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

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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.

Key Words

Lithium titanate, Gassing behavior, Quantitative analysis, Solid electrolyte interface film, Lithium ion battery

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 (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. Li^+/Li), which is more positive than the reduction potential of typically used carbonated based lithium ion electrolytes (~ 0.8 V vs. Li^+/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 cm^{-1}) and lithiated $\text{Li}_7\text{Ti}_5\text{O}_{12}$ (10^{-5} - 10^{-3} S cm^{-1}) inhibits the expansion of local short-circuits, making the LTO battery 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 a solid electrolyte interface (SEI), which eliminates chances of associated side reactions during the formation cycles [12,13], previous work has demonstrated that evolution of gases are associated with the presence of LTO electrode, where H_2 gas was the 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 the 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 differ 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/CO₂ gas species are dominants in LTO/LiM₂O₄ 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 (Li₂CO₃ and ROCO₂Li) and LiF were deposited on the surface of LTO electrode with LiCoO₂ 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 occurs 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. A 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_2O_4 (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. 1M LiPF_6 in a mixture of 1:1:1 vt% (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 pyrrolidinone. The detailed fabrication procedure of the battery is mentioned in our previous work [28]. The coating weight of the LTO electrode was controlled to 12.5 mg cm^{-2} while that of the LMO electrode was 20.8 mg cm^{-2} . 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 hours 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 is 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 $25 \pm 1^\circ\text{C}$ 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.

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.

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. The insulation layer was stripped from the tip of the wire using concentrated sulphuric acid at a length of 5 mm, and a tiny bit of lithium metal was attached afterward. A micro-reference electrode was inserted into the battery through the hole on the bottom mentioned above, which was then sealed with epoxy resin to prevent electrolyte volatilization.

2.3 Material Characterization

Batteries at different states (before formation, after formation, after 250 cycles) were disassembled in an Ar-filled glove box. The LTO electrodes were washed twice with DMC and heated in a vacuum at 60°C to remove the residual DMC. Cross-sectional and surface morphologies of LTO particles were examined by field emission scanning electron microscope (FE-SEM, Hitachi S4700, Japan) and FIB (Helios 600, FEI).

For FIB measurements, layers of Pt and W metal were first deposited on the electrodes to protect the outermost morphology. Thereafter, Ga^+ was sputtered on LTO particles on the working electrode after being accelerated at a high voltage (typically 30 kV). Thereby, a cross section of the LTO particles with a tilted angle of 52° relative to the ion sputtering direction was obtained.

3. Results and Discussion

3.1 The gassing behavior of LTO battery

The internal pressure of the LTO/LMO battery measured during the formation cycle is displayed in Fig. 2, where the formation current is simultaneously shown for comparative purposes. It can be seen that the two curves perfectly correspond to each other. During the first 0.02 C/1 h charging, a slight increase of the pressure appears if compared to the short flat plateau seen before activation. During the following 0.1 C

charge, the pressure significantly increases to 22.8 psi. The specific pressure increase rate, dP/dt , sharply declines at the start of 0.1 C compared to that observed at 0.02 C, and then gently decreases afterward. During the following 12 h of resting process, the internal pressure continues to grow at a relatively constant dP/dt , even without current flow. During the next 0.5 C discharging, the pressure significantly increases at constant dP/dt , with a sudden increase at the end.

Fig. 2. Pressure profile for the formation cycles of the LTO/LMO cylindrical battery. Current (black line) and calculated specific pressure increase rate dP/dt (blue line) included.

The pressure of the battery is nearly constant after fabrication, while the current flow initiates the pressure increase. This suggests that the starting gassing reaction is more likely to be an electrochemical reaction rather than a chemical process. Some studies have attributed the gassing behavior to the catalyzed decomposition of electrolytes by Ti^{3+} ions, as the gassing starts with the intercalation of Li^+ in LTO. Assuming that the catalytic properties of Ti^{3+} ions are responsible for the improved electrochemical-activity of the surface, the relatively higher dP/dt observed during the discharge process compared to the resting time would be hard to explain since no significant change in the concentration of Ti ions exists. Thus, novel methods should be proposed to explain those phenomena.

The paradox lies in the highest dP/dt at 0.02 C. It is well known that the lithium ion intercalation/deintercalation in LTO is a two-phase reaction mechanism, resulting in a flat potential plateau of LTO electrode during the charge/discharge, especially at low rates with less polarization [2]. To further describe the electrochemical reactivity on the electrode potential, a reference electrode is utilized to clarify the connection between the potential and dP/dt . Fig. 3 displays the relationship between the potential of both the cathode and anode electrodes during the formation cycle. It is clear that during the first 0.02 C charge, the potential of the anode decreases slowly and yet is positive than 1.8 V. During the following nearly 10h of charging at 0.1 C, the potential of the LTO electrode reaches a plateau potential of 1.53 V then stabilizes afterward, while the pressure rises as dP/dt reduces. This could be linked to either a reduction in the reactant or the reaction site. At the end of the charge, the potential quickly declines to reach 1.34 V, with a rapid increase of dP/dt as shown in Fig. 2. This means that the gases are mostly generated in a preferential range of potential of LTO electrode.

Fig. 3. Potential profiles for the formation cycle of the cathode and the anode electrode.

Under this assumption, the range of potential with high gassing reactivity should be clarified. To this end, an LTO pouch cells with an LTO electrode (5 cm × 5 cm) as working electrode, a Li-strip as counter electrode and reference electrode were immersed in 5 g electrolyte. To validate the correlation between the internal pressure

and the potential, the cell was then hold to 1.0, 1.4, 1.6, 1.8, and 2.5 V at 80°C, respectively. The variation of volume in the pouch cells are acquired after a 72 h-storage period using a drainage method and the results are shown in Table. 1. Two types of LTO with different particle sizes are present that could help to compare the effects of different surface morphology. The negative values are most likely due to experimental errors, suggested as negligible volume variation. Observable swelling is consistent with the apparent gassing performed during the first lithium intercalation. The gassing occurs mostly under a potential range of 1.5 - 2.5 V, which becomes more quickly when the potential is positive than 1.60 V. Different particle sizes with various specific areas show different reactivity as a function of potential. This implies that the state of the surface would effect the gassing process as it will be discussed later.

Table 1. Swelling ratios of batteries held at different electrode potentials at 80°C for 7 days for 2 kinds of particle sizes of LTO.

Swelling ratio (%)	2.5 V	1.8 V	1.6 V	1.5 V	1.4 V	2.0 V
LTO ($D_{50} = 0.6 \mu\text{m}$)	18.13	32.82	10.74	10.80	-0.86	-0.15
LTO ($D_{50} = 1.2 \mu\text{m}$)	21.17	11.77	-0.19	7.75	-0.14	0.02

The phenomena mentioned above are consistent with the gassing process occurring during the formation cycle. The resting potential of LTO electrode is almost stable at 1.55 V during the 12 h period, which is actually beyond the highest reactivity potential range of gassing, thus resulting alongside in a relatively low dP/dt . The pressure increases significantly during the discharge process as the potential is positive than 1.55 V. The sudden increase in dP/dt at the end of the discharge process could be related to the instantaneous increase in the potential, which is positive than 1.80 V as displayed in Fig. 3. This hypothesis has already been proposed by many studies, stating that the passivation of LTO electrode is a gradual process and the SEI film obtained during the first lithium intercalation process could slightly dissolve during the next lithium deintercalation process [22, 29].

After the battery formation, the internal pressure increases to 46.1 psi. It is believed that swelling is mostly attributed to the presence of hydrogen which resulting from the electrochemical reduction of trace of water in the battery following reaction 1[30, 31]. The measured moisture content of LTO electrode, LMO electrode, separator and the rest of components after drying acquired by Karl-Fisher titrator are recorded as 450 ppm, 260 ppm and 150 ppm, respectively. This is equivalent to a total of 0.28 mmol in the whole 18650 cell. If we assume that the entire amount of moisture is consumed to generate H₂, the internal pressure of the battery should be estimated to 9.9 psi, and the cavity volume of the battery is approximately 5.0 mL using drainage method, which is far below the tested value. Analysis of the compositions of gases in pouch cells by gas chromatography-mass spectrometry (Focus DSQ, Thermo electron), which experienced exactly the same testing procedures, shows 3.3% percent of H₂ in the whole. The result (shown in Tab. S1) is thought to have some reference meaning in the cylindrical LTO/LMO battery, further proving that moisture is not the determining factor of gassing behavior.

During the formation cycle, it is also clear that trend of dP/dt differs in the charge and discharge process, which infers tiny distinctions exist in the process of lithium ion intercalation and deintercalation of LTO. To further describe these differences, the battery was discharged at respective rates of 1 C, 2 C and 3 C after a 1 C CC-CV charge. The internal pressure curve depicted in Fig. 4, clearly shows a distinct decrease in pressure during the charge and a rapid increase during the discharge processes. Precisely, the pressure reduces in the galvanostatic charge (1 C) then slowly recovers during the following potentiostatic charge (2.7 V). As can be distinguished from Fig. 3, the potential of the anode slightly rises during the potentiostat charge process, confirming the sensitivity of the side reaction to LTO electrode potential.

Fig. 4. Charge/discharge curves of the LTO/LMO cylindrical battery at different rates. Current (black line) and calculated specific pressure increase rate dP/dt (blue line) included.

It is also important to note that the values of dP/dt vary as a function of discharge rate, where higher value is recorded at the rate of 3 C. Gieu et al. [32] proposed a new intercalation/ deintercalation module of LTO material which states that in a core-shell module, the shell of the LTO particles would always be surrounded by Ti^{4+} ions with a poor electrical conductivity if kept steady. Based on this assumption, an instantaneous increase in the electrochemical polarization would appear during the beginning of delithiation of LTO, leading to a transient potential rise of the LTO electrode. The transient polarization will be released when the lithiation/delithiation process reaches equilibration. In Fig. 4, the dP/dt displays an apparent increase at the beginning and the end of the discharging process. Under these two conditions, the potential of the LTO electrode become positive than the plateau at 1.55 V. The former is attributed to the electrochemical polarization and latter is originated from the delithiation of LTO, as discussed above.

The evolution of the pressure during battery cycling is also investigated after cycling at the rate of 1 C under 25°C for 250 cycles. A negligible degradation in capacity could be noticed during cycling. Fig. 5 exhibits the internal pressure profile

during the first 50 cycles. It can be seen that the regular patterns of pressure under different charge and discharge processes are similar to the curves displayed in Fig. 4. In addition, the general trend of the internal pressure increases to approximately 74.1 psi after 46 cycles and finally reaches constant. During the following 200 cycles, the pressure varies in the range of 2 psi, which can be explained by the influence of temperature. This is confirmed in LTO batteries when taking $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and LiCoO_2 as the cathode materials. As the number of cycles increased, the pressure of the batteries finally reach constant, further indicating that the gassing is associated with the side reaction which is determined by electrode potential and electrode/electrolyte interface, rather than the electrolyte decomposition or humidity.

Fig. 5. Pressure profile for the first 50 times 1 C cycle at 25°C of the LTO/LMO cylindrical battery.

3.2 The interface evolution on LTO electrode

Fig. 4 compares the variation in the pressure increase of the batteries resting for 24 h at 50% SOC before and after the rates testing with an interval of nearly 72 h. It will be noted that the potential of LTO electrode lies nearly at the plateau potential of 1.55 V. The internal pressure apparently rises during the testing hours, which is different from the stable state observed before formation. The total increase in pressure under these

two conditions is different. Before rates testing, the total increase in pressure is nearly 6.7 psi, while it decreases to 4.5 psi after the rates testing. This suggests that the gassing behavior is also in close correlation with the charge and discharge processes that would significantly change the surface state of the particle.

To clearly describe the inter-correlation between the internal pressure and passivating layer, the interface of the LTO/electrolyte is carefully observed by SEM and FIB and the results are shown in Fig. 6 and 7, respectively. A SEM image of the pristine LTO particles is displayed in Fig. 6a. It can be seen that the pristine LTO particle has a uniform morphology with a smooth surface and average particle size of about 0.6 μ m. The potential of LTO electrode examined by reference electrode is recorded as 2.87 V then the cell is dissected. The particle shows a totally different morphology (Fig. 6b), where it exhibits a rough surface with small salient points arising on its surface. As shown in Fig. 7a, the cross-sectional morphology of FIB displays indistinct electrode/electrolyte interface, indicating that the side reactions occurs under this potential. This contradicts what is generally believed, where the SEI film can only be formed when the potential of the electrode is below 1.0 V. The deposits of the side reaction significantly affect the surface morphology [33].

Fig. 6. SEM images of LTO electrode at different states (a) pristine (b) before formation (c) after formation (d) after 250 cycles.

Fig. 7. Secondary electron FIB images of cross-section of LTO electrode at different states (a) before formation (b) after formation (c) after 250 cycles.

After battery formation, the deposits extend the surface area to cover the entire particles surface, presenting the porous morphology shown in Fig. 6c. An apparent layer can be seen from the cross-sectional morphology in Fig. 7b, corresponding to the SEI film of the LTO electrode with a thickness of about 24 nm. After 250 cycles, thick deposits can be observed on the LTO particles, as indicated in Fig. 6d. This observation suggests that LTO electrode suffers from severe side reactions accompanying by the gassing behavior. However, the thickness of SEI film is measured as 23-27 nm in Fig. 7c, with no apparent increase but a much more distinct profile. This means that the SEI film becomes denser as the number of cycles increased.

The variation of the internal pressure and particle surface SEI morphology indicate the side reaction on LTO surface is the main cause that induces the gassing behavior. A potential-determined side reaction initiates the gassing and its deposits form the SEI film. The side reaction would not either decline or vanish after the formation cycle as the graphite electrode does [34-36], but continue gradually changing the particle surface morphology during cycling. The SEI film covers the active site between LTO and electrolyte and suppresses further side reaction. Whenever the surface of LTO is entirely covered with dense deposits, the side reaction can be restrained then the internal pressure stabilizes. XPS measurements, utilized on LTO electrode under different conditions show consistent results as mentioned above, displayed in Fig. S2. Through a semi-quantitative calculation of the C 1s, the compositions of the SEI film changes with cycles while no apparent difference in the peak intensity appears in the cycles. Further studies by using in situ measurements on LTO electrode will put forward the understanding of the relationship between SEI film evolution and the gassing behavior.

4. Conclusions

A pressure testing device is presented for the first time to acquire quantitative internal pressure of the 18650 cylindrical LTO/LMO batteries during the formation and cycling processes. The internal pressure increases significantly during the formation cycle and continues to grow during the following cycles. Under different formation steps of the battery, the internal pressure increases under various specific increasing pressure rate, dP/dt . In particular, the internal pressures increase during the discharge process, while decrease during the charging process. The analysis based on the electrode potential proposes a potential-determined side reaction mechanism, meaning that gases generate in a specific range of potential of the LTO electrode, which most likely to be more positive than 1.60 V. After 46 cycles, the pressure reaches constant at 74.1 psi.

Different values of pressure increase after being stored at 80°C at different stage of life states the influence of SEI film on gassing behavior. SEM and FIB are applied to explicitly study the surface and cross-section morphology of LTO particle at different

states. The results show that the deposits induced from the side reaction that contributes to the formation of the SEI film also influence the gassing behavior. The SEI film is mainly deposited during the formation cycle then densifies in the following cycles without an apparent thickness increase. The thickness of the LTO SEI is found to be approximately 23-27 nm.

In sum, the LTO electrode potential initiates the side reaction and the resultant gases cause severe swelling. The deposits form the SEI film which covers the electrode/electrolyte interface. The SEI film suppresses the direct contact of LTO particles and electrolyte, pushing the internal pressure to gently increase during the following cycles. Once the SEI film becomes dense and totally covers the electrode/electrolyte interface, the side reaction is suppressed and the internal pressure stabilizes. The stabilized pressure after certain cycles would put new lights on the solutions of swelling, especially for punch cells.

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Table 1. Swelling ratios of batteries held at different electrode potentials at 80°C for 7 days for 2 kinds of particle sizes of LTO.

Swelling ratio (%)	2.5 V	1.8 V	1.6 V	1.5 V	1.4 V	2.0 V
LTO ($D_{50} = 0.6 \mu\text{m}$)	18.13	32.82	10.74	10.80	-0.86	-0.15
LTO ($D_{50} = 1.2 \mu\text{m}$)	21.17	11.77	-0.19	7.75	-0.14	0.02