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In situ nano-sized spinel $Li_4Ti_5O_{12}$ powder fabricated by a one-step roasting process in molten salts

Wei-Wei Meng [a, b, c], Yong-Jun Xu [a, *], Bei-Lei Yan [b, c]

[a] School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 150001, China
[b] Pangang Group Research Institute Company Limited, Sichuan Province, Panzhihua 617000, China
[c] State Key Laboratory of Vanadium and Titanium Resources Comprehensive Utilization, Sichuan Province, Panzhihua 617000, China

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ABSTRACT

In this work, for the first time, a one-step roasting process to fabricate nano-sized spinel $Li_4Ti_5O_{12}$ powder (LTO-Ti) of which electronic conductivity was enhanced by doping unreacted titanium powder in the molten salts environment growing in situ directly from Ti powder is described. The crystal structure and morphology of LTO-Ti were examined with X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). When used as anodes for LIBs, the as synthesized nano-sized spinel $Li_4Ti_5O_{12}$ powder (LTO-Ti) manifest an excellent rate capability and a significantly enhanced cycling performance. At charge/discharge current of 0.5C, 1C, 2C, 5C, 10C and 15C, the discharge capacity of the LTO-Ti electrode is 170, 162, 149, 143, 131, and 110 $mAhg^{-1}$ respectively. After 200 cycles at current of 2C, its capacity retention was 96.7% with almost no capacity fading, exhibiting high capacity, superior rate property and outstanding cycling stability.

1. Introduction

In present, most of the pollutants are created from fossil fuels which supply us with 85% of energy [1]. As a result, severe air pollution, especially particulate matter (PM) pollution, threatens human health [2]. An increasing amount of clean, renewable and sustainable energies become the focus of energy research. Invention of recharge-able lithium ion batteries has actively changed the functionality of modern lifestyle and lithium ion batteries are considered to be the most promising energy-storage technology for hybrid, plug-in hybrid, and all electric vehicle applications [3–9]. But, nowadays, state-of-the-art lithium secondary batteries use graphite/carbon-related negative electrodes (anodes), which can cause serious safety concerns for large-size applications [10–12]. Due to the low lithium intercalating voltage of approximately 100 mV (vs. Li/Li^+), highly reactive metallic lithium forms easily under a fast charge rate. Such metallic lithium will deposit on the surface of the electrode particles and lead to high reaction risk with electrolyte or highly-charged cathode [13,14]. As a new anode material for lithium-ion battery, spinel $Li_4Ti_5O_{12}$ has attracted widespread attention because of its unique properties [15–17]. $Li_4Ti_5O_{12}$ is a lithium intercalation compound (or insertion host) with a high lithium insertion/extraction voltage (approximately 1.55 V), which is considerably higher than the formation potential of SEI (from reduction of the organic electrolyte) and dendritic lithium so that excellent safety can be obtained. Spinel $Li_4Ti_5O_{12}$ is a so-called zero-strain insertion material as the anode material of lithium secondary batteries [18–20]. This feature is suitable for storage batteries of new energy cars. In addition to being non-toxic and relatively inexpensive, the material experiences little change in volume during the lithium insertion/extraction processes and possesses high thermal stability which means a long cycling lifetime. Recently, $Li_4Ti_5O_{12}$ has been considerably deemed as a promising anodic material for LIBs used in electrochemical energy storage and electric vehicles [21,22]. However, $Li_4Ti_5O_{12}$ exhibits low electronic conductivity (in the range of ~10^{-8} to ~10^{-13} Scm^{-1}) and low lithium-ion diffusion coefficient (~10^{-9} to ~10^{-13} $cm^2\ s^{-1}$), which seriously limit its rate performance. Recently, contraposed the defects of the lithium titanate material, considerable research has been conducted on the morphological optimization, doping, and nano structuring of $Li_4Ti_5O_{12}$, or a combination of these, to improve its capacity and rate capability [23–27]. Conventional synthesis methods of lithium titanate include solid-state reaction [28] sol-gel method [29], and hydrothermal method [30]. All of these approaches have different problems. Solid-state reaction

* Corresponding author.
E-mail address: xuyongjun1218@126.com (Y.-J. Xu).

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requires high-temperature heating for a long time, and the product of which exhibits inhomogeneity, irregular morphology, and broad particle-size distribution; in another hand, sol-gel method and hydrothermal method both require difficult synthesis conditions and a large quantity of solvents organic materials, which are not suitable for mass production [31–34]. To solve the above problems, this paper adopts the molten salt synthesis method, which not only can ensure controlled product morphology and uniform particle distribution, but also suit industrial production. Synthesis of $Li_4Ti_5O_{12}$ anode material by the molten salt process can combine both advantages of liquid phase and solid phase synthesis.

This study examines the synthesis of $Li_4Ti_5O_{12}$ anode material by molten salt route, which is most likely to be realized for industrialization. In the molten salt synthesis of lithium titanate, titanium dioxide is usually used as the titanium source, and lithium carbonate as the lithium source to carry out high-temperature synthesis in the molten state salt [35,36]. Doping technique is effective at altering the structural properties and thus the performance of $Li_4Ti_5O_{12}$ [37]. By taking Ti_2O_3 as initial raw material, the Ti self-doped $Li_4Ti_5O_{12}$ material is prepared through solid-state reaction. The existence of Ti^{3+} is to enhance material electrochemical performance [38]. In this work, we prepare LTO-Ti anode material which is fabricated in situ directly from Ti powder with a synergistic effect of bulk doping, surface coating, and size reducing via a conventional molten salt route. In addition, compared with other reported metal ion doped $Li_4Ti_5O_{12}$ materials, our prepared LTO-Ti also shows improved performance, as shown in Table 1 [33,39–41], which indicates that the synergistic effect of LTO-Ti in-situ decoration should be responsible for thus outstanding performance. Moreover, introduction of LTO-Ti maintain the original spinel-like morphology, and Ti into the LTO-Ti sites changes Ti^{4+} into Ti^{3+} in the surface region so that the electronic conductivity of the LTO-Ti material is enhanced. At the same time, Ti nanoparticles are dispersed in the bulk of LTO-Ti, which further improves the conductivity of the electrode. Finally, the Ti modification is proved to suppress the growth of the LTO particles prepared via molten salt method, and the reduced particle size means a short distance for both Li^+ ion and electron conduction. The LTO-Ti has excellent electrochemical performance.

2. Experiment

2.1. Preparation of $Li_4Ti_5O_{12}$ powders in NaCl-KCl

In this study, $Li_4Ti_5O_{12}$ powders were prepared by two different methods. The precursors of LTO powder samples were synthesized using Li_2CO_3 (analytically pure 99.9%), TiO_2 (anatase, average particle size\0.8 μm, purity >99%, Panzhihua Tianlun Chemical Corporation, Panzhihua, China) (denoted as LTO-S), Li_2CO_3 (analytically pure 99.9%) and ultrafine titanium powder (average particle size\1–2 μm micron-sized, Pangang Group Research Institute Co. Ltd.) (denoted as LTO-Ti). Such precursors were mixed and grinded in a mortar with a pestle. The molar ration of TiO_2 and Li_2CO_3 was 5:2, Ti: Li_2CO_3 was 6:2. The molar ratio of the eutectic mixture of NaCl-KCl was fixed at 1:1which was used as solvent. The mixed salts were mixed thoroughly and grinded in a mortar with a pestle and dried under vacuum at 120 °C for 24 h, to minimize the water content in the molten salt (NaCl-KCl). Then, precursor and solvent were mixed in alumina crucibles and transferred to a muffle furnace immediately. The mixed precursor powders were calcined at 850 °C for 4 h and then naturally cooled to room temperature. The heating rate was 10 °C min^{-1} for all temperature settings. After sintering, a powder was immediately precipitated in the molten salt solution. After cooling and solidification, this solid mixture was immersed in deionized water, and all of the salt elements were dissolved. The precipitated powders were the metal oxide particles which are insoluble in water, so that all of the precipitates could be separated. The obtained particles were collected and vacuum treated again at 120 °C for 24 h to eliminate residual water on particle surfaces. The dried powders were then subjected to structural characterization and electrochemical measurements.

2.2. Composition and structure determination

The thermal decomposition behavior of the precursor was examined by thermogravimetric analysis and differential scanning calorimetry (TG-DSC) using the thermal analyzer (Netzsch STA 449 C) in static air at a heating rate of 10 °C min^{-1}. The phase composition was studied by X-Ray diffraction (XRD, Empyrean, Holland) using Cu Kα radiation in the range of 10°–80° (2θ) and operated at 40 kV and 30 mA with a scanning rate of 0.06°/s and for quantification analysis using Rietveld method. The morphology of the powders was observed by scanning electron microscopy (SEM, JSM-7001F, Japan) and an FEI Titan 80-300 transmission electron microscope (TEM). The chemical states of various elements at the surface were analyzed on a PerkinElmer PHI-5000C multifunctional X-ray photoelectron spectrophotometer (XPS). X-band Electron Paramagnetic Resonance (EPR) spectra were obtained using a Bruker EMX-10/12 EPRspectrometer.

2.3. Electrode preparation, coin cell assembly and electrochemical measurements

For electrochemical test, the working electrode was composed of a paste mixture of LTO as active material, with carbon black as electronic conductive additive, and polyvinylidene fluoride (PVDF) binder mixed in N-methyl-2-pyrrolidone (NMP), at a weight ratio of 80:10:10. Subsequently, the paste was coated onto a copper foil, and then vacuum-dried at 110 °C for 12 h (The electrode preparation process is the same, and the mass loading of active materials in the electrodes were controlled to be close and about 3 $mgcm^{-2}$). Experimental cells were assembled in an argon filled glove box (M-Braun) with the working electrode, metal lithium foil as the counter and reference electrode, and Celgard 2400 as the separator and 1 M LiPF6/EC-DMC (1:1, v/v) as the electrolyte. The cells were galvonostatically cycled between 1 V and 2.5 V (versus Li^+/Li) on a Land CT2001A battery-testing instrument. Cyclic voltammetry (CV) was measured using a VersaSTAT4 electrochemical workstation between 0 and 2.5 V (vs. Li^+/Li) with a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were

Table 1
Comparison of our LTO-Ti with other reported metal ion doped $Li_4Ti_5O_{12}$ materials.

Samples	Cycle number	Ref.	Additives (during electrode preparation)	At highest rates capacity ($mAhg^{-1}$)	Preparation method
$Li_4Ti_5O_{12}$-Ti	200	This work	Ti	110.2 (15C)	Solid-state reaction
$Li_4Ti_5O_{12}$-Ag	50	[33]	Ag	154.62 (10C)	Solid-state reaction
$Li_4Ti_5O_{12}$-Mo	200	[39]	Mo	210.8 (6C)	Solid-state reaction
$Li_4Ti_5O_{12}$-Au	100	[40]	Au	162.3 (60C)	Hydrothermal
$Li_4Ti_5O_1$-La	120	[41]	La	103.5 (10C)	Solid-state reaction