Heterostructured Li$_4$Ti$_5$O$_{12}$/TiO$_2$/carbon microspheres self-assembled by nanowires as high performance anodes for lithium ion batteries

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Abstract

We report a delicate design and controllable preparation of Li$_4$Ti$_5$O$_{12}$/TiO$_2$/Carbon (LTO-T/C) spherical heterostructure and its application as anode for Lithium Ion Batteries (LIBs). The as-prepared self-assembled LTO-T/C spheres exhibit a chrysanthemum-like structure with abundant nanowires on the surface, which provide a large specific surface area and many transmission channels for electrons and ions transport. The carbon layer around the sphere could further increase the conductivity of the sample. As expected, the tailored LTO-T/C electrode shows excellent rate performance and outstanding reversible capacity of 220 mAh g$^{-1}$ and 125 mAh g$^{-1}$ after 500 cycles at the current density of 1.0 A g$^{-1}$ and 10 A g$^{-1}$, respectively. The improved cyclic and rate performance are attributed to its unique heterostructure and self-assembled microsphere morphology.

1. Introduction

With the rapid development of the economy, the excessive usage of traditional fossil fuel such as petroleum and coal has caused many destructive environmental problems [1--6]. The environmental friendly renewable energy sources such as hydrogen energy and solar energy have attracted attention of researchers in the environment and energy fields [7--11]. Lithium-ion batteries (LIBs) are considered to be one of the most promising energy storage devices due to their high operating voltage, high specific capacity [4, 12--20]. At present, most of the commercial LIBs anode materials are various lithium-intercalated carbon materials, which have a great many of fatal defects such as limited theoretical capacity of 372 mAh g$^{-1}$, easily forming of solid electrolyte interface (SEI) film during the cycle, dramatic dropping of capacity and growth of lithium dendrites, which could cause many other serious safety problems [21--26].

Spinel Li$_4$Ti$_5$O$_{12}$ (LTO) has been regarded as one of the ideal candidates for LIBs with numerous outstanding characters: [21, 27--30] (1) the higher Li$^+$ insertion and extraction platform voltage (about 1.55 V versus Li$^+$/Li) prevent growing lithium dendrites and forming SEI film; (2) LTO known as ‘zero-strain’ structure material possesses excellent reversibility and longevity. But the characters of low intrinsic electronic conductivity (merely 10$^{-13}$ s cm$^{-1}$) and ionic conductivity restrict the application of LTO on LIBs [28, 31]. The following practices usually to be done to solve the mentioned problems: [32--35] (1) changing the particle size of LTO; (2) doping other metal elements with LTO; (3) regulating microstructure and morphology of LTO; (4) coating conductive materials (such as graphene, carbon nanotubes) on LTO.

TiO$_2$ has multifarious advantages such as strong redox reaction, non-toxic, abundant and low cost in addition to this TiO$_2$ also has a relatively high theoretical capacity of 336 mAh g$^{-1}$, so more and more researchers tried to form a hierarchical Li$_4$Ti$_5$O$_{12}$--TiO$_2$ structure, and they have made remarkable achievements. Zhang et
successfully prepared the Li$_4$Ti$_5$O$_12$-Rutile TiO$_2$ ternary phase composites by a facile hydrothermal way, as well as the capacities and rate performances were very well. Zhao et al. reported on a successful synthesis of porous Li$_4$Ti$_5$O$_12$ and TiO$_2$ nanosheet arrays via the solvothermal method and the rate performance possessed a capacity of 102.9 mAh g$^{-1}$ at a high current density of 1600 mA g$^{-1}$. Wang et al. reported the LTO nanosheets coated onto rutile TiO$_2$ through a one-pot hydrothermal synthesis process, and the rate capability was dramatically improved comparing with the pure LTO nanosheets\cite{31,36–38}. But the conductive of them were not very well and the method was a bit complicated.

Herein, heterostructured Li$_5$Ti$_4$O$_12$-TiO$_2$ (LTO-T) was synthesized through solvothermal and heat treatment methods then coated carbon with dopamine (DAP) to obtain LTO-T/C. Since the capacity and conductivity of TiO$_2$ were better than LTO, the capacity and rate performance of LTO-T were significantly improved. Forming uniform carbon layer accelerates the transmission speed of electrons and lithium ions. As anode material for LIBs, the LTO-T/C delivers excellent electrochemical performance.

2. Experimental

2.1. Materials synthesis

All of the chemicals were analytical reagents and used as-received.

2.1.1. Synthesis of LTO-T precursor

Precursor of Li$_5$Ti$_4$O$_12$ was prepared by solvothermal method. 2 ml tetrabutyl titanate (TBT), 0.12 g Tris and 0.22 g lithium acetate dihydrate (CH$_3$COOLi · 2H$_2$O) were dissolved into the mixture of 25 ml n-propanol and 5 ml glycerin with continuous stirring step-by-step. The obtained solution was transferred into a 100 ml Teflon-lined stainless-steel autoclave and kept at 180 $^\circ$C for 18 h. Then, white powder was gained after centrifugation, washing and drying as the precursor of LTO-T.

2.1.2. Synthesis of LTO-T

LTO-T was prepared by the low temperature calcination method. After grinding for 15 min, the powder was annealed in air at 400 $^\circ$C for 6 h with heating rate of 2 $^\circ$C min$^{-1}$ to obtain LTO-T.

2.1.3. Synthesis of LTO-T/C

Dopamine polymerization was utilized to form the carbon coating on the surface of LTO-T. 0.12 g Tris was added into 100 ml distilled water under magnetic stirring, obtaining the buffer solution with pH $= 8.5$. 0.2 g LTO-T was added into the buffer solution and stirring for 30 min subsequently, ensuring uniform dispersion. Then, 0.1 g dopamine was added into the solution under magnetic stirring. After stirring for 24 h, the black slurry was filtered and washed several times to gain LTO-T/DPA. Finally, carbonization was performed in an argon atmosphere at 600 $^\circ$C for 2 h with a heating rate of 2 $^\circ$C min$^{-1}$, the obtained black powder was marked as LTO-T/C.

2.2. Structural characterization

X-ray powder diffractometer (XRD, Rigaku D/Max-RA, graphite monochromatized CuK$\alpha$ radiation, $\lambda = 0.15406$ nm) was used to characterize the crystal structures of the samples. Field emission scanning electron microscopy (FESEM, S4800, JSM-5800, Hitachi) and transmission electron microscopy (TEM, JEM-2100F, JEOL) were used to obtain the topography and crystal lattices of the samples. The Brunauer–Emmett–Teller surface area measurement (BET, NOVA2200e) was used to measure the specific surface area and pore distribution of the samples. Thermogravimetric Analysis (TG, TGA-101) was used to analyze the carbon content in the samples. X-ray photoelectron spectroscopy (XPS) was used to characterize valences of the elements in the samples. Raman spectroscopy (labRAM ARAMIS) was used to characterize graphitization and defect degree of the sample.

2.3. Electrochemical analysis

The LIBs electrodes were prepared by mixing LTO-T/C with carbon black and polyvinylidene difluoride (PVDF) at a weight ratio of 8:1:1 drying at 60 $^\circ$C in vacuum for 6 h. Then dropped into N-methyl-2-pyrrolidone (NMP) with stirring for 30 min obtaining the slurry. The slurry was pressed on the copper foil and then dried at 80 $^\circ$C in vacuum for 12 h. The 2032-type coin cells were assembled in an argon-filled glove box (Sunnan220750) under the concentrations of oxygen and moisture below 1 ppm. The cells were assembled using the tailored LTO-T/C as the cathode, and lithium foil as the anode. Electrolyte was made from 1 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume). The electrochemical measurements for the cells were...
performed at Lanlike electrochemistry work station (CHI660D). The galvanostatic discharge/charge experiments were carried out on a galvanostatic meter (Land CT2001A).

3. Results and discussion

Figure 1 shows the x-ray diffraction (XRD) patterns of samples at different stages of the experiment. The XRD pattern of the precursor is shown in figure 1(a). The curve without crystallization peak indicates that the sample is amorphous. The XRD pattern of LTO-T treated at 400 °C for 6 h is shown in figure 1(b). As seen from figure 1(b), several main diffraction peaks can be found at 2θ values of 18.33, 35.57, 43.20, 57.00 and 62.00 corresponding to (111), (311), (400), (333) and (440) crystal planes of LTO, respectively (JCPDS Card NO.49–0207). Simultaneously, the main diffraction peaks observed at 2θ values of 27.45, 36.08, 41.20, 54.32 and 62.97 are related to (110), (100), (111), (211), and (002) crystal planes of rutile TiO₂, respectively (JCPDS Card NO. 21–1276). The result of the XRD pattern indicates that sample both exists LTO and TiO₂ and the reaction equations are as follows. LTO-T with highly crystalline and stable heterostructure contributes greatly to LIBs cycle performance.

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\begin{align*}
\text{Ti(C}_4\text{H}_6\text{O}_4)_{4} &\rightarrow \text{Ti(OH)}_{4} + 4\text{C}_4\text{H}_6\text{OH} \\
\text{Ti(OH)}_{4} &\rightarrow \text{TiO}_2 + 2\text{H}_2\text{O} \\
5\text{TiO}_2 + 4\text{CH}_3\text{COOLi} &\rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} + 2\text{CH}_3\text{COOCCH}_3
\end{align*}
\]

Table 1. The ICP result of LTO-T.

| Element rate | Molar rate | Mass rate |
|--------------|------------|-----------|
| Li:Ti        | LTO:TiO₂   | LTO:TiO₂  |
| 4:7          | 1:2        | 2.72:1    |

Figure 1. (a) XRD pattern of the precursor, (b) LTO-T treated at 400 °C for 6 h.

Table 1. The ICP result of LTO-T.
TEM was used to further demonstrate the distribution of C on the surface of LTO-T/C. The TEM images at different magnification are shown in figure 4. From figure 4(a), we can see that the darker part of the particle is the LTO-T sphere and the gray area surrounding the particle is the carbon layer. From figure 4(b) we can see that 10 nm thick carbon layer is continuously coated on the surface. The presence of carbon layer is of great significance for improving the electrochemical performance of LTO-T. During the charge and discharge process, the carbon layer provides a fast transmission channel for lithium ions and electrons improving the conductivity of the sample.
As we can see from the figures 5 (a) and (b), the specific surface area of the sample is 36.77 m$^2$ g$^{-1}$, and the surface pore size distribution is between 2–8 nm. Among them the 2–4 nm size range porous take a large proportion, which provide more active sites for the insertion of lithium ions and electrons. And the inset image in figure 5 (a) displays the N$_2$ adsorption–desorption isotherms of the LTO/TiO$_2$ composites structure without coating the Carbon layer, and the specific surface area is 64.15 m$^2$ g$^{-1}$. The decrease of LTO-T/C specific surface area could suppress side reactions between the active materials and electrolyte, and then improve its Coulombic efficiency [39].

The degree of graphitization of carbon can be monitored successfully by Raman scattering method. As shown in figure 5(c), there are two Raman characteristic peaks at around 1348 cm$^{-1}$ and 1590 cm$^{-1}$ respectively, corresponding to the D- and G-bands. The intensity of the D-band is proportional to the amount of disordered carbon and the lattice defects after graphitization; and the intensity of the G-band is proportional to the amount of ordered graphitic (sp$^2$) carbon contained in the graphitized DPA. Due to the -NH$_2$ functional group in DPA, the degree of graphitization is reduced and more defects are generated, which increases the peak intensity of the D-band in the Raman spectrum. In addition, due to some oxygen vacancies generated during the annealing process, the carbon layer produces more defects, which provide more effective active sites for the electrons and lithium ions on the surface of the sample, increasing the capacity of the LIBs, so that the capacity of the electrode more than the theoretical capacity of LTO [40].

The x-ray photoelectron spectroscopy (XPS) spectrums of full elements, oxygen element and carbon element are shown in figures 5(d)–(f). Figure 5(d) further indicates the existence of Ti, O, C, Li and N. As shown in figure 5(e), the O 1s spectra demonstrates the existence of Ti–O in the sample. The less intense characteristic peak at 530.9 eV demonstrates the presence of some oxygen vacancies on the lattice surface of the sample which reduce the band width and contribute LTO-T to combining with carbon, resulting in a uniform continuous carbon layer. In addition the N element in DPA remains in the carbon layer, enhancing the stability of carbon as well as increasing the insertion active sites of lithium ions.

Figure 5. (a) The N$_2$ adsorption–desorption isotherms (the N$_2$ adsorption–desorption isotherms of the LTO/TiO$_2$ composites structure without coating the Carbon layer inset), (b) pore size distributions, (c) Raman spectrum of LTO-T/C and (d)–(f) XPS spectrums of LTO-T/C.
The sample was heated from room temperature to 900 °C in air and the TG results are shown in figure 6. It can be seen that the mass of the sample not continuously reduce until 800 °C, which is due to the oxidation of C. From the image we can also learn that the carbon content in LTO-T/C is about 23%.

Figure 7 exhibits the initial three cycles of cyclic voltammetry (CV) curves at a voltage range of 0–3.0 V and scan rate of 0.1 mV s\(^{-1}\). A significant reduction peak during discharge seen at 1.0 V indicates that LTO with spinel structure combines with lithium ions to form lithiate compound. The relatively intense reduction peak at 1.8 V reveals the reaction between TiO\(_2\) with rutile structure and lithium ions forming lithium compound. On the contrary, the corresponding oxidation peaks at 1.5 V and 2.2 V represent the delithiation processes. Compared the oxidation peaks and the reduction peaks, the first reduction peak obviously differs from other cycles, implying irreversible electrochemical reaction, which could be caused by the formation of SEI film [33]. After second cycles, the profiles tend to almost overlap, which proved that the cycle performance was excellent. In addition, as the conductivity of the sample is improved, the polarization of the battery is reduced.

Figure 8 shows the charge and discharge profiles of 1st, 10th and 500th cycles for the LTO-T for a voltage window of 0–3.0 V and he current density of 1 A g\(^{-1}\), respectively. It can be seen from the first discharge curve that the discharge capacity of LTO-T is 216 mAh g\(^{-1}\), and the coulomb efficiency is nearly 100%, which is attributed to the high potential of LTO and TiO\(_2\). After 500 cycles, the stable charge and discharge plateaus indicates the excellent electrochemical reversibly and structural stability of LTO-T.

Figure 9 exhibits the cycling performance, rate performance and the electrochemical impedance spectroscopy (EIS) of the LTO-T and LTO-T/C, respectively. As we can see form figure 9(a), which was
measured at a current density of 1 A g$^{-1}$, the capacity of LTO-T with two-phase is 205 mAh g$^{-1}$ after 500th cycles. Compared with the LTO-T, the carbon-coated LTO-T/C represents a higher capacity, whose first discharge capacity is 227 mAh g$^{-1}$, and the coulomb efficiency is 95.64%. After 500 cycles the capacity of LTO-T/C is 220 mAh g$^{-1}$ and the coulomb efficiency remains over 95%. It also can be seen from the charge and discharge capacity curve that the cycle capacity drops slightly in the first 20 cycles, which may be caused by activation of the electrode during the cycle, and after that the capacity gradually rises and stabilizes. The result indicates that the chrysanthemum structure have a significant effect on improving transmission rate of electrons and ions and ensuring LIBs with more excellent cycling stability.

Figure 9(b) shows the rate performance of the LTO-T and LTO-T/C at 0.5 A g$^{-1}$, 1 A g$^{-1}$, 2 A g$^{-1}$, 5 A g$^{-1}$, 10 A g$^{-1}$ and 0.5 A g$^{-1}$, respectively. The LTO-T/C obtained corresponding reversible capacities: 245 mAh g$^{-1}$, 220 mAh g$^{-1}$, 174 mAh g$^{-1}$, 150 mAh g$^{-1}$ and 125 mAh g$^{-1}$. What we can see from the curve is that as the current density increases the capacity of the LIBs decreases, which could be caused by the low conductivity, but when the current density decreases the capacity can restore. The above facts prove that LTO-T/C maintains its original structure after continuous lithium insertion and extraction during cycle process, ensuring the excellent
rate performance and cycle life of LIBs. For example, when the current density increases from 5 A g⁻¹ to 10 A g⁻¹, the capacities of LTO-T and LTO-T/C are corresponding down to 80% and 83%, which could be caused by the heterostructure and carbon layer making up for the low conductivity of LTO. Figure 9(c) shows the Nyquist plots of LTO-T and LTO-T/C after 500 cycles. As shown in figure 9(c), the diameter of semicircle reflects the sum of the charge transfer resistance (Rt), which is the resistance between electrode material and electrolyte, and SEI impedance (RSEI), which caused by the SEI film forming on the surface of the electrode. It can be seen from the figure that the impedances of LTO-T/C is smaller than LTO-T, which proves that the carbon layers improve the electron transmission rate of LTO-T and accelerate the insertion and extraction of lithium under large current.

4. Conclusion

In summary, LTO/T composite with chrysanthemum structure was successfully fabricated by a hydrothermal method and followed by coating a uniform carbon layer on the surface to obtain LTO-T/C. The unique nanowire assembled structure of TiO₂ improves the reversible capacity and rate performance of LTO. The carbon layer on the surface improves the conductivity of the sample. When evaluated as an anode material for LIBs, the LTO-T/C exhibits excellent perform (220 mAh g⁻¹ at a current density of 1.0 A g⁻¹ after 500 cycles or 125 mAh g⁻¹ at a current density of 10 A g⁻¹ after 500 cycles).

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