Solvothermal synthesis method for dual-phase Li$_4$Ti$_5$O$_{12}$/TiO$_2$ composites for high-stability lithium storage

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Abstract

As a promising anode material, lithium titanate (Li$_4$Ti$_5$O$_{12}$) displays extremely stable cycling and high safety performance. Nevertheless, its application is hindered because of a low electron conductivity and low specific capacity. Herein, dual-phase Li$_4$Ti$_5$O$_{12}$/TiO$_2$ (LTO/TO) was synthesized by a straightforward solvothermal method utilizing crystallized water of lithium hydroxide to hydrolyse tetrabutyl titanate at high temperature and pressure conditions. This work demonstrated that LTO/TO composites have excellent electrochemical performance and indicated that the inherent defects of LTO can be improved by the decoration of TO. At a current density of 1.0 A g$^{-1}$ (~6 C), the discharge capacity of LTO/TO sample reached 197 mAh g$^{-1}$ after 100 cycles, while LTO exhibited 180 mAh g$^{-1}$. It appears that nanostructure LTO/TO composites may shorten the diffusion distance of electrons and lithium ions.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are gradually emerging because of the depletion of traditional fuels and are of interest to researchers worldwide. Due to their high power density, high efficiency and long cycle life, lithium-ion batteries are becoming the power source of choice for electronic products [1–4]. In particular, in recent years, more attention has been paid to the safety of lithium-ion batteries. However, the traditional carbon negative electrode has a serious safety problem due to lithium dendrites being generated at a low voltage. As a promising anode material, spinel lithium titanate Li$_4$Ti$_5$O$_{12}$ (LTO) has been explored intensively, and its excellent safety, zero-stain during charge/discharge processes, great structural stability are attractive properties [1, 5]. And it has a flat high voltage of 1.55 V (versus Li/Li$^+$) [6]. However, a relatively low theoretical specific capacity (175 mAh g$^{-1}$), low lithium ion diffusion coefficient, and poor ionic and electronic conductivity restrict its widespread application [7, 8].

A series of strategies have been implemented to improve the performance of LTO, such as multifarious structures, diverse synthetic methods, doping of various conductive metal cations, and coating with different electric materials [9–11]. Recently, many experiments have proven that hollow porous structure and multiphase LTO can promote material properties. Zhou et al [12] reported Li$_4$Ti$_5$O$_{12}$ porous fiber which exhibited discharge capacity of 141 mAh g$^{-1}$ at a high current density of 20 C (1 C = 175 mA g$^{-1}$). Chen et al [13] synthesized fluoride doping Li$_4$Ti$_5$O$_{12}$ nanosheets and it showed reversible capacity of 101.4 mAh g$^{-1}$ at 28.6 C. Repp et al [10] using Fe$^{3+}$ doped Li$_4$Ti$_5$O$_{12}$ nanoparticles and it displayed excellent cycling performance. Ding et al [14] obtained yolk-shell structure Li$_4$Ti$_5$O$_{12}$–SnO$_2$ which delivered a steady capacity of 253.2 mAh g$^{-1}$ at 1 C. Gu et al [15] gained Li$_4$Ti$_5$O$_{12}$/PPy particles and it exhibited the initial capacities of 186.2 mAh g$^{-1}$ at 0.1 C.

Titanium dioxide (TiO$_2$) is considered as a promising LIB material because of its considerable theoretical capacity (167–335 mAh g$^{-1}$) and fast Li-ion insertion/extraction [16–18]. Additionally, dual-phase Li$_4$Ti$_5$O$_{12}$/TiO$_2$ (LTO/TO) compounds have demonstrated that a combination of the two materials can improve electrochemical properties [19]. Noerochim et al [20] reported that the capacity of Li$_4$Ti$_5$O$_{12}$–TiO$_2$
nanowires electrode decreased less than 5% at a current density of 0.1 C. Zhang et al. [21] synthesized Li$_4$Ti$_5$O$_12$-TiO$_2$ composites and its first discharge capacities reached 174 mA h g$^{-1}$. Theoretically, Li$_4$Ti$_5$O$_12$ and TiO$_2$ lattices can match favourably with other materials at lattice boundaries due having the two same elements and similar crystal structures [22]. In this paper, a binary LTO/TO compound and pure LTO nanosheets composed of very small nanoflakes were successfully produced by a facile solvothermal method. Ethanol was used as the sole solvent in this work, and tetrabutyl titanate was hydrolysed by crystallized water. The LTO/TO composite shows preferable electrochemical properties compared with those of pure LTO.

2. Experimental

2.1. Material synthesis

The LTO and LTO/TO nanoparticle were synthesized via a one-step solvothermal method followed by further heat treating using lithium hydroxide (LiOH·H$_2$O) and tetrabutyl titanate (TBOT) as raw materials. Typically, 0.2 g LiOH·H$_2$O was completely dissolved in 50 ml of ethanol after ultrasonication for 30 min as solution A. And 4 ml of TBOT was dissolved in 10 ml of ethanol as solution B. Then solution B was slowly drop wise into solution A with magnetic stirring. The mixed solution was transferred into a 100 ml Te autoclave and reacted at 200 °C for 24 h. After natural cooling to ambient temperature, the precursor product was collected by centrifugation, washed with ethanol and ultrapure water for several times, and dried overnight at 80 °C. Finally, the LTO/TO sample had been obtained via calcining at 600 °C for 3 h in air. Though the same procedure, pure LTO can be synthesized by dissolving 2 ml of TBOT in 10 ml of ethanol to form solution B.

2.2. Material characterization

The crystalline phase was identified by X-ray diffraction (XRD) on a X Pert PRO (PANalytical) with a Cu–Ka radiation at a range of 3°~80°. The morphology of the samples was characterized by Field emission scanning electron (FESEM, Zeiss Supra 55VP). The crystalline microstructure was determined by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, Tecnai F20, FEI).

2.3. Electrochemical measurement

The electrochemical evaluation was performed with CR2032 coin-type cells. The anodes as working electrodes that consisted of 70 wt% the active material, 20 wt% conductive carbon black and 10 wt% polyvinylidene difluoride (PVDF) mingled in N-methylpyrrolidone (NMP) solvent adequately to form homogeneous slurry. Subsequently, pressed the mixture onto a copper foil and dried at 120 °C for 24 h. The coin cells were assembled in an Ar-filled glove box with pure lithium foil as the counter electrode, Celgard 2300 as the separator and 1 M LiPF$_6$ dissolved in a 1:1 of ethylene carbonate (EC), and diethyl carbonate (DEC) as the electrolyte. All tests were performed at a voltage range of 0.01~3.0 V (versus Li$^+$/Li). The galvanostatic discharge/charge measurements were performed on the electrochemical equipment of NEWARE test system. Electrochemical impedance spectroscopy (EIS) was conducted on a CHI760C electrochemical station between 0.01 Hz to 100 kHz.

3. Results and discussion

Figure 1(a) shows a synthetic schematic of LTO/TO and LTO. LiOH·H$_2$O and TBOT were added to ethanol that was adequately stirred. The mixed solution was placed inside an autoclave for reaction and dried to obtain a precursor. Finally, we received nanometre-scale material after sintering. We performed component analysis on the synthesized materials by XRD, as shown in figure 1(b). As shown in figure 1(b), all the diffraction peaks of the black line were indexed to spinel Li$_4$Ti$_5$O$_12$ (JCPDS No. 49-0207). In the two-phase materials (red line), the other peaks were indexed to single anatase phase TiO$_2$ (JCPDS No. 21-1272), except for the characteristic LTO peaks. These results indicate that we successfully synthesized pure LTO and dual-phase LTO/TO.

To analyse the morphology and microstructure of LTO/TO and LTO, SEM, TEM and HRTEM were performed, as shown in figure 2. The morphology of the pure LTO (figure 2(a)) comprises secondary particles of different sizes composed of nanoparticles. Obviously, the appearance of the LTO/TO (figure 2(b)) is similar to a homogeneous nanoflake, which is significantly distinct from that of the pure LTO. In figure 2(c), it is clear that the microstructure of the LTO consists of very small nanoparticles with a diameter of approximately 20 nm, which is consistent with figure 2(a). In figure 2(d), the LTO/TO comprises LTO nanoflakes, which have diameters of approximately 100 nm and thicknesses of approximately 5 nm, and TO nanoparticles with diameters of approximately 10 nm. Measurements indicated that the lattice spacing is 0.48 nm in figure 2(e) and corresponds to the (111) plane of spinel Li$_4$Ti$_5$O$_12$. As shown in figure 2(f), the large interplanar pitch is 0.48 nm, which is assigned to the (111) plane of spinel Li$_4$Ti$_5$O$_12$. Another interplanar spacing is 0.35 nm, which is...
assigned to the (101) plane of anatase TiO₂. The results obtained by HRTEM matched well with those from XRD, as shown in figure 1(b). High-magnification TEM images of LTO and LTO/TO are in good agreement with this result, as shown in figure 3. In figures 3(a)–(b), the LTO microstructure consisted of bitty nanoparticles with a diameter of about 20 nm. In figures 3(c)–(d), the LTO/TO is made up of LTO nanoflakes, which with diameter of about 100 nm and thickness of about 5 nm, and TO nanoparticles with diameter of about 10 nm. The SAED patterns of samples in figures 3(e)–(f) prove the well-crystallized feature of the LTO and LTO/TO, and also in good agreement with the XRD and HRTEM results.

The electrochemical performance tests in the potential range of 0.01 ~ 3 V (versus Li/Li⁺) of the samples and the corresponding schematic diagram are shown in figure 4. Figure 4(a) demonstrates the initial
galvanostatic charge/discharge curves of LTO and LTO/TO at a low current density of 0.1 A g\(^{-1}\) (\(\sim 0.6\) C). The two materials have a voltage plateau at approximately 1.5/1.6 V. The LTO/TO compound contains voltage plateaus at approximately 1.7/2.0 V. The first cycle discharge capacity of LTO/TO delivers a high capacity of 439 mA h g\(^{-1}\), but only has a coulomb efficiency of 66.3%. The LTO exhibits a discharge capacity of 322 mA h
−1 and a coulomb efficiency of 69.2%. This may be due to the selected voltage interval, causing the formation of an SEI film and providing a portion of the capacity along with the acetylene black in the electrode.\cite{22, 23}

In figure 4(b), the dQ/dV curves were implemented on LTO and LTO/TO at a scan rate of 0.1 mV·s−1. The LTO/TO exhibits two pairs of cathodic/anodic peaks at 1.5/1.6 V and 1.7/2.0 V, while the LTO has an additional pair of redox peaks located at 1.5/1.6 V, which corresponds to the typical charge and discharge plateau for Li+ intercalation and removal in Li4Ti5O12 (equation (1)). This weak peak at 1.7/2.0 V indicates the redox reactions of the Ti4+/Ti3+ couple in TiO2 (equation (2))\cite{24, 25}. The dQ/dV curves correspond well with the first charge/discharge diagram.

\[
\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3\text{e}^- \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12} \quad (1)
\]

\[
\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \quad (2)
\]

In figure 4(c), the stability of LTO and LTO/TO samples were probed at a current density of 0.2 A g−1 and 1 A g−1. From the picture, the LTO and LTO/TO shown nearly the same discharge capacities about 200 mA h g−1 at a current density of 0.2 A g−1. It can be clearly seen that the capacity of LTO/TO is approximate at different current densities. For comparison, table 1 shows the cycling performance of LTO-based materials in recent reports. Figure 4(d) presents a comparison of the rate performance of the two materials at different current densities. In the fifth cycle at current densities of 0.1, 0.2, 0.5, 1.0, 0.1 A g−1, discharge capacities of approximately 216, 200, 183, 172, and 212 mA h g−1 can be obtained for pure LTO and 258, 222, 204, 191, and 251 mA h g−1 for LTO/TO, respectively. The result is the same as the cycle diagram figure 4(c), where LTO/TO shows better rate performance than LTO.

| Materials       | Current densities (A g−1) | Cycle number | Specific capacity (mAh g−1) | References |
|-----------------|---------------------------|--------------|----------------------------|------------|
| LTO/TO          | 1.00                      | 500          | 170                        | This work  |
| LTO/C           | 1.75                      | 2000         | 140                        | [4]        |
| LTO/TO          | 0.18                      | 200          | 172                        | [26]       |
| LTO/TO          | 0.18                      | 100          | 151                        | [27]       |
| Ti4+/LTO/TO     | 0.50                      | 4000         | 85                         | [28]       |
| LTO/TO          | 4.00                      | 100          | 110                        | [29]       |

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|-----------------|---------------------------|--------------|----------------------------|------------|
| LTO/TO          | 1.00                      | 500          | 170                        | This work  |
| LTO/C           | 1.75                      | 2000         | 140                        | [4]        |
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| LTO/TO          | 0.18                      | 100          | 151                        | [27]       |
| Ti4+/LTO/TO     | 0.50                      | 4000         | 85                         | [28]       |
| LTO/TO          | 4.00                      | 100          | 110                        | [29]       |

Figure 5. (a) cycling performance at 1.0 A g−1, (b) electrochemical impedance spectra of LTO and LTO/TO and (c) the lithiation/delithiation mechanism of LTO/TO electrode during charge/discharge process.
The diagram of long cycle properties at high current density was shown in figure 5(a). And the discharge capacities of LTO and LTO/TO samples reached 142 mA h g$^{-1}$ and 170 mA h g$^{-1}$, respectively, at a current density of 1.0 A g$^{-1}$ after 500 cycles. And both of LTO and LTO/TO batteries shown good stable cycling performance. Figure 5(b) shows the AC impedance spectrum of the two materials after different cycles at a current density of 0.2 A g$^{-1}$. Evidently, the charge-transfer resistances of the LTO/TO are lower than those of LTO. This suggests that the grain boundary and phase interfaces of Li$_4$Ti$_5$O$_{12}$ can be enriched by the incorporation of TiO$_2$, which can effectively improve the electrochemical performance [22, 24]. Two-phase LTO/TO sample has excellent electrochemical properties. Figure 5(c) depicts the lithiation/delithiation mechanism of the LTO/TO composite electrode. The lithium ions and electrons can be rapidly transported in the bulk LTO/TO, of which a thin SEI film formed on the surface during the charge and discharge process.

4. Conclusion

In summary, we report a novel strategy to synthesize binary LTO/TO and pure LTO. Crystallized water from lithium hydroxide monohydrate was used to hydrolyse dibutyl phthalate and synthesize two-phase LTO/TO in situ. The obtained material has prominent cycle stability and rate performance. It is likely that this synthetic method is feasible and can be applied to the synthesis of other similar electrode materials.

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