20: 10 in N-methyl pyrrolidinone (NMP), and pasted the mixture on copper foil current collector. Afterwards, the electrodes were dried under vacuum at 110 °C for 12 h, lithium foil served as the counter electrode, and polypropylene films were used as separator. The electrolyte was a 1 mol L^{-1} $LiPF_6$ solution with a 1:1 (V: V) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The test cell assembly process was carried out in an argon-filled glove box. Galvanostatic charge–discharge experiments were performed at different current densities between 1 and 2.5 V (*vs.* Li^+/Li) using a LAND CT2001A cell test instrument. The cyclic voltammetry (CV) measurements were carried out on an electrochemical work station (CH Instruments, mode 760E).

3. Results and discussions

The synthetic processes of tablet-like porous TiO_2 and $Li_4Ti_5O_{12}$ are shown in Fig. 1. Large scale preparation of MIL-125 (Ti) could easily be realized on the basis of a reported procedure [35]. MIL-125 (Ti) can be described as the centered cubic structure, and the atoms are replaced by polymers of edge-sharing and corner-sharing $TiO_5(OH)$ octahedra. 1, 4-benzene dicarboxylates substitute the connection between atoms and create a 3D structure [36].

The structure and purity of MIL-125(Ti) is verified through X-ray diffraction (XRD) as displayed in Fig. S1, which is the same as previous reported [37]. In order to investigate the thermal stability of MIL-125 (Ti), TG and DSC tests were conducted in air atmosphere, as exhibited in Fig. S2. The MIL-125(Ti) precursor degrades in succession due to initial loss of water, methanol and DMF in the range of 50 through 250 °C. Further degradation between 250 and