

# Enhanced electrochemical performance of $\text{La}_2\text{O}_3$ -modified $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material for Li-ion batteries

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**Abstract.** 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  sample is prosperously synthesized through a polymeric method followed by calcination at 500 °C for 5 hours in air. The 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to confirm the structure and morphology. After the modification process, the lattice structure of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is not changed and a  $\text{La}_2\text{O}_3$  coating layer has formed on the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles. The 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  exhibits a superior rate capacity, with charge capacity between 0 and 3 V of 235.2, 224.8, 214.1, 202.2, 194.5 and 181.9 mAh g<sup>-1</sup> at rates of 0.2, 0.5, 1, 3, 5, and 10 C (1 C = 250 mAh g<sup>-1</sup>), respectively.

## 1. Introduction

In recent years, many efforts have been devoted to develop the lithium ion batteries (LIBS) because of their potential applications in electrical vehicles, hybrid electric vehicles and electrical energy systems [1-3]. Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) has been regarded as an ideal anode material for long-life LIBS due to its negligible volumetric change during the insertion/extraction of the lithium ion. Furthermore, in comparison with commercial carbon-based materials, LTO is a safer material because of its high thermal stability and high discharge plateau (at about 1.5V vs  $\text{Li}^+$ ), which prohibits the formation of metallic lithium dendrites on the electrodes' surfaces. Although LTO has the above-mentioned advantages, it still has some problems in the power LIBS industries with large-scale applications. The gas generation is a severe drawback of LTO when using LTO as anode material in LIBS. The main reason for the gassing behavior may be the interfacial reactions between LTO and electrolyte [4, 5].

Surface modification has been demonstrated to be an effective way to prevent LTO from reacting with electrolyte. For example, carbon [6-9], metal [10-12] and metal oxide [13-16] all have been used to modify the LTO to suppress the electrolyte decomposition and enhance the electrochemical performance. To the best of our knowledge,  $\text{La}_2\text{O}_3$  with excellent thermal stability has been used in various applications. In particular, when  $\text{La}_2\text{O}_3$  is used as an additive, it greatly decreased the overpotential in the ternary alkaline metal carbonate system and protected the transition metal ions from dissolving into the electrolyte [17-19]. In this present work, we use  $\text{La}_2\text{O}_3$  to modify pure LTO. The structure and electrochemical performance of the  $\text{La}_2\text{O}_3$  modified LTO samples are studied and reported below.



## 2. Material and methods

### 2.1 Synthesis and characterization

Pure LTO powder (Shenzhen beiterui new energy Limited by Share Ltd),  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aladdin) and polyvinyl alcohol (PVA, degree of polymerization is 1500) were purchased for this work. In brief, The 3 g of LTO was dispersed in deionized water by 0.5 hour sonication followed by 2 hours stirring. The calculated 1.0 wt.% of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  to form  $\text{La}_2\text{O}_3$  and 1.0 wt.% polyvinyl alcohol were dissolved in warm deionized water and added dropwise to the dispersed LTO. The mixture was continuously stirred for 3 hours at 25 °C and continuously stirred at 100 °C to evaporate the water, then the mixed solid powder was calcined at 500 °C for 5 hours in air to obtain the 1.0 wt.%  $\text{La}_2\text{O}_3$  modified LTO sample.

Powder X-ray diffraction (XRD, Ultima IV, Rigaku) with  $\text{Cu K}_\alpha$  radiation was used to characterize the phase composition and crystal structures of all the samples. The diffraction patterns were collected at room temperature by step scanning in the range of 10–90° at a scanning rate of 0.02° per 10 s. The morphology of the materials was characterized by SEM (Hitachi S-4800, Japan).

### 2.2 Electrochemical measurements

The electrochemical properties of LTO samples were measured using a CR2032 coin-type half-cell in which the cathode and Li metal anode were separated by a porous polypropylene film (Celgard 2400, Celgard Inc., USA). The cathode slurry was prepared by homogeneously mixing the active material (LTO materials), Supper-P, and a polyvinylidene fluoride (PVDF) in a mass ratio of 90:5:5 in N-methyl-2-pyrrolidone (NMP) solvent. Then the slurry was cast onto a Cu foil and dried for 12 h in vacuum at 105 °C. Finally, the electrode laminate was punched into disks (10 mm in diameter) and dried in a vacuum oven at 105 °C for 24 h. The coin cell was assembled entirely in an argon-filled glovebox. The electrolyte (Capchem Technology (Shenzhen) Co., Ltd.) was a solution of 1 mol  $\text{L}^{-1}$   $\text{LiPF}_6$  in ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1, in volume).

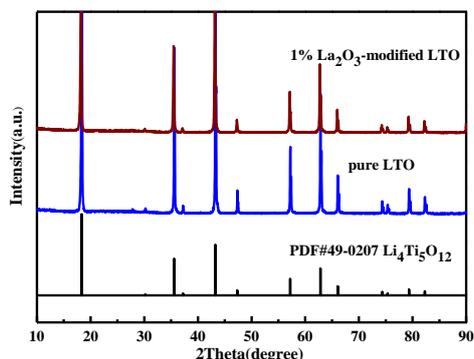
Galvanostatic charge-discharge tests were carried out on an automatic galvanostatic charge-discharge unit (Land 2001A, Wuhan, China) between 0 and 3 V at C-rates of 0.2C, 0.5C, 1C, 3C, 5C and 10C (1C = 250 mAh  $\text{g}^{-1}$ ) at 25 °C.

## 3. Results and discussion

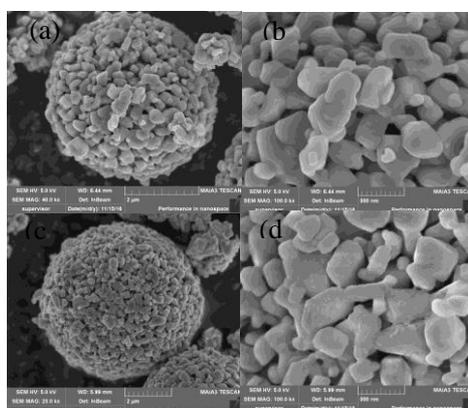
### 3.1 Material characterization

Figure 1 shows the XRD patterns of pure LTO and 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO sample. All the XRD diffraction patterns of 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO are indexed to the standard spinel structure of LTO (card NO. 49-0207) with  $\text{Fd}3m$  space group and no peaks of  $\text{La}_2\text{O}_3$  are present due to low quantity. The XRD patterns prove that the structure of 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO sample is not destroyed after  $\text{La}_2\text{O}_3$  modification process.

Figure 2 shows the SEM images of pure LTO and 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO sample. It can be observed that pure LTO has a smooth surface as clearly shown in Figure 2a-b. However, after  $\text{La}_2\text{O}_3$  modification, the surface of 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO becomes rough as shown in Figure 2c-d. Such phenomenon is attributed to that the  $\text{La}_2\text{O}_3$  layer on the surface of LTO.



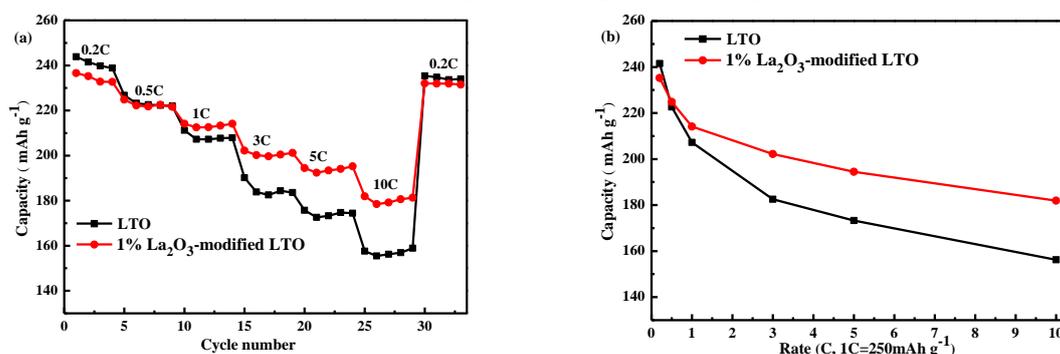
**Figure 1:** XRD patterns of pure LTO, 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO and the standard XRD patterns of LTO .

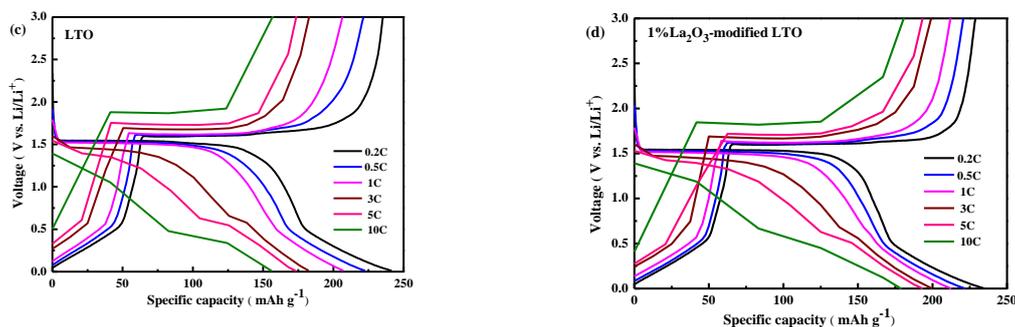


**Figure 2:** SEM images of (a-b) pure LTO and (c-d) 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO.

### 3.2 Electrochemical properties

Figure 3a-b displays the rate capacity of pure LTO and 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO at C-rates from 0.2–10 C between 0 and 3 V. 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO showed a higher rate capacity than pure LTO at high C-rates. The galvanostatic charge-discharge curves of pure LTO and 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO at C-rates of 0.2–10 C between 0–3 V are shown in Figure 3c-d, respectively. The 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO displayed a smaller potential difference between the charge and discharge platforms than pure LTO, especially at high C-rates. This confirms that  $\text{La}_2\text{O}_3$  modification is favorable for reducing electrode polarization, thereby enhancing the rate capacity of LTO. The charge capacity values of pure LTO were 241.5, 222.6, 207.2, 182.5, 173.3 and 156.2  $\text{mAh g}^{-1}$  at 0.2, 0.5, 1, 3, 5, and 10 C, respectively, while for 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO these values were 235.2, 224.8, 214.1, 202.2, 194.5 and 181.9  $\text{mAh g}^{-1}$ , respectively. This indicates that 1.0 wt.%  $\text{La}_2\text{O}_3$ -modified LTO had a higher charge capacity than pure LTO, especially at higher rates.





**Figure 3:** (a) Rate capacity of pure LTO and 1.0 wt.% La<sub>2</sub>O<sub>3</sub>-modified LTO from 0.2C to 10C, (b) charge capacity as a function of the C-rates for pure LTO and 1.0 wt.% La<sub>2</sub>O<sub>3</sub>-modified LTO and (c-d) galvanostatic charge-discharge curves at different C-rates for pure LTO and 1.0 wt.% La<sub>2</sub>O<sub>3</sub>-modified LTO between 0 and 3 V (1C = 250 mAh g<sup>-1</sup>).

#### 4. Conclusion

After La<sub>2</sub>O<sub>3</sub>-modification process, the results indicated that a La<sub>2</sub>O<sub>3</sub> coating layer was formed on the surface of LTO. The electrochemical results show that 1.0 wt.% La<sub>2</sub>O<sub>3</sub>-modified LTO displays a superior rate capacity between 0 and 3 V. The improvement in electrochemical properties is attributed to the La<sub>2</sub>O<sub>3</sub> coating layer on the surface of LTO, which suppresses the electrolyte reduction decomposition. Therefore, application of the La<sub>2</sub>O<sub>3</sub> modification process has potential to be an efficient strategy for improving the electrochemical performance of pure LTO for lithium ion batteries.

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