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Scalable synthesis of hierarchical hollow $Li_4Ti_5O_{12}$ microspheres assembled by zigzag-like nanosheets for high rate lithium-ion batteries

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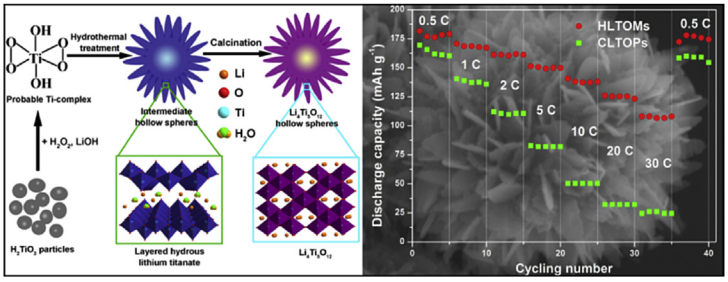
HIGHLIGHTS

- 3D hollow $Li_4Ti_5O_{12}$ microspheres assembled by zigzag-like nanosheets were prepared.
- Low-cost industrial H_2TiO_3 particles were chosen as titanium sources.
- Four parameters were found correlative and optimized to obtain pure $Li_4Ti_5O_{12}$.
- A high yield of $Li_4Ti_5O_{12}$ microspheres up to 120 g L^{-1} was achieved.
- The products exhibit outstanding rate performance and cycling stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical performance, abundance and cost are three crucial criteria to comprehensively evaluate the feasibility of $Li_4Ti_5O_{12}$ as an electrode material for lithium-ion batteries (LIBs). Herein, hierarchical hollow $Li_4Ti_5O_{12}$ microspheres (HLTOMs) assembled by zigzag-like nanosheets are synthesized by hydrothermal treatment of scalable lithium peroxotitanate complex solution using low-cost commercial H_2TiO_3 particles as titanium sources, followed by a calcination treatment. Precursor solution concentration, Li/Ti ratio, hydrothermal temperature and duration are found correlative and should be optimized to obtain pure $Li_4Ti_5O_{12}$ products. A high yield of HLTOMs up to 120 g L^{-1} was achieved. Due to the unique morphology, the HLTOMs deliver an outstanding rate capability of 139, 125 and 108 mA h g^{-1} at 10, 20 and 30 C, respectively, and exhibit 94% capacity retention after 1000 cycles at 30C indicating excellent stability. These values are much superior to those of commercial $Li_4Ti_5O_{12}$ particles (CLTOPs), showing HLTOMs are promising anode materials for LIBs.

1. Introduction

Lithium ion batteries (LIBs) have been the power source for most portable electronic devices, and are now being the optimal energy storage candidate for modern electric vehicles (EVs) and stationary off-peak energy storage systems [1,2]. Selecting suitable electrode materials is the key to improve the performance of LIBs. Commercial graphite is currently used as anode materials in LIBs, however, i) serious safety issues arise from lithium dendrite formation when the Li-insertion potential of graphite approaches almost 0 V vs. Li/Li^+, ii) poor rate performance is induced by their low Li^+ diffusion coefficient and iii) poor cycle stability is caused by volume change

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(ca. 9–13%) during lithium insertion/extraction processes [3–5]. Ergo, it is highly imperative to develop better anode materials with superior safety, high energy/power density, and long cycle life for next generation of LIBs.

Ti-based materials have proven to be potential alternative anode materials for LIBs [6–9]. Especially, spinel $Li_4Ti_5O_{12}$ (LTO), which is viewed as the most promising one due to its inherent advantages, has been extensively investigated [10,11]. LTO exhibits a stable voltage plateaus at about 1.5 V vs. Li/Li^+, which is high enough to avoid electrolyte reduction on the surface of the electrode and prohibit lithium dendrite formation, thus making batteries safe. Also, as a zero strain lithium insertion host, LTO can accommodate up to three lithium ions per molecule with negligible volume change, resulting in good reversibility and cycling stability [12–14]. Therefore, it is not surprising that LTO was firstly employed to replace the traditional graphite as anode material for LIBs in EVs and advanced energy storage devices by companies such as Toshiba [15,16] and Altairnano [17].

However, pristine $Li_4Ti_5O_{12}$ is an electronic insulator due to the presence of only Ti^{4+} with a d^0 electronic configuration. Although works by Song et al. [18] and Kim et al. [19] demonstrated that pristine LTO could be cycled fairly well without any carbon additives because a few percent Li insertion into LTO could increase the electronic conductivity by a factor of ca. 10^6 [20], a comparative study of carbon free and carbon containing $Li_4Ti_5O_{12}$ electrode by Pohjalainen et al. [21] showed that the feasibility of carbon free LTO electrodes highly depend on the properties of LTO (particle size and surface area). At the same time, several other strategies have been implemented to improve the rate performance of LTO electrode. One strategy is to increase its electrical conductivity by surface conductive coating or foreign atom doping [22–27]. Another good choice is to shorten the electrons/lithium ions transport length by tailoring its morphology and reducing the particle size to nanometer scale. Ganapathy et al. theoretically proved that size reducing and shape tailoring could significantly increase the storage capacity by density functional theory calculations [28]. Experimentally, wet synthesis methods are considered the optimum methods to prepare nanostructured LTO materials compared to solid state reaction, because the latter usually results in severe unwanted particle agglomerations at high temperature for a long period [29]. Chen et al. successfully prepared sawtooth-like LTO nanosheets by hydrothermal reaction, and the nanosheets exhibited an exceptional high rate performance up to 132 mA h g^{-1} even after 200 cycles at 57 C (1C = 175 mA g^{-1}) [30]. Cheng et al. synthesized hierarchical hollow LTO urchin-like microspheres through template-assisted hydrothermal reaction, and the materials showed a discharge capacity of 120 mA h g^{-1} at 20 C with just <2% decay after 100 cycles [31]. Other micro-nanostructured LTO materials, such as submicron donut-like structures [32], mesoporous submicrospheres [33], and mesoporous hollow spheres [34], have also been reported to exhibit outstanding rate performance.

A consensus that sustainability is the guiding principle for the next generation batteries including element abundance, cost, toxicity and scalability, has been reached [2]. However, since it is difficult for inorganic titanium salts such as $TiCl_4$ and $Ti(SO_4)_2$ to form a stable aqueous solution except in a strongly acidic environment [35], the titanium sources used in these alkaline solution methods are almost organometallic titanium compounds, i.e., titanium alkoxides like tetrabutyl titanate [22,25,31,34,36–40] and titanium isopropoxide [4,5,26,30,32,33]. The high cost of organic Ti sources used to supply Ti element which occupies 52.2% mass percentage of $Li_4Ti_5O_{12}$, and the potential environmental issues caused by correlatively used organic solvents obstruct the scalable synthesis of LTO nanostructured materials.

We showed in a previous result that, inorganic peroxotitanate complex solution was an appropriate precursor to synthesize Ti-based nanostructured materials with tailed morphology and controlled crystal phase [41]. Inspired by that idea, herein, lithium peroxotitanate complex solution using low-cost industrial H_2TiO_3 particles as Ti source was exploited to synthesize LTO nanomaterials with designed structures in large scale. The peroxotitanate complex precursor solution was obtained by dissolving H_2TiO_3 particles in LiOH solution with the help of H_2O_2. As expected, hierarchical hollow $Li_4Ti_5O_{12}$ microspheres (HLTOMs) assembled by zigzag-like nanosheets were obtained by hydrothermal reaction and a following calcination treatment. Factors including precursor solution concentration, Li/Ti ratio, hydrothermal temperature and duration were found to determine the final morphology and crystal phase of the products. Benefiting from the unique structures, the as-prepared HLTOMs exhibited remarkable rate capability (139 mA h g^{-1} at 10 C and 108 mA h g^{-1} at 30 C) and excellent cycling stability (the capacity retention ratio after 1000 cycles at 30 C is 94%). Compared to commercial LTO particles (CLTOPs), the electrochemical performance of HLTOMs was significantly improved, especially at high rates.

2. Experimental

2.1. Materials synthesis

The Li-Ti-O materials were synthesized by a hydrothermal reaction of peroxotitanate complex precursor solution followed by a calcination treatment. The precursor solution was obtained via the same approach as that in our previous result [41]. Typically, 21.5 mmol of $LiOH \cdot H_2O$ was dissolved in 50 ml deionized water. 5 mmol of commercial H_2TiO_3 powder (ca. 1 μm in diameter) and 4 ml of H_2O_2 (30%) were then added into the solution. After magnetic stirring for 1.5 h at 30°C, a pale yellow precursor solution was obtained and transferred into a 75 ml Teflon-lined stainless steel autoclave, which was subsequently heated at 150°C for 6 h. White-color products were filtered and washed by deionized water several times, and then dried at 80°C for 3 h. Finally, the dried powders were calcined at 550°C for 4 h to obtain the HLTOMs. Different precursor solution concentrations, Li/Ti ratios, hydrothermal temperatures and durations were also investigated using a similar procedure, as summarized in Table 1. The precursor solution was designated as S-X-Y, where S, X, and Y correspond to solution, concentration of Li and Ti in the solution, respectively. For example, S-0.43M-0.10M means a precursor solution with 0.43 M Li and 0.10 M Ti.

2.2. Materials characterization

The phase compositions of the samples were identified by X-ray diffraction (XRD, D8 Advance, Bruker) with Cu K_a ($\lambda = 0.15418$ nm) radiation. The morphologies were characterized using field emission scanning electron microscope (FE-SEM, JEOL JSM-7800F Prime) and transmission electron microscope (TEM, JEOL JEM-2100, 200Kv). The nitrogen adsorption/desorption isotherms were obtained by a Micromeritics TriStar II 3020 apparatus. The thermogravimetric analysis was performed on a TA discovery TGA at a heating rate of 10°C/min in air. The tap density is tested by an intelligent density tester (PF-100B, Litian magnetoelectrican Science &Technology Co. Ltd).

2.3. Electrochemical measurement

The working electrodes were prepared by mixing the active materials, carbon black, and polyvinylidene difluoride (PVDF) at a weight ratio of 80: 10: 10 in *N*-methylpyrrolidone (NMP). The