



# Quantitative investigation of the gassing behavior in cylindrical $\text{Li}_4\text{Ti}_5\text{O}_{12}$ batteries



Qian Wang<sup>a</sup>, Jian Zhang<sup>a,\*</sup>, Wei Liu<sup>b</sup>, Xiaohua Xie<sup>a</sup>, Baojia Xia<sup>a</sup>

<sup>a</sup> Research Center for New Energy Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, 200050, China

<sup>b</sup> Shanghai Nanotechnology Promotion Center, Shanghai, 200237, China

## HIGHLIGHTS

- Quantitative internal pressure is acquired with self-designed testing device.
- The side reaction of gassing is associated with the anode electrode potential.
- A visual image of the SEI film of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode is achieved.
- The internal pressure can reach constant after the SEI film is densely formed.

## ARTICLE INFO

### Article history:

Received 28 September 2016

Received in revised form

23 December 2016

Accepted 17 January 2017

### Keywords:

Lithium titanate

Gassing behavior

Quantitative analysis

Solid electrolyte interface film

Lithium ion battery

## ABSTRACT

The  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  gassing behavior is a critical limitation for applications in lithium-ion batteries. The impact of electrode/electrolyte interface, as well as the underlying mechanisms involved during the gassing process, are still debated. Herein, a quantitative evolution of the internal pressure in 18650-type cylindrical  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  batteries is investigated using a self-designed pressure testing device. The results indicate that the internal pressure significantly increases during the formation cycle and continues growing during the following cycles. After several charge and discharge cycles, the pressure finally reaches constant. Simultaneously, the formation of the solid electrolyte interphase (SEI) film is also investigated. The results suggest that the initial formed SEI film has a thickness of 24 nm, and is observed to shrink during the following cycles. Furthermore, no apparent increase in thickness accompanying the pressure rising is noticed. These comparative investigations reveal a possible mechanism of the gassing behavior. We suggest that the gassing behavior is associated with side reactions which are determined by the potential of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode, where the active sites of the electrode/electrolyte interface manage the extent of the reaction.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The lithium titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , LTO) is considered as one of the most promising anode material candidates in long-life lithium-ion batteries due to its high safety and cycling stability [1]. When compared to carbonaceous graphite ( $\text{LiC}_6$ , 16 vol%) and silicon ( $\text{Li}_{4.2}\text{Si}$ , 400 vol%) [2–4], LTO exhibits nearly no volume expansion during lithium ion intercalation and deintercalation (expansion less than 0.1 vol%). The relatively high working potential of LTO (~1.55 V vs.  $\text{Li}^+/\text{Li}$ ), which is more positive than the reduction potential of

typically used carbonated based lithium ion electrolytes (~0.8 V vs.  $\text{Li}^+/\text{Li}$ ), eliminates the risk for formation of lithium dendrite during the charging [5–7]. In addition, the distinct difference in the electrical conductivity between  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  ( $10^{-13}$ – $10^{-9}$  S  $\text{cm}^{-1}$ ) and lithiated  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  ( $10^{-5}$ – $10^{-3}$  S  $\text{cm}^{-1}$ ) inhibits the expansion of local short-circuits, making the LTO batteries extraordinary safe [8,9]. Hence, LTO has attracted tremendous attention for application in hybrid electric vehicles and energy storage systems.

During the past years, studies of cells containing LTO have, unfortunately, revealed severe volume swelling due to gas evolution, especially at elevated temperatures [10,11], which would seriously deteriorate the power density and cyclic stability of the batteries. Though LTO is expected to lack solid electrolyte interface (SEI), which eliminates chances of associated side reactions during the

\* Corresponding author.

E-mail address: [zjskycn@mail.sim.ac.cn](mailto:zjskycn@mail.sim.ac.cn) (J. Zhang).

formation cycles [12,13], previous work has demonstrated that evolution of gases were associated with the presence of LTO electrode, where H<sub>2</sub> gas was found to be the dominant species. This conclusion facilitated the viewpoint of the influence of humidity. To examine the influence of humidity on volume expansion during the formation cycle, water was intentionally added into the electrolyte by Bunes et al. [14]. Their results confirmed that presence of water can directly lead to greater evolution of hydrogen gas. However, no linear correlation was found between the swelling ratio and the water content, and no obvious detrimental effects were noticed on the cell performance. Wu et al. [10] also injected redundant water into the electrolyte in order to analyze the influence of the electrode moisture. Their findings showed that gas species and their ratios differed according to the utilized electrolytes, making the impact of the electrode moisture negligible. The influence of the moisture and the gas species were challenged thereafter. Recently, Liu et al. [15] found that CO/CO<sub>2</sub> gas species were dominants in LTO/LiM<sub>2</sub>O<sub>4</sub> pouch cells containing different types of electrolytes, making the gassing mechanism of LTO-based batteries more ambiguous.

The reactivity of LTO towards common carbonates based electrolytes was questioned afterward, and the existence of SEI was further debated. Studies performed by El Ouatani et al. [16] using X-ray Photoelectron Spectroscopy (XPS) analysis revealed that during the first charge, carbonates salts (Li<sub>2</sub>CO<sub>3</sub> and ROCO<sub>2</sub>Li) and LiF were deposited on the surface of LTO electrode with LiCoO<sub>2</sub> as the cathode electrode material. Other important research related to gassing process was also reported by He [17], where he demonstrated that the gas release occurred through electrolyte decomposition. Therefore, a better understanding of the electrode/electrolyte interface becomes essential.

Approaches of XPS [18,19], Fourier transform infrared spectroscopy (FTIR) [20,21], Atomic Force Microscope (AFM) [22], Scanning Tunneling Microscopy (STM) [23], and electrochemical impedance spectroscopy (EIS) [24] etc. have been proposed to systematically investigate the SEI film. Some authors believe the deposits of electrolyte decomposition during the charge-discharge cycle form the SEI film and originate in the gas generation [25]. Others thought that the species were firstly formed at the positive electrode before being adsorbed at the LTO electrode surface, either by diffusion or migration processes [26]. Although much information about the SEI film has been acquired using various spectroscopic and electrochemical techniques, the formation mechanism of the SEI is still widely debated, and its correlation with the gassing are still not fully understood. Hence, efforts should vigorously be pursued to create a comprehensive understanding of the electrode/electrolyte interface and the gassing behavior.

Many studies suggested that the LTO batteries suffered severe swelling at elevated temperatures with a qualitative thickening of the pouch cell, while it scarcely affected at ambient temperature [7,27]. However, our results strongly suggest that the LTO batteries suffer severe swelling even at ambient temperature. Herein, we aim to establish a direct correlation between the gassing process and performance of the battery. For this purpose, we designed a pressure testing device of the 18650-cylindrical battery to quantitatively reveal the generation law of gases along with the cycle life. Focused ion beam (FIB) technology was used to directly follow the evolution of morphological formation of SEI film upon repeated cycles. The investigations are in effort to reach a better understanding of causes dealing with gassing behaviors.

## 2. Experimental

### 2.1. Cell assembling and electrochemical characterization

In this study, 18650-type cylindrical batteries were prepared to

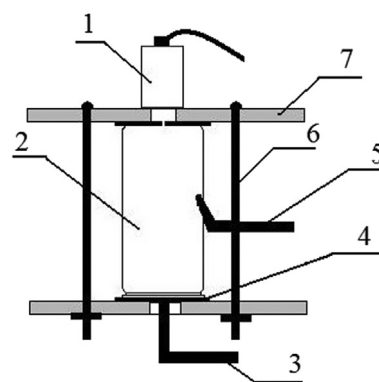
evaluate the performance of the batteries. Spinel LiMn<sub>2</sub>O<sub>4</sub> (LMO) (Shanshan Co., Ltd., China) and LTO (BTR, China) were used as the cathode and anode materials, respectively. The detailed information on the active material was shown in Fig. S1. 1 M LiPF<sub>6</sub> in a mixture of 1:1:1 v/v/v ethylene carbonate, diethyl carbonate, and dimethyl carbonate (DMC) was used as the electrolyte. The separator, Celgard 2325 PP/PE/PP (Celgard Inc., USA), was dried overnight at 60 °C under vacuum prior to use. The electrode was prepared by mixing the active material, carbon black, and poly(vinylidene fluoride) at a certain weight ratio (LMO cathode = 93.5:3.5:3, LTO anode = 90:5:5) in *N*-methyl pyrrolidone. The detailed fabrication procedure of the battery has been mentioned in our previous work [28]. The coating weight of the LTO electrode was controlled to 12.5 mg cm<sup>-2</sup> while that of the LMO electrode was 20.8 mg cm<sup>-2</sup>. After cell assembly and baking, a Karl-fisher titrator (KF831, Metrohm) was applied to examine the traces of water in the electrode and other components before electrolyte injection.

After electrolyte injection, the batteries were stored for 24 h at ambient temperature to ensure good electrolyte wetting. The formation of the as-prepared 18650-type LTO battery included 2 steps of galvanostatic charging processes (0.02 C/1 h and 0.1 C to 2.7 V) and a 2.7 V-potentiostatic charging process. This was further followed by a 12 h resting at 100% SOC. Galvanostatic charge/discharge measurements were conducted over a voltage window of 1.5–2.7 V on BT2000 equipment [A'bin Instrument (TJ) Co., Ltd.]. The batteries were cycled using constant-current (CC) mode at 1 C rate at 25 ± 1 °C for 250 cycles.

### 2.2. Device processing for pressure testing

A device for quantitatively measuring the internal pressure of the cylindrical battery was designed, and the simulated configuration profile is shown in Fig. 1. The real-time internal pressure was acquired using a pressure sensor ([MSP300, Measurement Specialties (China) Ltd.] with a precision of 0.2 psi. The pressure sensor was connected to the cell interior by perforating a hole ( $\phi = 1$  mm) on the flat bottom. The cell was then sealed with three screws at a torque of 10 N·m, and the height between the two clamping plates was kept identical using vernier caliper. A seal ring was placed in the middle to prevent gas leakage.

To analyze the gassing behavior and its effect on performance, the batteries were equipped with the testing device after electrolyte injection. A battery with a reference electrode was also fabricated for comparison. The micro-reference electrode was prepared from a polyester enamelled copper wire with a diameter of 0.5 mm.



**Fig. 1.** Schematic diagram of a simulated device to test the internal pressure of cylindrical battery, the numbers are indexed as: 1—pressure sensor, 2—18650-type cylindrical battery, 3—the positive terminal, 4—seal ring, 5—the negative terminal, 6—clamping screw, 7— clamping plate.

Download English Version:

<https://daneshyari.com/en/article/5149442>

Download Persian Version:

<https://daneshyari.com/article/5149442>

[Daneshyari.com](https://daneshyari.com)