Destructive gas generation with associated swelling has been a major challenge to the large-scale application of lithium ion batteries (LIBs) made from Li$_4$Ti$_5$O$_12$ (LTO) anodes. Here we report root causes of the gassing behavior, and suggest remedy to suppress it. The generated gases mainly contain H$_2$, CO$_2$ and CO, which originate from interfacial reactions between LTO and surrounding alkyl carbonate solvents. The reactions occur at the very thin outermost surface of LTO (111) plane, which result in transformation from (111) to (112) plane and formation of (101) plane of anatase TiO$_2$. A nanoscale carbon coating along with a stable solid electrolyte interface (SEI) film around LTO is seen most effective as a barrier layer in suppressing the interfacial reaction and resulting gassing from the LTO surface. Such an ability to tune the interface nanostructure of electrodes has practical implications in the design of next-generation high power LIBs.

Lithium ion batteries (LIBs) have been widely applied in many electronic devices due to their high energy densities, flexible design, light weight and long lifespan compared to other types of batteries, such as Ni-Cd, Ni-MH and lead acid batteries. For the same reasons, they also have been considered as an excellent power source for electric vehicles (EVs) and energy storage stations (ESSs) that require high energy density, long cyclic life and excellent safety performance. At present, various forms of carbons are the dominant source of anode materials for LIBs, which, however, have shown some critical issues, including poor cyclic life, high reactivity with electrolyte solution that easily contribute to the thermal runaways of battery under certain abusive conditions. Myriad investigations have hitherto been conducted to develop new electrode materials that possess much improved electrochemical and safety performance.

Spinel Li$_4$Ti$_5$O$_12$ (LTO) anode has a theoretical capacity of 175 mAh g$^{-1}$ within the voltage range of 2.5–1.0 V, and exhibits excellent reversibility due to its zero volume change during charge/discharge cycles. In addition, LTO demonstrates excellent safety and cyclic performance, making it a potential anode material for high power applications. Unfortunately, LTO shows a low intrinsic electronic conductivity and lithium-ion diffusion coefficient, resulting in poor high-rate charge/discharge capabilities. A number of strategies, including carbon coating, metal and nonmetal ion doping, hybridization with carbon and metal powders, reduction in particle size, and formation of micro-scale secondary particles consisting of nanostructured primary particles, have been devised to improve the electrochemical performance of LTO anodes with varied success.

Even after a decade of tremendous efforts based on the above approaches, however, LTO anode is not considered the most preferable choice for large-scale applications by the power LIB industries mainly due to severe gassing during charge/discharge cycles and storage, especially at elevated temperatures. Gassing in lead-acid batteries is known to be caused by overcharging or short circuits inside the battery. However, gassing in LTO-based LIBs is little understood although it leads to serious swelling and hence becomes a grave safety concern, a main obstacle to widespread use of LTO-based batteries. The battery industries are expecting an effective remedy for the gassing problem so as to pave the way for the vast applications of LTO powder battery in EVs and ESSs. To date, there are only a few reports that specifically refer to the gassing behavior of LTO electrodes. Very recently, the gas generated inside the LTO/Li$_4$Mn$_2$O$_4$ cells has been confirmed to mainly consist of H$_2$, CO$_2$ and CO. It is suggested that H$_2$ is possibly derived from a trace of H$_2$O, while CO and CO$_2$ result from the decomposition of electrolyte solution initiated at relatively high temperatures by PF$_5$ that is a strong Lewis acid and one of the decomposition products of the electrolyte, LiPF$_6$. However, gassing always occurs even when the LTO-based battery is not cycled and only stored at room temperature. Moreover, commercial graphite anodes soaked in LiPF$_6$ electrolyte do not show similar gassing behavior during storage or cyclic
As presented above, five conditions were designed to simulate the gassing process between LTO and electrolyte (See Table 1 for details). Interestingly, obvious swelling also occur when LTO or rutile TiO₂ is soaked in solvents (Condition A) or electrolyte solution (Condition B) (not subject to any electrochemical process), whereas there is no obvious swelling when there is only electrolyte solution in the absence of LTO or rutile TiO₂ (Condition C). This difference can be clearly identified from the volume of gas generated under Conditions A, B and C (Fig. 2e). The above results indicate that the gassing behaviors are intimately related to LTO or rutile TiO₂.

The gas components were analyzed by gas chromatograms and the results are summarized in Table 2 and Table S1. The gassing behaviors of LTO with electrolyte solution or solvent under different conditions are schematically depicted in Fig. 2a–d. CO₂ is the only component generated when LTO is soaked under Conditions A and B, whereas H₂, CO₂, CO and a trace of gaseous hydrocarbons are generated when the NCM/LTO batteries are stored (Condition D) and cycled (Condition E) where H₂ fraction is over 50 wt%. Note that H₂ and CO are generated in the batteries that were subjected to charge/discharge cyclic test, suggesting that the charged LTO promotes the generation of H₂ and CO which are driven by electrochemical reactions.

PF₆, a strong Lewis acid and one of the decomposition products of LiPF₆, has been mistakenly considered as the major source of initiating the gassing reactions in the presence of trace amount of water²⁶,³³. In sharp contrast, our observation indicate that gassing always occurs even when LTO is soaked in solvents under Condition A (totally free from LiPF₆) and CO₂ is the only gas component (Fig. 2e and Supplementary Table S1). That is to say that PF₆ originated from LiPF₆ is not mainly responsible for the generation of CO₂.³³,³⁴ As discussed above, much less gassing occurs under Condition C (totally free from LTO or rutile TiO₂) as compared to the cases under Conditions A and B. It is therefore concluded that CO₂ generation is mainly attributed to the intrinsic reaction between LTO or rutile TiO₂ and alkyl carbonate solvents. Unexpectedly, the volume of gas generated of LTO or rutile TiO₂ soaked under Condition A is obviously larger than that under Condition B, although the component of gas is exactly the same (CO₂) (Fig. 2e). This further indicates that LiPF₆ does not favor the gassing reactions, but rather suppresses it to a certain extent (details will be discussed below).

As is expected, the reactivity of solvents and electrolyte solutions with LTO or rutile TiO₂ at 50 °C is higher than that at 25 °C, which suggests that the higher temperature also promote the above reactions. This can explain why the LTO-based battery is easily swelling at high temperature. For the same reason, we discuss in details the LTO soaked in solvent or electrolytes at 50 °C to image the gassing behaviors more distinctly.

The volume of the generated gas as demonstrated in Fig. 2e also indicates that the reactivity of rutile TiO₂ with electrolyte is apparently lower than that of LTO counterpart. In view of the above findings and a very small amount of rutile TiO₂ contained in LTO, the

### Results

**Gassing behaviors under Conditions A–E.** Nano-structured active materials have a high reactivity with electrolyte, making it very difficult to detect the intrinsic reactions taking place between the electrode and electrolyte. Therefore, micro-sized cubic LTO powders were synthesized to study the gassing reactions in this work. The particle size of LTO is ~1 μm as confirmed by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations (Supplementary Fig. S1a–b). The X-ray diffraction (XRD) patterns of the LTO is in good agreement with the spinel structure of LTO with the space group Fd3m (Supplementary Fig. S1c). Weak diffraction peaks of rutile TiO₂ are detected, indicating an existence of small fraction of rutile TiO₂ nano-coating that can improve the rate performance of LTO⁶⁻⁸.

The soft packed NCM/LTO batteries were assembled with Li(Ni₁/₃Co₁/₃Mn₁/₃)O₂ (NCM) as the cathode, the LTO prepared above as the anode, and 1 M LiPF₆/EC+DMC+EMC as the electrolyte solution. Using such soft packed NCM/LTO batteries, the specific capacities of the LTO measured at the 1st and 400th cycles are 148.7 and 138.5 mAh g⁻¹, respectively (Fig. 1a). It is noted that very obvious swelling is observed for the battery after cyclic test under Condition E (Fig. 1e–f). Even the fully charged battery that was only stored at 25 °C for 3 months (Conditions D) also presents similar gassing behavior (Fig. 1c–d). It is apparent that the swelling results from the gas generated in the soft packed batteries. The rate of gassing gradually decreases with increasing the storage and cyclic period.

| Conditions | Remarks |
|------------|---------|
| Package containing LTO (or rutile TiO₂) soaked in electrolyte-free solvents at 25 or 50 °C for 3 months | 1 M LiPF₆/EC; Diethyl carbonate (DEC); Dimethyl carbonate (DMC); Ethylene carbonate (EC); Ethylene methyl carbonate (EMC); Propylene carbonate (PC) |
| Package containing LTO (or rutile TiO₂) soaked in electrolyte solution at 25 or 50 °C for 3 months | 1 M LiPF₆/EC+DMC+EMC |
| Electrolyte solution stored at 25 or 50 °C for 3 months in absence of LTO | Same as Condition D |
| Fully charged soft-packed battery stored at 25 °C for 3 months | NCM/LTO or NCM/(LTO/C) battery (see details in Experimental section) 1 M LiPF₆/EC+DMC+EMC is used as electrolyte solution |
| Soft-packed battery cycled 400 times at 25 °C at a charge/discharge rate of 0.5C |
swelling of NCM/LTO batteries is mainly ascribed to the intrinsic reactions of LTO with electrolyte solution.

**Carbon coating to suppress gassing in NCM/LTO battery.** Here, carbon coating is employed as a thin barrier layer to control the gassing reaction by isolating the LTO particles from electrolyte solution. Carbon coated LTO (LTO/C) was prepared (see Methods) and its XRD pattern is in good agreement with the JCPDS file (card No. 49-0207) (Supplementary Fig. S3a). Low diffraction peaks of rutile and anatase TiO₂ are observed and LTO/C has a well-defined crystal structure with a particle size of around 300 nm (Supplementary Fig. S3b–e). The Raman spectra of LTO/C indicate that the carbon is mainly amorphous judging from the high the intensity ratio (ID/IG \(=\) 2.99) of D- and G-band peaks (Supplementary Fig. S4a). Based on the thermogravimetric analysis (TGA), the carbon content is roughly estimated to be \(3.0\ \text{wt}\%\) (Supplementary Fig. S4b).

The soft-packed NCM/(LTO/C) batteries were prepared using LTO/C as the anode and the specific capacities measured after the 1ˢᵗ and 400ˢᵗ cycles at 0.5C/0.5C are 151.2 mAh g⁻¹ and 151.3 mAh g⁻¹, respectively (Fig. 1b). These values present much higher cyclic stability than the corresponding values of the uncoated LTO (Fig. 1a), testament to the beneficial effect of the carbon coating. In particular, no visible swelling occurs for the LTO/C-based battery after storage and cyclic test under both Conditions D and E (Fig. 1g–j) unlike the uncoated LTO batteries (Fig. 1c–f). This observation suggests that the carbon coating is very effective in suppressing the gassing behavior of LTO batteries.

Note that both the LTO and LTO/C-based batteries were prepared using the same condition. No apparent gassing occurs in the LTO/C-based batteries, indicating that H₂ is not generated in the LTO/C-based batteries unlike the LTO-based batteries. This observation further hints that H₂ generated in LTO-base batteries is not caused by the reactions of Li ions (or Li metal) with the trace H₂O (or HF) that are present in both LTO-based and LTO/C-based batteries. This means that the gassing based swelling of LTO-based batteries originates from the intrinsic reactions of electrolyte and LTO subjected to charge/discharge cyclic test.

Based on the above results, we can conclude that the gas generated in the swollen LTO-based batteries originates from the intrinsic reactions between the electrolyte solution and LTO, and is hardly related to PF₅ and H₂O. In the next section, the gassing reaction mechanisms of LTO with electrolyte solution under different conditions are discussed in more detail and the role of carbon coating in suppressing the gassing behavior of LTO batteries is elucidated.

**Discussion**

Gassing processes of LTO in presence of alkyl carbonate solvents under different conditions are discussed in details as follows. LTO soaking in electrolyte-free solvent (DEG as a typical solvent for Condition A) is discussed at first. The original LTO has a well-defined crystal structure as indicated by the high-resolution TEM...
soaked in DEC (totally free from LiPF6 as electrolyte), an apparent 
ment with that of the (111) plane of spinel LTO. After LTO was 
HRTEM image (Fig. 3a), and the 
Figure 2 | Schematics of gassing behaviors of LTO electrodes with 
| (HRTEM) image (Fig. 3a), and the 
\[ \frac{d}{d_0} = \frac{0.489}{0.241} \] is in agree-
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The spinel crystallographic structure of LTO presents that the 
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Therefore, the above discussion suggests that the decarboxylation 
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Table 2 | Gas generated for LTO soaked under Conditions A and B, and NCM/LTO batteries stored and cycled under Conditions D and E, respectively

| Condition | CO2 wt% | H2 wt% | CO wt% | C2H4 wt% | C2H6 wt% | C3H8 wt% | CH4 wt% |
|-----------|---------|--------|--------|----------|----------|----------|----------|
| A         | 100.00  | /      | /      | /        | /        | /        | /        |
| B         | 100.00  | /      | /      | /        | /        | /        | /        |
| D         | 30.41   | 55.65  | 10.00  | 2.09     | 1.10     | 0.32     | 0.43     |
| E         | 31.72   | 52.67  | 13.24  | /        | 1.34     | /        | 1.03     |

This is the main reason why the addition of LiPF6 in the solvents 
reduces the reactivity of LTO with electrolyte and somewhat retards 
the gassing reactions.
The O 1s XPS profile presents a large peak at 532.4 eV which is assigned to C-O-C species, while two small peaks at 531.7 and 533.5 eV are attributed to the C=O species and the oxygen atom of lithium alkyl carbonates bonding to two carbon atoms, respectively (Supplementary Fig. S5h). The C 1s detailed spectrum indicates that the C-O species are the main reaction products between LTO and electrolyte solution. The peaks assigned to carbonates are hardly detected (Supplementary Fig. S5m). The FTIR spectrum (Supplementary Fig. S6d) of LTO after soaking presents three main peaks at 1634, 1167 cm\(^{-1}\) and 1024 cm\(^{-1}\), which are associated with C=O, C-O-C and ROLi species, respectively, and these results are in accordance with the XPS results. Only CO\(_2\) is generated during LTO soaking under Condition B as a result of the decarboxylation reactions of solvents, similarly to Condition A (DEC). These reactions are also associated with the removal of Li\(^+\) and O\(^{2-}\) ions at the outermost surface of LTO leading to the formation of (222) plane and anatase TiO\(_2\) (101) plane (Fig. 3d and Supplementary Fig. S8f). In view of the formation of many C-O-C species on the surface of LTO after soaking under Condition B, LTO may initiate the ring-opening polymerization of EC, which results in the formation of PEO-like oligomers (-CH\(_2\)-CH\(_2\)-O-)\(_n\) and CO\(_2\) (Figure 4b)\(^{33,43}\).

The reacted surface of LTO is also covered by a SEI film with \(~\hbox{2 nm}\) in thickness resulting from the interfacial reaction, which is much thicker than that of LTO soaked under Condition A.

Figure 3 | TEM images of LTO and LTO/C electrodes. (a) As-prepared LTO. (b, c) LTO soaked under Condition A (DEC at 50 °C). (d) LTO soaked under Condition B (1 M LiPF\(_6\)/EC+DMC+EMC at 50 °C). (e) LTO in fully charged NCM/LTO battery stored under Condition D. (f) LTO in NCM/LTO battery cycled under Condition E. (g) As-prepared LTO/C. (h) LTO/C in fully charged NCM/(LTO/C) battery stored under Condition D. (i) LTO/C in NCM/(LTO/C) battery cycled under Condition E. Note that the LTO and LTO/C batteries tested under Conditions D and E were fully discharged before TEM examination.
Based on the above analysis, the components and the thickness of the SEI film formed at the surface of LTO under Condition B are quite different from that subjected to Condition A. With the exception of the decomposition products of solvents, Li$_2$TiF$_6$ and LiF formed on LTO under Condition B can further separate the LTO from the surrounding solvents thereby leading to an obviously less reactivity of LTO in electrolyte solution than in LiPF$_6$-free solvents.

After NCM/LTO batteries were subjected to storage and cyclic tests (Conditions D and E), similar gassing behaviors were found as expected. The (111) plane at the outermost surface of LTO transforms to (222) plane, which is covered by a thin SEI film formed by the products derived from the interfacial reaction between LTO and electrolyte solution when LTO batteries were subjected to Conditions D and E (Fig. 3e–f). The thicknesses of the phase-change layers (from (111) to (222) plane) for LTOs under both conditions (storage and cyclic test) are almost the same (~3 nm), which are, interestingly, similar to that of the LTO soaked under Condition A. It is thought that the phase-change occurs only in a very thin surface layer (~3 nm). As discussed above, the phase change is attributed to the loss of Li$^+$ and O$_2^-$ ions from the (111) plane by the interfacial reactions between LTO and electrolyte solution. Both the phase-change surface along with newly formed (222) plane and the SEI film formed on top of the phase-change surface become the barrier to separate the LTO from the surrounding electrolyte solution, which can restrain the further interfacial reactions and loss of Li$^+$ and O$_2^-$ ions from the interior part of LTO. Therefore, it is said that the interfacial reactions between LTO and electrolyte solution mainly occur at the early stage of the storage or cyclic test. As such, the gassing rate gradually decreases as storage and cyclic test continue.

The XRD patterns show that the LTO electrodes tested under Condition D or E maintain the original spinel structure (Supplementary Fig. S8c). However, the XPS (Ti 2p and O 1s) spectra offer no information for unreacted LTO, a strong evidence of the reacted LTO particles being covered completely by the SEI film of reaction products (Supplementary Fig. S5d–e and S5i–j). The detailed XPS results (C 1s) and FTIR spectra indicate that the C-O species are the main components of the SEI film on LTO after storage and cyclic test, which is similar to that of LTO soaked under Condition B (Supplementary Figs S5m–o and S6e–f).

However, it should be mentioned that the formation mechanism of SEI film on LTO electrode is totally different from that on graphite anode. The formation of SEI film on graphite anode is attributed to the reduction reaction of electrolyte solution (~0.7 V) along with gassing and Li$_2$CO$_3$ and ROCO$_2$Li are the main components of the SEI film. Because the reduction potential of most solvents is ~0.7 V, the
The reduction reaction of electrolyte solution occurs rapidly when the graphite anode is discharged to below 0.7 V. Thus, the formation of SEI film only occurs in the first several cycles during the battery formation and stops in the following cycling. After formation, the gassing behavior stops in the graphite anode battery due to a stable and complete SEI film that can separate the graphite from electrolyte solution and suppress the reduction decomposition of electrolyte.

In contrast, the formation of SEI film on LTO is resulted from the interfacial reactions between LTO and electrolyte solution, not the reduction of the electrolyte solution. The rate of interfacial reactions in LTO batteries is much lower than that of the reduction reaction of electrolyte solution in graphite-based batteries, and therefore a complete SEI film cannot be formed on LTO electrode during the battery formation process like the case of graphite electrode. Thus, the interfacial reaction further occurs during battery cycling test and long-term storage, which results in the continuous gas-release. The SEI film on LTO electrode is formed gradually with the processing of interfacial reaction, which leads to the decrease in the continuous gassing rate of LTO based battery accordingly. Moreover, the SEI film formed on the surface of LTO after the cyclic test under Condition E is much thicker than that LTO after storage under Condition D. It is well-known that the electrolyte solution is consumed during the battery cyclic tests gradually increasing the SEI film thickness.

Gases such as H2, CO2 and CO were generated under both Conditions D and E. CO2 is derived from the decarboxylation reactions of solvents, similarly to Conditions A and B. As discussed above, H2 does not arise from the reactions of Li ions (or lithium metal) with H2O (or HF). The alkyl groups in alkyl carbonate are the only species that can provide the H proton in the battery. Therefore, the dehydrogenation of the alkyl group in solvents may be promoted by LTO subjected to charge/discharge cycles and are responsible for the generation of H2. The intermediates of solvent dehydrogenation can further accept electrons and Li ions leading to the decarboxylation reactions and generation of CO26. The possible reaction mechanism is described in Figure 4c. CO2 can also be reduced to form CO according to Figure 4d33,46–48. Therefore, it can be concluded that the LTO electrodes induce decarboxylation, dehydrogenation and dehydrogenation reactions of solvents, directly accountable for gassing in LTO batteries.

Carbon coating around LTO is found as an effective method to suppress the gassing behavior of NCM/LTO batteries. The d-spacing measured from the HRTEM image of the as-prepared LTO/C is 0.481 nm (Fig. 3g), which matches well with the (111) plane of spinel LTO. The HRTEM images suggest that the LTO surface (e.g. the 0.481 nm (Fig. 3g), which matches well with the (111) plane of spinel measured from the HRTEM image of the as-prepared LTO/C is complete SEI formation, which can further protect the LTO from the surrounding electrolyte solution, eliminating the possible interfacial gassing reaction46.

The HRTEM images exhibited that the morphologies of the interface between LTO and carbon coating hardly changed under Conditions D and E, proving a stable interface existing between them (Fig. 3h–i). Therefore, it can be said that carbon coating is an effective strategy to fully suppress the interfacial reaction and gassing on the LTO surface.

In summary, the gassing phenomenon in LTO electrodes has been one of the most serious obstacles to their large-scale applications in LIBs. PF5, as a strong Lewis acid of decomposition product of LiPF6, has been erroneously regarded as a major source for gassing in the presence of trace amount of water. This paper clarifies that the gassing reactions, including decarboxylation, dehydrogenation and dehydrogenation reactions of solvents, are initiated not by PF5, but by LTO on the outermost surface of LTO (111) plane. The interfacial reactions between LTO and electrolyte solution generate gasses like H2, CO2 and CO, which are the main sources for swelling of battery pack. The gassing involves the plane transformation of LTO from (111) to (222) and the formation of (101) plane of anatase TiO2 and the outermost surface Li+ and O2− ions of the LTO (111) plane are removed from LTO by the interfacial reactions.

Constructing a barrier layer is an effective strategy to control the interfacial reactions between LTO and the surrounding electrolyte solution, and a nanoscale carbon coating on LTO is proven to suppress the gassing of LTO batteries. The coated carbon, together with the stable SEI film formed around the coating offer significant synergy to separate LTO from the surrounding electrolyte solution and prevent the interfacial gassing reactions. The modification of LTO surface is a simple yet very effective strategy, which can both improve the high-rate charge/discharge performance of batteries and suppress the gassing behavior of LTO battery.

**Methods**

**Synthesis of rutile TiO2, LTO and LTO/C.** Rutile TiO2 was obtained by sintering the precursor amorphous TiO2 at 900 °C for 8 h. The LTO powder was synthesized by solid-state reaction of the mixture containing amorphous TiO2 with LixCO3 in air. The TiO2 and Li2CO3 were mixed at a Li:Ti molar ratio of 4:2.5. Carbon coated LTO (LTO/C) composites were also prepared based on a similar solid-state reaction using the precursor mixture plus glucose in argon atmosphere. The details of the synthesis route can be found elsewhere51,52.

**Preparation of soft-packed NCM/LTO batteries.** Commercial 034352 type soft packed NCM/LTO batteries, of dimensions 3 mm thick, 43 mm wide and 52 mm long, were assembled to investigate the gassing behaviors of LTO batteries. The batteries were made of Li(Ni0.5Co0.2Mn0.3)O2 (NCM) (Tianjiao Technology, Shenzhen, China) as the cathode, as-prepared LTO or LTO/C as the anode, polyethylene as the separator, and 1 M LiPF6/EC+DMC+EMC as the electrolyte solution. The NCM cathode consisted of 85 wt. % NCM, 9 wt. % Super-P and 6 wt. % poly(vinylidene fluoride)(PVDF) binder, whereas the LTO anode consisted of 80 wt. % LTO, 10 wt. % Super-P and 10 wt. % PVDF. These components were rolled together to form the battery core and assembled into aluminum-plastic laminated film packages. Batteries were charged and discharged three times between 1.5 and 2.8 V at a rate of 0.3C for stabilization before storage and cyclic tests under Conditions D and E.

**Gassing behaviors (Conditions A–E).** As demonstrated in Table 1, five different conditions were designed to clarify the root causes of the gassing behaviors and the gases generated under all these conditions were analyzed on a gas chromatograph (Agilent 7890A GC System) using the GB/T 9722-2006 method.

**Conditions A and B:** LTO (or rutile TiO2) soaked in electrolyte-free solvent or electrolyte solution. 1.6 g of LTO or rutile TiO2 powders was put into aluminum-plastic laminated film packages, and 4 mL LiPF6-free solvent or LiPF6-based electrolyte solution was added before sealing of the packages in an argon-filled glove box (See Table 1 for details of the solvents and electrolytes used). The electrode packages were stored at 25 or 50 °C for 3 months. The volumes of the packages before and after storage were monitored using the water displacement method.
**Condition C** Electrolyte solution (1 M LiPF6/EC+DME+ EMC) stored at 25 or 50°C for 3 months in the absence of LTO. This condition is designed to evaluate the role of LiPF6 in the gassing reactions.

**Condition D**: Storage test of soft-packed NCM/LTO or NCM/(LTO/C) batteries. The assembled fully charged batteries were stored at 25°C for 3 months.

**Characterization of structure and morphology changes of LTO and LTO/C under different conditions.** The LTO and LTO/C electrode materials were rinsed after tests using DMC to remove the electrolyte and dried in the glove box antechamber to remove the residual DMC. XRD patterns of the samples were obtained on a diffractometer (Rigaku D/max 2500 PC) using Cu Kα radiation. The morphologies were examined using a TEM (JEOL JEM-2100F, Japan). XPS measurements were conducted using Physical Electronics PHI5020 instrument using X-rays magnesia anode (monochromatic Kα X-rays at 1253.6 eV) as the source. The C 1s region was used as a reference and was set at 284.8 eV.

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**Additional information**

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