Pomegranate-like high density LTO anode material for lithium-ion batteries

1 | INTRODUCTION

Spinel Li$_4$Ti$_5$O$_12$ (LTO) as an alternative anode material for lithium ion batteries has been paid great attention recent years [1–3]. Compared with traditional graphite anode, LTO presents a relatively high discharge platform (1.55 V vs Li/Li$^+$), which can effectively avoid the discharge of solid electrolyte interface film and facilitate the coulombic efficiency of LIBs [4–6]. Besides, LTO presents a better high/low temperature characteristics (−40–55 °C), zero strain effect, which can enhance the cycle performance, reversibility, long stability and safety property of LIBs [7, 8]. However, the commercialization of LTO anode is still limited by its low electronic conductivity of 10–13 S cm$^{-1}$ and medium Li$^+$ diffusion coefficient of 10$^{-13}$–10$^{-9}$ cm$^2$ S$^{-1}$ [3, 9].

To overcome the issues, researchers have developed approaches in three aspects [1, 3, 10, 11]. The first one was to prepare various nano-morphological LTOs to reduce the diffusion distance of Li$^+$ and the electron transport path, thereby accelerating the insertion/extraction reaction of lithium ions into LTO [12–14]. Sun et al. [13] used hydrothermal method to synthesize nanosheet-like LTO with high capacity of 180 and 110 mAh g$^{-1}$ at 1 C and 20 C, respectively. The second method was designing a conductive layer on the surface of LTO to promote the conductivity of the composite [15–18]. Song et al. [19] synthesized Li$_4$Ti$_5$O$_12$ with a hierarchical porous carbon (derived from bagasse) on the surface. The obtained sample showed a reversible capacity of 170.7 mAh g$^{-1}$ after 1000 cycles at 1 A g$^{-1}$ and 91.2 mAh g$^{-1}$ even after 3000 cycles at a high current density of 10 A g$^{-1}$. The other strategy is by element doping [20, 21]. Zhou et al [2] synthesized Ni-doped LTO, it presented a high specific capacity of 180 and 110 mAh g$^{-1}$ at 1 C and 30 C, respectively.

The previous strategies were mostly designing a nano structural LTO for LIBs. However, the low tap density will dramatically affect the volumetric capacity and inhibits its commercialization [22]. While the in situ synthesizing LTO on top of the microstructural TiO$_2$ can significantly improve the electrochemical properties comparing with micro LTO. And the total volume of the composite is similar as the micro TiO$_2$ precursor. Therefore, the LTO/TO composites maintain high volume energy density as well as good rate property [23].

We mainly focus on finding a low-cost and simple method to prepare LTO nano/micro structural composites, making large-scale applications and industrial production of LTO possible.

In this work, the TiO$_2$ and LiTiO$_2$ composites were synthesized by using a simple reaction with micro-TiO$_2$ and LiOH-H$_2$O. The mixture was firstly treated by a hydrothermal method and then calcined at 700 °C in air to form a pomegranate-like nano/micron LTO-TO composites. Compared to the original TiO$_2$, the LTO-TO composites showed better capacity and rate property, with a discharge capacity of 157.3 mAh g$^{-1}$ at 0.5 C and 102.3 mAh g$^{-1}$ at 10 C. The results demonstrate this strategy presents a high potential in designing commercial LTO anode materials.

2 | EXPERIMENTAL SECTION

2.1 | Materials preparation and characterization

All chemicals were purchased from Aladdin and Sinopharm and did not require further purification. 0.0060 mol of lithium hydroxide monohydrate (LiOH-H$_2$O, 99%) was dissolved in 15 mL of deionized water to form a 0.4 M lithium hydroxide solution, and 0.0074 mol of titanium dioxide (TiO$_2$, 99%) was added to the solution (the molar ratio of LiOH-H$_2$O to TiO$_2$ was fixed at 4:5) and stirred for 2 h. The resulting solution was transferred to stain steel autoclave, sealed and incubated at 180 °C for 2 h. The precipitate was centrifuged by filtration, washed with deionized water and ethanol, separated in a high-speed centrifuge (3000 r/min, 10 min), and then dried at 60 °C for 4 h. Then the dried precursor was put into muffle furnace and calcined in air at 700 °C for 2 h to obtain an LTO-TO-4. LTO-TO-1 and LTO-TO-6 were obtained in the same manner using a 0.1 M and 0.6 M lithium hydroxide solution. The obtained original TO, LTO-TO-1/4/6 samples were subjected to powder X-ray diffraction (Bruker, XRD), scanning electron microscope (Phenom ProX, SEM), and transmission electron microscope (FEI, TEM) characterization.
2.2 Electrochemical measurements

Electrochemical tests were made using CR2032 coin-type half cells. The electrode composed of anode composite, conductive carbon black and PVDF (8:1:1), then coated on copper foil. Constant current discharge/charge experiment was performed on a CT-4008 battery cycler (Shenzhen Neware Electronics Co., Ltd., China) with a voltage range of 1–3 V (vs Li/Li⁺). Cyclic voltammetry (CV) was tested using an electrochemical workstation (CHI-660E, Shanghai) at a scan rate of 0.1–10 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was measured on an electrochemical workstation (ZAHNER IM-6, USA) in the frequency range of 100 kHz to 0.1 Hz.

3 RESULTS AND DISCUSSION

The concentration of LiOH·H₂O is crucial for the ratio of LTO to TiO₂ during the reaction process. In this work, LTO-TO dual phase anode materials were prepared by using different concentrations of LiOH·H₂O. The composition of the samples was analysed by XRD (shown in Figure 1). The XRD patterns acquired from LTO-TO-1 exhibit a weak LTO peak, LTO-TO-4 shows a moderate LTO and TO anatase phase peak, and LTO-TO-6 shows a strong LTO peak as well as a weak TO peak. The high ratio of LTO in LTO-TO-6 was prepared by a high concentration of LiOH·H₂O, while the lower LTO content of LTO-TO-1 was obtained by using lower concentration of LiOH·H₂O. Obviously, increasing the concentration of the reactants facilitates the formation of the LTO phase.

The microstructure of the LTO-TO composite was observed by SEM. The morphology of TO, LTO-TO-1/4/6 samples with the same magnification as shown in Figure 2. It can be seen that the original TiO₂ is composed of micro-scale particles (Figure 2(a)). However, there is a small amount of particles on the surface of LTO-TO-1, and new uniform particles on the surface of LTO-TO-4, while LTO-TO-6 has no particles on its surface. It clearly disclosed that LTO is a surface grown on TO. It can be seen that LTO-TO-4 exhibits a pomegranate structure, and the uniformly growing LTO small-size particles completely loaded on the surface of TO, which indicates that LTO-TO-4 has a good two-phase structure of LTO and TO.

The microstructure of the sample was observed by TEM as well, as shown in Figure 3. The low resolution TEM image (Figure 3(a)) reveals the layered structure of the LTO-TO composed of nanospheres clearly. An HR-TEM image (Figure 3(b)) shows the coexistence of spinel LTO and anatase TiO₂ crystal planes in a single nanosphere. The enlarged region obtained from Figure 3(b) exhibits that most of the regions are the LTO regions (Figure 3(c)). Moreover, some of the LTO regions are doped with the elongated TO region, in which the two phases are
shared (Figure 3(d)). It may show that it is difficult for Li\(^+\) to be inserted into the TO to form LTO when the TO size is large, it forming an LTO coated on the surface of the TO, and the narrow TO area in the LTO region may be a gap between the LTOs. The lattice fringe on the surface of LTO and TO have lattice spacings of 0.4841 and 0.349 nm respectively, corresponding to (111) and (101) crystal plane, which are in accordance with the standard cards of Li\(_4\)Ti\(_5\)O\(_{12}\) and TiO\(_2\) acquired from XRD. It recorded that the boundaries of grain in LTO-TO composites might contribute to the promotion of Li\(^+\) diffusion and more Li storage offered by active sites [23]. Therefore, the prepared composite is likely to possess excellent electrochemical properties.

The electrochemical properties of the LTO-TO-1/4/6 anode materials were measured by CV, as shown in Figure 4. The samples were tested at a scan rate of 0.5 mV s\(^{-1}\) (Figure 4(a)). The anode and cathode peak ratios of LTO-TO-4 is sharper than LTO-TO-1 and LTO-TO-6, indicates its superior electrochemical Li\(^+\) intercalation/deintercalation kinetics. LTO-TO-4 was characterized by a scan rate of 0.2 mV s\(^{-1}\). Except for the characteristic anode and cathode peaks of the LTO (1.66 and 1.50 V, respectively), it can be observed the anatase TiO\(_2\) at 2.21 and 1.68 V. The CV curves of the second and third circles almost completely coincide, indicates that LTO-TO-4 has excellent reversible properties. These CV results well characterized the dual phase properties of the samples and agree well with the XRD results (Figure 1). Therefore, it is believed that the LTO-TO-4 anode presents a better electrochemical performance.

The rate performance of three anode materials measured sequentially at 0.5 C to 10 C was compared in Figure 5(a), with each rate performance being 10 cycles. The LTO-TO-4 exhibits better capacity than the original LTO-TO-1 and LTO-TO-6 at different current density. The discharge capacities of LTO-TO-4 at a rate of 0.5 C, 1 C, 3 C, 5 C, and 10 C (taken from the last cycle of each current rate) were 137.1 (the tenth cycle), 127.9, 112.9, 106.7, and 92.6 mAh g\(^{-1}\), respectively. While LTO-TO-1 and LTO-TO-6 corresponding discharge capacities were 47.7 (the tenth cycle), 34.0, 17.1, 12.0, 7.2 mAh g\(^{-1}\) and 111.9 (the tenth cycle), 105.0, 91.7, 84.1, 69.3 mAh g\(^{-1}\), respectively. The promoted capacity in the LTO-TO-4 indicates that a reasonable LTO size and a certain amount of TO are beneficial to promote the electrochemical performance of the LTO-TO composite.

The cycle stability of LTO-TO-1/4/6 tested at 0.5 C was demonstrated in Figure 5(b). The three samples sustained long-span cycling stability over 500 cycles. LTO-TO-4 still provided a high discharge capacity of 126.4 mAh g\(^{-1}\) after the 500 cycles. LTO-TO-1 and LTO-TO-6 presented a discharge capacity of 19.8 and 54.4 mAh g\(^{-1}\) after 500 cycles respectively, with capacity retention ratio were 30.1% and 67.7%, relative to the discharge capacity in the second cycle (65.7 and 80.5 mAh g\(^{-1}\)). The results of cycle performance confirmed the positive effect of reasonable LTO size and content on the electrochemical performance enhancement of LTO-TO hybrid anodes once again. Figure 5(c) exhibited the cycle performance of LTO-TO-4 measured at a high current of 10 C. It indicated that the LTO-TO-4 still provided a discharge capacity of 95 mA h g\(^{-1}\) after the 450 cycles, with a high capacity retention of 92.7% relative to the second cycle (105.4 mAh g\(^{-1}\)), which demonstrated the good cycle performance of LTO-TO-4 at high current.

Figure 5(d) displayed a voltage capacity profile of the LTO-TO-4 measured at a rate of 0.5 C. There is a stable charge and discharge platform in the whole cycles. At the 1st and 10th cycles, it is apparent that in addition to the charge and discharge platform near 1.55 V, there is also a platform near 1.78 V. The two platforms are the charge and discharge platforms of LTO and TO, respectively, which is a good indication of the dual phase properties in samples, identify with the XRD result (Figure 1) and the CV results shown in Figure 4. After 100 cycles, the TO platform disappeared, indicating that TO only provides capacity at the beginning. As the cycle progresses, TO
will no longer provide capacity and only play a role in enhancing the performance of LTO-TO composites, which can explain the quick capacity drops in the starting of the 30 cycles (Figure 5(b)). The excellent performance of LTO-TO-4 was further explained.

The electrochemical impedance spectroscopy (EIS) of the TO-TO-1, LTO-TO-4 and LTO-TO-6 electrodes are shown in Figure 6. The Nyquist diagram of the three spectra consists of a concave semicircle, high-frequency, intermediate-frequency and low-frequency oblique lines. The semicircles in the high and intermediate frequency regions are two overlapping semicircles, which represent the SEI impedance ($R_f$) and charge transfer impedance ($R_{ct}$), respectively. The bias line in the low frequency region reflect to the diffusion of Li$^+$. The unevenness of the layered electrode material and the rough surface may also cause a concave semicircle at high frequency [23]. The Z-view software fits the EIS spectra of the two samples represent by the equivalent circuit (the inset of Figure 6) The $R_{ct}$ of LTO-TO-1/4/6 were 289.7, 247.7, and 1067 $\Omega$, respectively. Clearly, a reasonable LTO size and content effectively promote ion, e$^-$ conductivity and charge transfer, which agree well with its better capacity, rate performance and cycle life.
4 | CONCLUSION

Three kinds of Li$_4$Ti$_5$O$_12$-TiO$_2$ dual-phase composites were prepared by using different concentrations of Li$_4$Ti$_5$O$_12$ and TiO$_2$ as lithium source and titanium source, then three samples were compared as electrode. The LTO-TO-4 microspheres achieved high reversible discharge capacities of 157 and 92 mAh g$^{-1}$ at 0.2 C and 10 C, respectively. Studies on different current density discharge/charge curves have shown that anatase TiO$_2$ phase may not benefit to Li storage in high current densities on account of extraordinary short discharge/charge times and serious polarization, but with Li$_4$Ti$_5$O$_12$ phase synergies may have appeared which increase the capacity of the mixture. The outstanding electrochemical characteristics of the Li$_4$Ti$_5$O$_12$@TiO$_2$ dual phase electrode indicates its potential as an anode for lithium-ion batteries.

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