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

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Abstract. 1.0 wt.% La$_2$O$_3$-modified Li$_4$Ti$_5$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.% La$_2$O$_3$-modified Li$_4$Ti$_5$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 Li$_4$Ti$_5$O$_{12}$ is not changed and a La$_2$O$_3$ coating layer has formed on the Li$_4$Ti$_5$O$_{12}$ particles. The 1.0 wt.% La$_2$O$_3$-modified Li$_4$Ti$_5$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$^{-1}$ at rates of 0.2, 0.5, 1, 3, 5, and 10 C (1 C = 250 mAh g$^{-1}$), 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 Li$_4$Ti$_5$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 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, La$_2$O$_3$ with excellent thermal stability has been used in various applications. In particular, when La$_2$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 La$_2$O$_3$ to modify pure LTO. The structure and electrochemical performance of the La$_2$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), La(NO₃)₃·6H₂O (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 La(NO₃)₃·6H₂O to form La₂O₃ 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.% La₂O₃ modified LTO sample.

Powder X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu Kα 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 L⁻¹ LiPF₆ 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 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.% La₂O₃-modified LTO sample. All the XRD diffraction patterns of 1.0 wt.% La₂O₃-modified LTO are indexed to the standard spinel structure of LTO (card NO. 49-0207) with Fd3m space group and no peaks of La₂O₃ are present due to low quantity. The XRD patterns prove that the structure of 1.0 wt.% La₂O₃-modified LTO sample is not destroyed after La₂O₃ modification process.

Figure 2 shows the SEM images of pure LTO and 1.0 wt.% La₂O₃-modified LTO sample. It can be observed that pure LTO has a smooth surface as clearly shown in Figure 2a-b. However, after La₂O₃ modification, the surface of 1.0 wt.% La₂O₃-modified LTO becomes rough as shown in Figure 2c-d. Such phenomenon is attributed to that the La₂O₃ layer on the surface of 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 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 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.
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