Enhanced electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode material for lithium-ion batteries with different carbons as support

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Abstract

Nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites with various structures are designed using tetrabutyl titanate as a precursor via a facile in situ liquid deposition method in the presence of three different carbons (multiwalled carbon nanotubes, spherical conductive carbon black super-P and ordered macroporous carbon). The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites with various morphologies are formed depending on the carbon matrixes used. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles obtained are approximately 100 nm in size and homogeneously dispersed in different carbon matrixes. It is found that the structures of the carbon matrixes have a close relation to the discharge capacities of the composites. At the discharge current density of 875 mA g^{-1} , the discharge capacities of nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites with 10 wt% carbon are 138.6, 120.8 and 120.9 mAh g^{-1} for carbon nanotubes, super-P and porous carbon as the carbon supports, respectively. The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon using carbon nanotubes as support exhibits superior performance with large reversible capacity, excellent cycle stability and good rate

capability. Capacity retention of 99 % can be maintained after 100 cycles, suggesting its promising potential as anode materials.

Keywords: Lithium titanate; Composites; Carbons; Anode materials; Lithium-ion batteries

1. Introduction

Spinel lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been regarded as one of the most promising anode materials for long-lifetime and high-rate lithium ion batteries owing to its inherent advantages. For example, it can accommodate up to three lithium ions without volume change during lithiation, which is also called as a zero-strain material. Moreover, it exhibits a flat charge/discharge plateaus at ~ 1.55 V (vs. Li^+/Li), which circumvents the solid electrolyte interphase (SEI) film formation and suppresses the lithium dendrite deposition [1-6]. Unfortunately, some kinetic problems with poor electrical conductivity (10^{-13} S cm^{-1}) and low lithium diffusion coefficient (10^{-9} to 10^{-13} $\text{cm}^2 \text{s}^{-1}$) limit its high discharge specific capacity at high charge/discharge rates [7-9]. Therefore, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ might not be suitable for high rate applications in its native form. To overcome the above problems of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, several strategies have been proposed and explored to improve the conductivity, and one of the most common strategies is to synthesize nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials with different morphology such as nanorods, nanowires and nanosheets [4, 6, 10-13]. Other attractive ways are to dope the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with metal or non-metal ions in the Li, Ti or O sites [14-20] or to modify surface using conductive materials to enhance the surface electrical conductivity [21-27].

Recently, nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has attracted much attention. Its large surface area increases the electrolyte/electrode contact area, which leads to a decrease of charge transfer resistance at the electrode/electrolyte interface. Furthermore, nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can facilitate both the electrons and lithium ions transport by reducing their transport distances, thus resulting in improved kinetic performance. However, nanoparticles have a tendency to aggregate together

during the heat treatment because of their high surface energy, which leads to a decrease in surface area and an increase in the interparticle contact resistance. Carbon surface modifications have proven to be an effective means of improving the electrochemical performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials due to their low cost and high conductivity. Using different carbon structures (e.g., amorphous carbon [24], carbon nanotubes [26], and graphene [25]) to form $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites can have a synergistic effect through minimizing particle size, enhancing specific surface area, and preventing nanoparticles from agglomerating. This can provide good electrical conductivity as well as fast lithium ion diffusion of such $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon anode materials, and thus improve the electrochemical performance in terms of specific capacity, cycling performance, and rate capability.

In this paper, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites using multiwalled carbon nanotubes (CNTs), spherical conductive carbon black super-P (SP), and macroporous carbon (PC) as carbon supports were prepared via a facile in situ liquid phase deposition technique. The process was based on mutual electrostatic interactions of two species, and the Ti^{4+} ions were uniformly adsorbed on the surface of carbon matrixes. The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites with different structures have solved the aggregation problem of the nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles, and high specific capacity could be expected for these composites. The effects of carbon structures on the electrochemical performance of the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites were compared and discussed.

2. Experimental

The CNTs purchased from Shenzhen Nanotech Port Co. Ltd. were purified by ultrasonic treatment in 2.6 M HNO_3 for 0.5 h to improve their dispersibility by introducing oxygen

containing functional groups on their side walls. PC was prepared using SiO_2 colloidal crystals with the size of 450 nm as the template according to the reported procedure [28]. SP and commercial $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were kindly provided by Shenzhen Bak Battery Co. Ltd. All other reactants were analytically pure and used without further purification.

The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites were synthesized by an in situ liquid phase deposition method in the presence of different carbons matrix. The predetermined amount of carbon content in nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites was 10 wt.%. Take the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs composites for example, 0.3 g purified CNTs were ultrasonically dispersed in 24 mL ethanol for 1 h, followed by the addition of tetrabutyl titanate solution (5.1 g) to form a suspension. Then, 0.832 g lithium acetate was dissolved into water (2 mL) and ethanol (24 mL), and then slowly dropped into the above suspension. After stirring for 24 h, the mixture was treated at 60 °C to remove the solvents gradually and then ground in a mortar. The obtained precursor was calcined at 900 °C for 90 min in a nitrogen atmosphere to obtain the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs composites. The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /PC and nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /SP were also prepared using the same method as mentioned above. For comparison, pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by a similar procedure except for the absence of carbon matrix.

The crystal structures of the as-prepared materials were characterized by X-ray diffraction measurements (XRD, Rigaku/mac250) using $\text{Cu K}\alpha$ radiation in the 2θ range of 10-90°. The morphology and microstructure of the as-synthesized materials were investigated by field emission scanning electron microscopy (FE-SEM, ZEISS supra 55) and transmission electron microscopy (TEM, JEOL JEM-200CX). The carbon content in nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites was measured by a carbon-sulfur analyzer (EMIA-820V).

The electrochemical measurements were performed using two-electrode 2032 coin-type cells. The working electrodes were fabricated by mixing active materials, carbon black (Super P), and polyvinylidene fluoride at a weight ratio of 8:1:1 in N-methylpyrrolidinone. After coating the above slurry on copper foil, the electrodes were dried at 60 °C for 6 h to remove the solvent. Then the electrodes were cut into disks and dried at 120 °C for 12 h in vacuum. Test cells were assembled in an argon-filled glove box using Li foil as the counter electrode and Celgard 2400 as the separator. The electrolyte was 1 M LiPF₆ in a 1:1:1 (in volume) mixture of ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate. The galvanostatic charge–discharge curves were recorded between 1 and 2.5 V (vs. Li⁺/Li) using a battery test system (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd.). Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) measurements were carried out using an electrochemical workstation (CHI660C, Shanghai Chenhua). EIS were measured from 100 kHz to 0.01Hz with alternating voltage amplitude of 5 mV.

3. Results and discussion

Fig. 1 presents the XRD patterns of pure Li₄Ti₅O₁₂, nano-Li₄Ti₅O₁₂/SP, nano-Li₄Ti₅O₁₂/PC and nano-Li₄Ti₅O₁₂/CNTs, respectively. The main peaks of all the products can be assigned to well-crystallized Li₄Ti₅O₁₂ with the spinel structure (JCPDS Card No.49-0207) and there are no other peaks observed for impurities, which suggests that the addition of carbon does not influence the formation of spinel Li₄Ti₅O₁₂ during heat treatment. In addition, there is no evidence for the diffraction peaks of SP or PC in nano-Li₄Ti₅O₁₂/SP or nano-Li₄Ti₅O₁₂/PC composites, which indicates that SP and PC are amorphous. It is noted that a low broad diffraction peak centered at $2\theta=26^\circ$ can be detected in the pattern of the nano-Li₄Ti₅O₁₂/CNTs,

which corresponds to the (002) plane of the stacked graphene layers in the CNTs. Results obtained from the carbon sulfur analyzer indicate that the amount of carbon in the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites as CNTs, SP, and PC for carbon supports is about 9.86 wt.%, 9.79 wt.%, and 9.83 wt.%, respectively.

The morphologies and microstructures of various carbons, pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /SP, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /PC and nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs were elucidated by FE-SEM and TEM measurements. The randomly entangled multi-walled CNTs have a diameter of 40–60 nm (Fig. 2a) and PC prepared using SiO_2 colloidal crystals has a pore size of 100–450 nm (Fig. 2b). Conductive carbon black SP shows spherical-like particles with a size of about 50 nm (Fig. 2c). The size of the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle (Fig. 2d and Fig. 3a) is about 200–500 nm and these particles aggregate with each other. The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /SP composites consists of secondary quasi-spherical microparticles with the diameters of 0.5–2 μm (Fig. 2e). TEM observation at a higher magnification reveals that each microsphere is actually a random dispersion of primary $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles (~ 100 nm), and the SP is dispersed among $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles to form a two-dimensional network structure (Fig. 3b). This interpenetrating nanostructure should be very helpful for preventing aggregation and growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles during heat treatment. From the image of nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /PC composites, it is clear that the nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with spherical-like structure is distributed on the surface of the PC (Fig. 2f). The TEM image displays that large much of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles with a size of 50–100 nm are imbedded in PC matrix and that some of the smaller particles (< 50 nm) are attached to the carbon wall (Fig. 3c). It has been known that there are many defective sites located at the walls of the porous carbon, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nuclei

can easily form on it. During the calcinations process, these defective sites may act as the active centers, which prevent the growth of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. For nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs composites, it can be seen that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles with a size of ~ 100 nm are uniformly anchored on the surface of CNTs, and the CNTs intertwine with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles together to form a three-dimensional network structure (Fig. 2g, Fig. 3d). It is worth noting that during the heat treatment, the nanoparticles are still strongly anchored on the surface of CNTs with a high density, suggesting a strong interaction between nanoparticles and CNTs.

The charge–discharge curves of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites synthesized with different carbon supports at the current density of 875 mA g^{-1} are shown in Fig. 4. It can be seen that nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /SP, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /PC, and nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs have similar charge–discharge plateaus as compared with the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which indicates that the addition of carbon did not affect the electrochemical reaction process of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Furthermore, the differences between the charge and discharge potentials of nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites are obviously smaller than those of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. It is reasonable to assume that the low polarization of the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites is related to their small particle sizes and the improvement of the electrical conductivity. Among these nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites, the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs composite has the lowest polarization.

To examine the effectiveness of different carbon matrixes in improving the electrochemical performance of the electrodes, the rate capabilities of nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes were investigated in Fig. 5. The discharge capacities of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ decrease steeply

with increasing discharge rate, whereas nano-Li₄Ti₅O₁₂/carbon composites decrease much slower at the same rate. As seen in table 1, it is clear that the capacity obtained by nano-Li₄Ti₅O₁₂/carbon composites at the current density of 875 mA g⁻¹ is higher than that obtained at the current density of 175 mA g⁻¹ for pure Li₄Ti₅O₁₂ (the capacity is calculated based on the total weight of the composites). A significantly improved rate capability is clearly achieved for the nano-Li₄Ti₅O₁₂/carbon composites. Furthermore, the effectiveness of CNTs in improving the rate capability of Li₄Ti₅O₁₂ is significantly better than that of SP and PC. The nano-Li₄Ti₅O₁₂/CNTs composite also exhibits excellent cycling stability with no noticeable decrease over 100 cycles at the current density of 875 mA g⁻¹ (Fig. 6). The discharge capacity of nano-Li₄Ti₅O₁₂/CNTs composite slightly decreases from 138.6 to 137.8 mAh g⁻¹, and it still retains over 99 % of the initial capacity. This result demonstrates that the structure of the composite is very stable, and the electrochemical Li⁺ insertion/extraction process is quite reversible even at high rates. For the nano-Li₄Ti₅O₁₂/SP and nano-Li₄Ti₅O₁₂/PC composites, the losses of the discharge capacities are more than 6% at the current density of 875 mA g⁻¹. The high rate capability and cycling stability of nano-Li₄Ti₅O₁₂/CNTs electrode can be attributed to the small size of Li₄Ti₅O₁₂ uniformly anchored on the surface of CNTs and the improvement of electrical conductivity.

To understand the improved high-rate performance after introducing conducting carbon matrixes into Li₄Ti₅O₁₂, the EIS of as-prepared materials were measured. Fig. 7 presents the EIS curves of Li₄Ti₅O₁₂, nano-Li₄Ti₅O₁₂/SP, nano-Li₄Ti₅O₁₂/PC and nano-Li₄Ti₅O₁₂/CNTs after three charge/discharge cycles at the stable voltage of 1.56 V. The EIS result demonstrates that each curve is consisted of a depressed semicircle at high-middle frequency

region and an inclined straight line at low frequency region. The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon electrodes exhibit much lower charge-transfer resistance than that of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, and the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs electrode displays the lowest charge transfer resistance in all the electrodes. The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon electrodes have lower charge-transfer resistance than pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, which could be attributed to two reasons: (1) the addition of SP, PC and CNTs to the precursor hinders particle agglomeration and growth during the calcination process, resulting in smaller particle sizes, and thus shortening the transport path of lithium ions and electrons. (2) The SP, PC and CNTs work as highly conductive matrixes for quickly providing electrons to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. Among these nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /CNTs electrode shows the minimum charge-transfer resistance which indicates that the conducting network of CNTs allows for the efficient charge transport in the composite electrode. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles are well anchored on the surface of CNTs as spacers to effectively reduce the degree of restacking of CNTs and consequently keep their large active contact area between the electrode and electrolyte solution.

4. Conclusions

Nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites with three different structures were successfully prepared by in situ liquid deposition technique and their electrochemical properties as anode materials for high performance lithium-ion batteries were compared. The nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites exhibit the lower polarization, excellent cyclic stability, and good rate capability compared to the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The superior electrochemical performance of the nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /carbon composites electrode is due to the formation of nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles on the carbon supports. The nano-sized particles of the

nano-Li₄Ti₅O₁₂/carbon composites enable fast electron and ion transport during charge-discharge process. Among these nano-Li₄Ti₅O₁₂/carbon composites, the effect of CNTs on improving rate capability of Li₄Ti₅O₁₂ is the most significantly and the nano-Li₄Ti₅O₁₂/CNTs composite exhibits a large reversible capacity, excellent cyclic performance, and good rate capability. The flexible structure of three dimensional CNTs and the strong interaction between Li₄Ti₅O₁₂ nanoparticles and CNTs in nano-Li₄Ti₅O₁₂/CNTs composites are capable of effectively utilizing the good conductivity, high surface area, and good electrochemical performance of CNTs.

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Table.1 The discharge capacity vs current density of the samples

Samples	Discharge capacity/mAh g ⁻¹				
	35 mA g ⁻¹	175 mA g ⁻¹	350 mA g ⁻¹	875mA g ⁻¹	1750 mA g ⁻¹
Commercial	163.3	131.6	99.8	68	46
LTO	165.8	125.1	92.8	60	39
LTO/SP	157	150.4	143.5	120.8	109
LTO/C450	150	143.7	135.7	120.4	93
LTO/CNTs	156	154	150	140	121

Figure Captions

Fig. 1 XRD patterns of (a) pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PC}$, (c) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SP}$ and (d) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ composites.

Fig. 2 SEM images of (a) SP, (b) PC, (c) CNTs, (d) pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (e) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SP}$, (f) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PC}$ and (g) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ composites.

Fig. 3 TEM images of (a) pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, (b) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SP}$, (c) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PC}$ and (d) nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ composites.

Fig. 4 Galvanostatic charge/discharge curves of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PC}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SP}$ and nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ at the current density of 875 mA g^{-1} .

Fig. 5 Comparison of the rate capability of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PC}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SP}$ and nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ at different rates.

Fig. 6 Cycle performance of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PC}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SP}$ and nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ at the current density of 875 mA g^{-1} .

Fig. 7 The EIS curves of pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{PC}$, nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{SP}$ and nano- $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{CNTs}$ electrodes at the voltage of 1.56 V.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7