



Li₄Ti₅O₁₂ composited with Li₂ZrO₃ revealing simultaneously meliorated ionic and electronic conductivities as high performance anode materials for Li-ion batteries



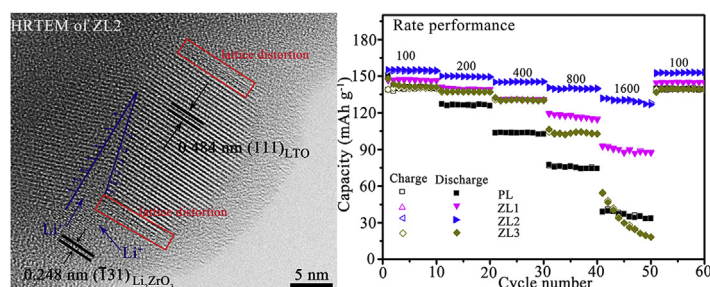
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HIGHLIGHTS

- Li₄Ti₅O₁₂ (LTO) composited with tetragonal Li₂ZrO₃ was simply fabricated.
- Li₄Ti₅O₁₂ composited with Li₂ZrO₃ exhibits excellent cycle and rate performance.
- Li₂ZrO₃ and superficial Zr⁴⁺ doping enhance the conductivities of LTO.

GRAPHICAL ABSTRACT



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ABSTRACT

Li₄Ti₅O₁₂ (LTO) is inherently a poor ionic and electronic conductor, and the modification methods available could solely meliorate either ionic or electronic conductivity. In order to simultaneously improve both the ionic and electronic conductivities, LTO was composited with Li₂ZrO₃ accompanying with superficial Zr⁴⁺ doping by the simple reaction between Zr(NO₃)₄·5H₂O and LiNO₃ on the LTO surface. From the comparative experiments, the as-modified LTO with a Li₂ZrO₃/LTO mass ratio of 0.009 and sintered at 750 °C exhibits the most excellent rate performance (achieving capacities of 155.3, 149.6, 145.4, 139.6, 130.2 and 153.2 mAh g⁻¹ at 100, 200, 400, 800, 1600 and 100 mA g⁻¹, respectively) and long-term cyclability (retaining a capacity of 102 mAh g⁻¹ after the 2000th cycle at 500 mA g⁻¹). By the detailed structural characterization and electrochemical impedance spectra analysis, the formation of the tetragonal Li₂ZrO₃ with good ionic conductivity and the superficial Zr⁴⁺ doping with improved electronic conductivity is responsible for the markedly enhanced cycling and rate performance of LTO.

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1. Introduction

Energy is crucial to the development of science and technology, but the resources become scarce due to the undue use. Developing

lithium ion batteries (LIBs) is one of the solutions for the present energy crisis. LIBs possess large energy density, high output voltage and friendliness toward environment. However, the anode materials used in current LIBs (dominantly carbon materials) could not meet the demands of many energy fields, especially electric vehicles and hybrid electric vehicles [1]. In order to obtain LIBs with better electrochemical performance, exploring new materials or modifying the currently available materials is an effective method.

Li₄Ti₅O₁₂ (LTO) could interact with three Li⁺ to form Li₇Ti₅O₁₂

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and restore to LTO around a stable plateau of 1.55 V (vs. Li/Li⁺) in the potential range of 1.0–2.5 V, yielding a theoretical capacity of 175 mAh g⁻¹ and almost zero volume change in charge and discharge process [2,3]. But the performance of LTO at high charge and discharge rates is not satisfactory due to the poor electronic conductivity (<10⁻¹³ S cm⁻¹) [4,5] and low ionic conductivity [6]. In order to overcome these shortcomings, some measures have been taken, such as doping alien ions [7–9], coating carbon materials [10], metal oxides [11–13], and Li-containing fast ion conductors [14,15]. However, the cycling stability is still unsatisfactory due to the uncontrollability of these measures. As a simple controllable method, forming composite would be a good choice. As has been reported, compositing LTO with carbon [16,17], TiO₂ [18], Fe₂O₃ [19], SiO₂ [20] and other compounds [21] could improve the electrochemical performance, but the ionic conductivity of carbon and metal oxides is very low. Li-containing fast ion conductors, such as Li₂SiO₃ [22], Li₂TiO₃ [23], Li₃ZrO₆ [24] and Li₂ZrO₃ [25,26] possess relatively high ionic conductivity, and have been applied in LIBs. Among the ionic conductors, tetragonal Li₂ZrO₃ as a metastable inorganic electrolyte are beneficial to Li⁺ transfer during charging and discharging [27]. According to the literature [28], the Li₂ZrO₃ formed using appropriate zirconium precursor could provide Zr⁴⁺ to diffuse into the surface of cathode material to enhance the electronic conductivity [29]. On the basis of the properties and investigations on Li₂ZrO₃, it is hopeful to simultaneously increase the electronic and ionic conductivities of LTO by rationally designing the reactions to yield Li₂ZrO₃ composited with LTO by combining the Li⁺ transfer ability of Li₂ZrO₃ with the superficial Zr⁴⁺ doping in LTO. In a previous research [15], Li₂ZrO₃-coated LTO was prepared by mixing 0.043 g Zr(NO₃)₄·5H₂O and 0.02 g CH₃COOLi·2H₂O with 4.591 g LTO powder in absolute alcohol, followed by sintering the dried mixture at 850 °C for 6 h. However, owing to the low amount of Li₂ZrO₃ (about 0.33 wt%) and high sintering temperature, the improvement in electrochemical performance was not distinct.

In terms of that the modification methods available could merely meliorate either ionic or electronic conductivity of LTO, in this work, the ionic conductor of Li₂ZrO₃ was composited with LTO by a simple reaction between Zr(NO₃)₄·5H₂O and LiNO₃ at suitable sintering temperatures, the simultaneous formation of Li₂ZrO₃ and superficial Zr⁴⁺ doping in LTO results in the simultaneously enhanced ionic and electronic conductivities of LTO. Various preparation conditions (including the mass ratio of Li₂ZrO₃/LTO, sintering temperature, etc.) were attempted to achieve the optimal modification effect, and detailed characterizations were conducted to understand the modification mechanism involved.

2. Experimental

2.1. Preparation of the composite of LTO and Li₂ZrO₃

The chemicals employed are analytically pure without further purification. The preparation of the composite of LTO and Li₂ZrO₃ is divided into two steps. The first step is preparing LTO, which is similar to that reported in our previous work [30]. The solution of 25.6 g tetrabutyl titanate dissolved in 50 mL anhydrous ethanol was added drop by drop into the 20 mL water solution containing 2.6 g LiOH·H₂O under magnetic stirring, followed by drying in an oven for 12 h and sintering in a tube furnace at 600 °C for 5 h.

The second step is preparing the composite of LTO and Li₂ZrO₃ (ZL) with various mass ratios of 0, 0.007, 0.009 and 0.018 for Li₂ZrO₃/LTO, and the products sintered at 750 °C for 5 h are designated as PL, ZL1, ZL2 and ZL3, respectively. Typically, the corresponding mass of Zr(NO₃)₄·5H₂O and LiNO₃ was dissolved in 40 mL water in a crucible, then the as-prepared LTO of 1.5 g was

added into the crucible under magnetic stirring. After thoroughly drying at 105 °C, the mixture was sintered at 750 °C for 5 h.

2.2. Material characterization

In order to know about the phase structure, composition of the as-prepared products, a series of measurement methods were adopted. A Rigaku Dmax-2500 diffractometer was used to obtain X-ray diffraction (XRD) patterns at a scanning rate of 4° min⁻¹ with Ni filtered Cu K α radiation (V = 50 kV, I = 100 mA), and Raman spectra are obtained through Lab-RAM HR800 Raman spectroscopy with 632.81 nm laser excitation. High angle annular dark field (HAADF)-Scanning transmission electron microscope (STEM), energy-dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM) were conducted in a JEOL JEM-2200FS microscope equipped with a Bruker Quantax 400 EDS system with an XFlash 5060 detector to examine the microstructure and composition. KARTOS XSAM800 X-ray photoelectron spectroscopy (XPS) was adopted to acquire the compositions using Al K α radiation as the excitation source.

2.3. Electrochemical assessment

2025 coin-type half-cells were assembled in an argon-filled glove box utilizing Li foils as the counter electrode and Celgard 2300 as separator. The mass ratio of active materials, acetylene black and polyvinylidene fluoride (PVDF) is 8: 1: 1. They were mixed for about 1.5 h and coated onto copper foils. After drying in a vacuum oven at 120 °C for 12 h, the electrodes of 14 mm in diameter were punched from the copper foils with the mass loading of active materials about 3 mg on each electrode and then dried in the vacuum oven at 80 °C for 1 h. The electrolyte consists of the solution of 1 M LiPF₆ in a 1: 1 (v/v) EC/DMC. Galvanostatic charge and discharge were performed at diverse current densities in the potential range from 1.0 to 2.5 V (vs. Li/Li⁺) at 25 °C on a Land CT2001A battery test system. The electrochemical impedance spectra (EIS) were tested from 100 kHz to 0.01 Hz with an AC signal amplitude of 5 mV on an IviumStat electrochemical workstation.

3. Results and discussion

3.1. Structure of the as-prepared products

The crystal structure of the as-prepared products was identified by XRD patterns (Fig. 1a). The diffraction peaks of PL correspond well with those for the spinel LTO (JCPDS49-0207, belonging to space group of Fd3m (227)) with a lattice constant of 8.38 Å. The diffraction peaks of ZL1, ZL2 and ZL3 are similar to those of PL except for the weaker peaks of ZL2 and ZL3 than PL, implying that compositing with Li₂ZrO₃ lowers the crystallization degree of LTO. The crystallite size calculated by the Scherrer Equation ($d = K\lambda / B\cos\theta$) [31] using the (111) plane is 57.9, 45.0, 33.5 and 42.3 nm for PL, ZL1, ZL2 and ZL3 respectively, demonstrating that the formation of Li₂ZrO₃ could suppress grain growth of LTO during sintering to a certain degree. The crystallite size was also examined by TEM (Fig. S1), which is similar to the XRD result. As a rule of thumb, the active materials with smaller crystallite size are favorable to achieve enhanced electrochemical properties [32]. In order to know about the subtle variation in structure, the (111) plane of the samples was zoomed in (Fig. 1b). Apparently, the (111) diffraction of LTO broadens when composited with Li₂ZrO₃, and the widened peak could be deconvoluted into two peaks. Taking ZL2 as an example, the two peaks situating at 18.28 and 18.07° could be clearly distinguished in the inset of Fig. 1b. The peak at 18.28° is close to that for PL, while the one at 18.07° corresponds to a lattice

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