



Gassing behavior of lithium titanate based lithium ion batteries with different types of electrolytes



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HIGHLIGHTS

- Swelling behavior of LTO/LMO battery stored at elevated temperature is observed.
- Swelling degree of LTO/LMO battery are observed at different SOC.
- The differences of SEI layer compositions based on EC and PC solvents are discussed.
- The reaction mechanisms of LTO electrode with electrolyte solvents are proposed.

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ABSTRACT

Gassing behavior of $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ full cell with different electrolytes that stored at elevated temperature of 70 °C is investigated. Scanning electron microscope (SEM), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) are used to study the solid electrolyte interphase (SEI) layer formed in battery formation and storage processes. The results suggest that the SEI film is formed as a consequence of intrinsic reaction between $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode and electrolyte solvents. A smooth SEI layer is formed on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode with full coverage in propylene carbonate (PC) based electrolyte during lithium intercalation process while gradually dissolved with lithium extraction. Moreover, the gas specificities generated in the different electrolyte solvents are also determined by gas chromatography–mass spectrometer (GC–MS) analysis and the reaction mechanisms of LTO electrode with electrolyte solvents are proposed.

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1. Introduction

The shortages of lead-acid, Ni–Cd and Ni–MH batteries are obvious, such as short service lives, low energy densities and environment pollution. Recently, lithium ion batteries (LIBs) have gradually occupied the consumer market of portable electronic devices and been considered the most promising battery for electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to significant progress in energy density, cycling and storage performance [1,2].

As a new anode material for LIBs, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has drawn tremendous attentions [3,4]. It can be embedded with three lithium ions to become $\text{Li}_7\text{Ti}_5\text{O}_{12}$, and its negligible structural

difference between pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and lithiated $\text{Li}_7\text{Ti}_5\text{O}_{12}$ during charge–discharge process leads to an infinite cycle lifetime in theory. In addition, LTO has a higher discharge voltage (approximately 1.55 V vs. Li/Li^+) to avoid lithium dendrite penetration into the separator during the discharging process, therefore, it has high security [5,6]. Based on these advantages, LTO has been considered one of the anode materials that could replace carbon materials. However, it also has some drawbacks that cannot be ignored, such as low battery voltage and intrinsic poor electronic conductivity (only $10^{-9} \text{ s cm}^{-1}$) [7]. The worst of its limitations for commercial application is its severe gassing problem during cycling and storage processes, especially at higher temperatures [8,9]. The gasses generated in the batteries will cause an increase in the volume and the cathode/anode to not be in close contact, which results in capacity fading, lifetime shortening and even exploding.

Recently, there have been several studies focused on the swelling inside LTO-based batteries that found the gases generated

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are mainly H_2 , CO , CO_2 and alkanes [10]. The reason for gassing is contraction, and some authors believed that this phenomenon could be attributed to the electrolyte's high reduction reaction activity on the LTO surface. The gas species depended on the electrolyte components. There were three opinions for the gassing mechanism. The first one is that LTO absorbs water easily, and the sorption of water easily becomes crystal water. Crystal water is difficult to remove and reacts with the electrolyte to generate gases. The second one is that the electrolyte has a higher redox reaction activity on LTO surfaces, and LTO surfaces may have catalytically active sites to catalyze electrolyte degradation to generate gases. The third one is that TiO_2 may exist in LTO, and it may have catalytic activity for gassing.

The existence of SEI films on LTO surfaces was also still heavily debated in the literature. Because LTO batteries were always cycled above 1 V, it was generally accepted that SEI layer could not form on the surface of LTO particles. However, K. Amine et al. had noted that a composite of phosphorous, fluorine, and manganese would coat the LTO electrode surface, which would decrease the cell capacity [11]. R. Dedryve confirmed that a passive film composed of inorganic substances (LiF) and organic deposits formed on the LTO surface [12,13]. Y. B. He et al. revealed that the SEI film formed on the LTO electrode was related to the discharge voltage and particle morphology [14]. C. P. Han et al. revealed that the SEI layer formed on the surface of C/LTO electrode is thicker and denser than NC/LTO, while the SEI layer of latter covers the whole surface of NC/LTO electrode more uniformly than the SEI film on C/LTO electrode [15]. M. S. Song had proposed that the presence of carbon in the electrode would increase the reactivity of LTO towards the electrolyte [16].

In this paper, we discussed the gassing behavior of LTO/LMO batteries at elevated storage temperature. The surface morphologies of LTO electrodes before and after formation were compared. And the SEI layer was confirmed to be formed in this process. The volume of swelling gases was related to the state of charge and the electrolyte solvent. Moreover, the reaction mechanisms of LTO electrode with electrolyte solvents are proposed.

2. Experimental

$Li_4Ti_5O_{12}$ was synthesized via a solid-state reaction. Analytically pure Li_2CO_3 (purity > 99.5%, Shanghai Element International, Shanghai, China) and fine anatase-phase TiO_2 ($D_m = 30$ nm, purity > 99.0%, Sinopharm Shares Chemical Reagent CO., LTD, Shanghai, China) were used as the Li and Ti precursors, respectively. After weighing Li_2CO_3 and TiO_2 corresponding to an Li/Ti ratio of 4.1/5.0 to synthesize 100 g of $Li_4Ti_5O_{12}$ powder, the mixture was mixed in 200 mL of ethanol with 5 wt% amount of pitch, heated at 80 °C with strong stirring for 30 min. Then, these slurries were exposed to 1 h of milling (MiniCer, Netzsch, Germany) operated at 1000 rpm using 1-mm beads. After drying the slurries at 80 °C in a magnetic stirrer for uniform mixing, the mixture were heat treated at 850 °C for 10 h in an N_2 atmosphere at a heating rate of 5 °C/min. $LiMn_2O_4$ cathode material used as received without any further treatment (Gejiu Superhoo Industries Co., Ltd).

The proportions of active material in both LTO and LMO electrodes were 92% with additional 8% as conducting agent and binder. LTO/LMO batteries were designed with a capacity of 20 Ah. Soft package batteries were assembled using LTO/C as the anode and LMO as the cathode. Celgard 2500 was used as the separator. The electrolytes were 1 mol L^{-1} $LiPF_6$ for the solvents based on PC (propylene carbonate), EC (ethylene carbonate), EMC (methyl ethyl carbonate), DEC (diethyl carbonate), DMC (dimethyl carbonate), which included PC + EMC (w:w = 1:1), EC + EMC (w:w = 1:1), PC + DEC (w:w = 1:1), EC + DEC (w:w = 1:1), PC + DMC

(w:w = 1:1), and EC + DMC (w:w = 1:1). The cells were dried in a vacuum oven at 75 °C for 24 h. Then, they were pre-sealed after electrolyte injection and stored for 24 h at 45 °C to ensure good electrolyte wetting before the formation process. During the pre-sealing, extra Al plastic laminate foil (called air bag) were set aside to generate possible gasses in the following step.

During the formation process, a BK-7632L/60 charge and discharge tester was used. Constant current/constant voltage

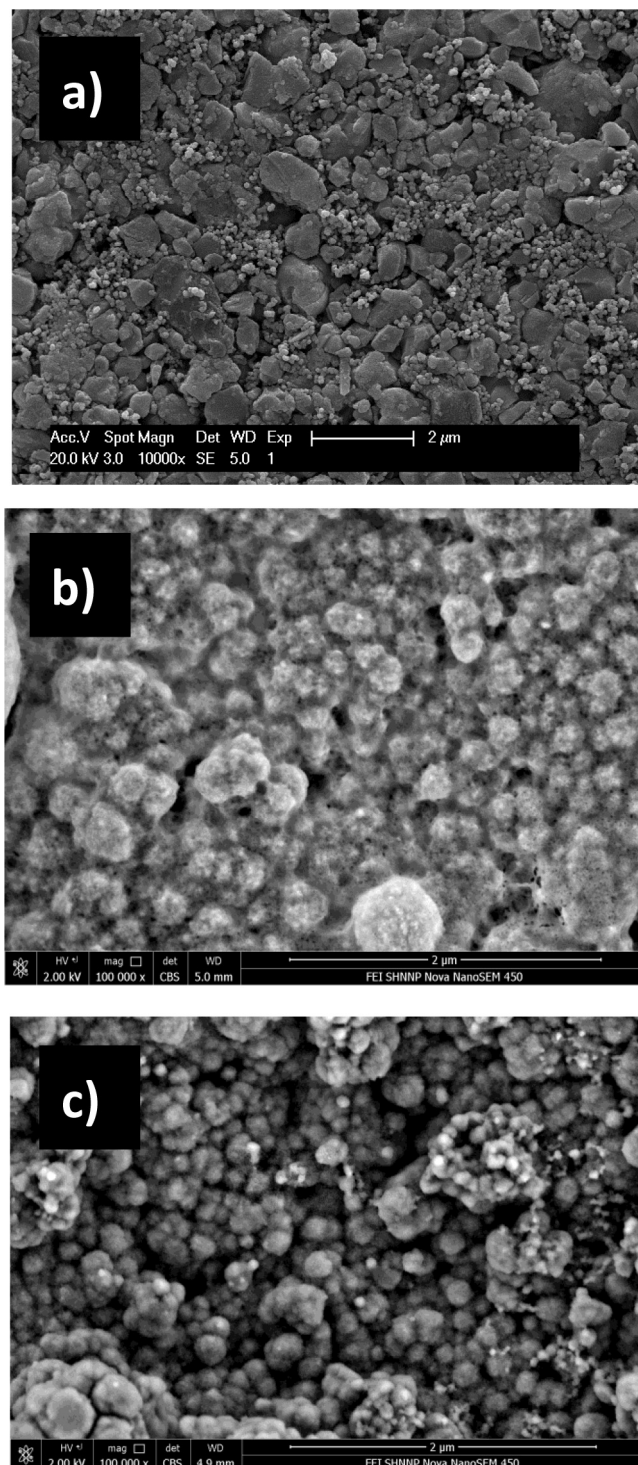


Fig. 1. SEM photos of LTO electrodes before and after formation.

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