Unique mesoporous spinel Li$_4$Ti$_5$O$_{12}$ nanosheets as anode materials for lithium-ion batteries

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** Highlights**
- Unique mesoporous LTO nanosheets are prepared for the first time.
- The mesoporous LTO nanosheets display remarkable surface lithium storage.
- The surface lithium storage is attributed to its advanced microstructure.
- The surface lithium storage contributes to its improved performances.
- The mesoporous LTO nanosheets are attractive for high performance anodes.

**Abstract**
Spinel Li$_4$Ti$_5$O$_{12}$ (LTO) has been intensively investigated as promising anode materials for lithium-ion batteries (LIBs) due to its remarkable structural stability and excellent safety. In this paper, unique LTO nanosheets with porous microstructure are successfully prepared for the first time by a facile approach without any additives and template under hydrothermal conditions following calcination. Particularly, compared with traditional LTO microspheres and smooth LTO nanosheets, the newly prepared mesoporous LTO nanosheets demonstrate extra surface lithium storage reaction and much improved electrochemical performances, delivering ultrahigh reversible capacity of 169 mAh g$^{-1}$ at 1C and superior rate performance of more than 140 mAh g$^{-1}$ at 30C between 1.0 and 2.5 V vs. Li$^+$/Li. The beneficial surface lithium storage is mainly attributed to its advanced microstructure, which can facilitate the transfer of lithium-ions and electrons. The exceptionally improved electrochemical performance of the mesoporous LTO nanosheets will undoubtedly make this microstructure attractive for high performance electrode materials of LIBs.

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1. Introduction

In recent years, lithium-ion batteries (LIBs) are receiving more and more attentions and will have broader and more crucial applications in the future due to the advantages of high energy/power density and good cycling stability along with the demand for green...
energy sources [1–5]. However, graphite, a widely used anode material for commercial LIBs, suffers from serious safety problems when high charge/discharge rate are required [6]. Among the possible candidates, spinel Li$_4$Ti$_5$O$_12$ (LTO) has attracted considerable attentions, because its relatively high operating voltage (1.55 V vs. Li$^+$/Li) can avoid the reduction of electrolyte as well as the formation of the solid-electrolyte interphase (SEI) layer (usually occurring below 1.0 V vs. Li$^+$/Li), and prevent the plating of metal lithium [7,8]. Furthermore, LTO acting as a zero-strain insertion material has excellent insertion/extraction reversibility, structural stability and excellent safety, which are highly desirable for power LIBs [9–11]. However, low electron conductivity and lithium-ion diffusion coefficient lead to severe polarization, thus greatly limiting the practical applications of LTO anodes [12–16].

Extensive research has been devoted worldwide to the improvement of power performances of LTO. Generally, the LIBs electrodes should have both excellent lithium-ion and electron conductivity to achieve a fast reaction rate [17–19]. Nanostructured electrode materials are commonly used in LIBs due to their higher reversible capacity and better rate performances [20,21]. It is worth noting that nanostructured LTOs are beneficial for shortening the diffusion paths of lithium-ions and electrons, and enhancing the intercalation kinetics due to their relatively higher electrode/electrolyte contact area [22]. In particular, LTO hollow microspheres assembled by mesoporous shells of tunable thickness using a templating method, delivering remarkable rate capability of 131 mAh g$^{-1}$ at 20C and stable long-term capacity retention [24]. Also, hierarchically porous LTO microspheres assembled by well-crystalline nanoparticles displayed very stable coulombic efficiency, ultrahigh rate capability at higher rates of 95 mAh g$^{-1}$ at 20C [25]. In addition, Kim et al. prepared mesoporous LTO microspheres via hydrothermal synthesis, showing high capacity retention [26]. Although nanostructured LTOs with multifarious morphologies possessed high reversible capacity and excellent rate performances, the explored synthesis approaches were usually very complex [20–26]. Moreover, to our best knowledge, no investigation was reported on the synthesis and application of mesoporous LTO nanosheets for LIBs.

In this report, we introduced a facile route to prepare a new type of mesoporous LTO nanosheets without any additives and template under hydrothermal conditions following by calcination. The as-prepared mesoporous LTO nanosheets exhibited prominent electrochemical performances with higher reversible capacity as well as much improved rate performances for LIBs, which was mainly ascribed to the remarkable surface lithium storage reaction resulting from its advanced microstructure. It was therefore concluded that mesoporous LTO nanosheets would be a promising anode candidate for power LIBs.

2. Experimental

2.1. Synthesis

The mesoporous LTO nanosheets were synthesized using a one-pot hydrothermal procedure. Typically, 0.189 g (4.5 mM) of LiOH·H$_2$O was completely dissolved in 25 ml of absolute ethyl alcohol at room temperature. Then, the 1.7 ml (5 mM) of tetraethyl titanate (TBT) was dropwise added into it with stirring. The solution was mixed thoroughly using a magnetic stirrer in a closed container placed in dry environment for 12 h until it formed an ivory solution. Next, the ivory solution was transferred into a 100 ml stainless-steel autoclave and placed in an oven at 180 °C for 36 h. The white precipitation at the bottom of the reactor was collected by centrifugation, washed with ethyl alcohol five times, and then dried in vacuum oven at 55 °C for 12 h. Finally, the as-prepared precursor was calcined in a muffle at 700 °C for 6 h to prepare the mesoporous LTO nanosheets.

2.2. Structural characterization

The composition and crystal structure of the products were characterized by powder X-ray diffraction measurement (XRD) using a Rigaku Dmax-2000 diffractometer with Cu Kα$_1$ radiation. The morphology and microstructure were studied using a JEOL 6701F scanning electron microscope (SEM) and JEOL JEM-2010 transmission electron microscopy (TEM). Thermogravimetric and differential scanning calorimetric analysis were conducted on a TG-DSC simultaneous thermal analyzer (Netzsch STA449F3). Nitrogen adsorption–desorption measurements were performed using a Micromeritics ASAP 2010 instrument. The pore size distribution was calculated from the adsorption branch of the sorption isotherms using the Barret–Joyner–Halenda (BJH) method.

![XRD patterns of the as-obtained sample calcinated at 700 °C for 6 h in air.](image-url)

Fig. 1. (a) The wide and low angle (insert) X-ray diffraction (XRD) patterns of the as-obtained precursor after hydrothermal; (b) XRD pattern of the as-obtained sample calcinated at 700 °C for 6 h in air.
2.3. Electrochemical characterization

Electrochemical measurements were carried out in a CR2032-type coin cell with lithium metal as the positive electrode. The working electrode was fabricated by compressing a mixture of the active materials, conductive material (acetylene black (AB)), and binder (polytetrafluoroethylene (PTFE)) with a weight ratio of 8:1:1 onto a copper foil at 10 MPa. The electrodes were punched in the form of disks typically with a diameter of 12 mm and dried at 120 °C for 24 h. The thickness of the electrode was about 30 μm, and the loading mass of active materials was about 8.5 mg cm⁻². The cell assembly was operated in a glove box filled with pure argon. The electrolyte solution was 1 M LiPF₆/ethylene carbonate (EC)/propylene carbonate (PC)/diethyl carbonate (DEC) (1:1:1 by volume). The cell was galvanostatically cycled between 1.0 and 2.5 V vs. Li⁺/Li at various current densities from 1 to 30C (where 1C corresponded to complete discharge in 1 h, the charge and discharge current densities were identical during each cycle) at about 25 °C. Cyclic voltammograms were recorded using a three-electrode cell, the metallic lithium was used as a counter and reference electrodes. The experiment was performed using an electrochemical workstation (Precision PARC) at a scan rate range of 0.4-5 mV s⁻¹ between 1.0 and 2.5 V vs. Li⁺/Li.

3. Results and discussion

Fig. 1a shows wide and low angle X-ray diffraction (XRD) patterns for the as-prepared precursor. It could be seen that the hydrothermal process led to an intermediate phase with a layered titanate structure (orthorhombic Li₁₈H₀.₁₉Ti₂O₅∙nH₂O, JCPDS Card No. 47-0123) [27]. Moreover, the result of the low-angle XRD pattern (inset of Fig. 1a) suggested that there was no ordered mesoporous arrangement in the as-obtained precursor [28]. Figure S1 displays the TG curve of the as-prepared precursor over a temperature range from 20 to 800 °C in air. No obvious weight loss was observed when temperature was above 700 °C, suggesting the completion of phase transformation. According to the TG results, the as-prepared precursor was calcinated at 700 °C for 6 h. Its XRD pattern (Fig. 1b) indicated that the spinel LTO (JCPDS No.49-0207) was generated [29]. No impurity phase such as rutile or anatase TiO₂ [28] was detected based on the XRD pattern. Therefore, the well-defined and sharp peaks belonging to spinel structures confirmed the formation of LTO with pure phase and high degree of crystallinity. The calculated lattice parameter of the prepare LTO sample was 8.357 Å, which was in good agreement with the value for pristine Li₄Ti₅O₁₂ (a = 8.356 Å) [25].

The unique mesoporous nanosheet morphology of the as-prepared precursor and LTO were clearly identified by using TEM images (Fig. 2a and c). A mean pore size of ~5 nm of the mesoporous precursor and LTO nanosheets were further confirmed in HRTEM images as shown in Fig. 2b and d. Fig. 2d indicated a lattice fringe of 0.484 nm, corresponding to (111) crystal plane spacing of LTO.

Nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore-size distribution analysis were employed to determine the surface area and pore size distribution. As shown in Fig. 3, the adsorption–desorption isotherms of the as-obtained LTO showed an apparent capillary condensation step at a relative pressure (P/P₀) of 0.42-0.72 (corresponding to a pore size of ~5 nm), which well agreed with the pore size evaluated by using TEM images. The specific surface area of the as-obtained LTO was 150.6 m² g⁻¹. Accordingly, all of these physical characterization data verified that the mesoporous LTO nanosheets were successfully prepared through a facile hydrothermal method.

To elucidate the formation mechanism of the mesoporous LTO nanosheets, XRD and TEM were performed to reveal the crystal structure and morphology of precursor with only 2 h hydrothermal treatment. As shown in Figure S2 and S3, the precursor was amorphous and exhibited smooth nanosheets morphology without porous microstructure in the initial stage of the hydrothermal reaction, which indicated that elongating hydrothermal treatment time was the key to the formation of the porous microstructure [30]. In previous studies, the porous structure was formed by
localized Kirkendall effect resulting from a difference in diffusion rates between two components in a diffusion couple [17,30] during the hydrothermal process. In this work, the mesoporous structure formation of LTO nanosheets could be explained by a similar mechanism. The formation process was discussed below.

At the initial stage of the hydrothermal reaction, amorphous lithium titanate nanosheets were formed. During the hydrothermal process, OH- and H2O diffused into the amorphous lithium titanate nanosheets and interacted with the titanium ions and/or lattice oxygen to form titanium hydroxyl species (probably HTiO3/C0). Then, the porous nanosheets were formed by outward transport of fast-moving HTiO3/C0 through the oxide layer and a balancing inward flow of vacancies to the vicinity of the hydrous titanium oxide interface [17]. Moreover, no obvious change of the microstructure between the precursor with 36 h hydrothermal treatment and the as-prepared mesoporous LTO nanosheets could be observed from Fig. 2. Consequently, the schematic illustration for the preparation of the porous LTO nanosheets was summarized in Fig. 4. Generally, the porous structure can offer rich channels for the sufficient interaction between active materials and electrolytes, which facilitates the transfer of lithium-ions and electrons, thereby leading to high capacity and excellent rate capability [17,28,31–33].

Furthermore, the mesoporous LTO nanosheets were studied as the anodes in LIBs. Obvious plateaus in the potential range between 1.5 and 1.6 V vs. Li+/Li were observed at all current densities in the galvanostatic charge–discharge curves when cycled in the voltage range of 1.0–2.5 V vs. Li+/Li (Fig. 5). Even at a high current density of 30C, the flat potential plateaus were still retained. Upon increasing charge–discharge rates, the gaps between the charge and discharge plateaus were still smaller than 0.1 V, suggesting insignificant polarization. Fig. 6 compares charge–discharge capacities of the mesoporous LTO nanosheets during cycling at different current rates between 1.0 and 2.5 V vs. Li+/Li. It was worth noting that the sample displayed a high specific capacity of 169 mAh g−1 at 1C and could be operated at 30C for 30 cycles with slight capacity decay. Also, when the current density was returned to 1C after cycling at various rates, a high capacity of 169 mAh g−1 was totally recovered.

Fig. 7 provides a comparison of rate performance for three different LTO anodes including mesoporous LTO nanosheets, mesoporous LTO microspheres [17], and smooth LTO nanosheets [34]. The loading mass of the mesoporous LTO microspheres and the smooth LTO nanosheets were about 6.5 and 10 mg cm−2, respectively. Among the three samples, the mesoporous LTO nanosheets exhibited the best rate performance. The reversible capacity of the mesoporous LTO nanosheets in the voltage range of 1.0–2.5 V was 97.6%, 93.5%, 88.9%, 84% of 1C discharge capacity when high current densities of 5, 10, 20, 30C were conducted. However, those were 92.5%, 87.5%, 81.3%, 75% and 94.6%, 81.1%, 75.7%, 61% for the mesoporous LTO microspheres and smooth LTO nanosheets, respectively. Even at 30C rate, the reversible capacity of the mesoporous LTO nanosheets was higher than 140 mAh g−1 whereas this value was only 120 and 90 mAh g−1 for the mesoporous LTO microspheres and smooth LTO nanosheets, respectively.

To better understand the kinetics and mass transport of the mesoporous LTO nanosheets during the charge–discharge process, cyclic voltammetry experiments at different scan rates were carried out as shown in Fig. 8. In particular, differing to smooth LTO nanosheets and mesoporous LTO microspheres [17,34], two peaks could be detected in the cathodic process of the mesoporous LTO nanosheets at all scan rates. It is well known that the relation between peak currents and scan rates indicates the different electrochemical reaction characteristics, including solid phase diffusion-controlled or surface-confined charge-transfer processes [29,35,36]. The dependence of the peak current on the square root
of the scan rate indicated an obvious diffusion limited reaction for the peaks at relatively high potential in the cathodic process for the mesoporous LTO nanosheets. However, the peaks at relatively low potential showed a linear relationship between peak currents and scan rates, revealing the surface lithium storage process corresponded to the faradaic reaction. Apparently, this indicated that the electrode reaction of the mesoporous LTO nanosheets was controlled by a mixed process of the faradaic pseudocapacitive and diffusion-limited reaction. It has been well known that the faradaic pseudocapacitive reaction is a quick lithium-ion insertion process, yielding an extra capacity. Therefore, the pseudocapacitive effect was responsible for the improvements of reversible capacity and high-rate capability of the mesoporous LTO nanosheets. Although the mesoporous LTO nanosheets and microspheres all had a rough surface and large specific surface area, the "plane-to-plane" contact mode of the mesoporous LTO nanosheets contained more contact interfaces. This could provide more electrochemically active sites, which was more favorable for achieving the faradaic pseudocapacitive reaction compared to the "point-to-point" contact mode of the mesoporous LTO microspheres. We anticipated that this preliminary study would offer an advanced nanostructure for improving electrochemical performance of electrode materials for next generation LIBs.

4. Conclusions

In summary, we have successfully prepared a new type of mesoporous LTO nanosheets through a simple sol-hydrothermal followed by a calcination treatment in air at 700 °C. The favorable surface lithium storage (faradaic pseudocapacitive effect) induced by the advanced microstructure significantly contributed to the ultrahigh reversible capacity and remarkable rate performance. The mesoporous LTO nanosheets possessed three distinct advantages: (1) the novel mesoporous nanosheets provided larger contact areas and more electrochemical active sites; (2) the extra surface lithium storage reaction significantly reduced the polarization and further enhanced the electrochemical performance at high rates; (3) excellent cycling stability and safety. Therefore, the mesoporous
spinel LTO nanosheets would hold great promise to be an advanced anode materials for next-generation power LIBs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.08.038.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.08.038.

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