Dendrite-accelerated thermal runaway mechanisms of lithium metal pouch batteries

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Funding information
Beijing Municipal Natural Science Foundation, Grant/Award Number: Z200011; National Key Research and Development Program, Grant/Award Number: 2021YFB2500300; National Natural Science Foundation of China, Grant/Award Numbers: 22179070, 22075029, U1932220; the "Shuimu Tsinghua Scholar Program of Tsinghua University; Mercedes-Benz AG

Abstract
High-energy-density lithium metal batteries (LMBs) are widely accepted as promising next-generation energy storage systems. However, the safety features of practical LMBs are rarely explored quantitatively. Herein, the thermal runaway behaviors of a 3.26 Ah (343 Wh kg\(^{-1}\)) Li | LiNi\(_{0.5}\)Co\(_{0.2}\)Mn\(_{0.3}\)O\(_2\) pouch cell in the whole life cycle are quantitatively investigated by extended volume-accelerating rate calorimetry and differential scanning calorimetry. By thermal failure analyses on pristine cell with fresh Li metal, activated cell with once plated dendrites, and 20-cycled cell with large quantities of dendrites and dead Li, dendrite-accelerated thermal runaway mechanisms including reaction sequence and heat release contribution are reached. Suppressing dendrite growth and reducing the reactivity between Li metal anode and electrolyte at high temperature are effective strategies to enhance the safety performance of LMBs. These findings can largely enhance the understanding on the thermal runaway behaviors of Li metal pouch cells in practical working conditions.

KEYWORDS
battery safety, lithium metal dendrites, lithium metal pouch cells, solid electrolyte interphase, thermal runaway, whole life cycle
1 | INTRODUCTION

The rechargeable batteries are of great significance to various energy storage processes for the environmental sustainability and the availability of renewable energy.1–3 With the booming development of electric vehicles and portable electronic devices, advanced electrode materials and high-energy-density battery systems are urgently demanded.4–7 Lithium metal batteries (LMBs) are promising to achieve a theoretically high energy density due to the lowest potential (−3.04 V vs. the standard hydrogen electrode) and ultra-high specific capacity (3860 mAh g⁻¹) of the Li anode.8–10 Actually, LMBs were previously tried into the commercial products and their high-energy-density feature rendered the practical applications.11,12 However, the frequent fire accidents led to the abandon of LMBs while the safe lithium ion batteries (LIBs) based on the intercalation principles achieve great success since 1990s. Therefore, the safe operation of LMBs is among the most urgent issues before the practical applications.13,14

During practical operations of batteries, abuse conditions can occur, such as mechanical abuse,15–17 electrical abuse,18–21 and thermal abuse,22–25 leading to safety problems of batteries. Under these abuse conditions, thermal runaway is the intrinsic feature of safety risk, mainly controlled by the thermal balance between the heat generated (exponentially) and the heat dissipated (linearly) of the cell.26 The main trigger for thermal runaway involves a series of uncontrolled exothermal chain reactions contributed by the components inside a battery, including the anode, the cathode, and the electrolyte.27–29 Calorimetric techniques such as C80 microcalorimeter,30,31 and extended volume-accelerated rate calorimetry (EV-ARC),32–35 and differential scanning calorimetry (DSC) are adopted to evaluate the contribution of different exothermic reactions to the thermal runaway.36 EV-ARC can measure the intrinsic thermal safety of the battery under adiabatic conditions. Working with DSC, EV-ARC can provide accurate quantification of the thermal runaway properties of cells. These methods are beneficial to enhance the understanding of the thermal runaway processes of LMBs. However, the thermal runaway behaviors of high-energy-density LMBs are rarely investigated quantitatively.

Compared to the LIBs, LMBs suffer from problems such as dendritic Li deposition and unstable solid electrolyte interphase (SEI).37–42 During cycling, the SEI is continuously broken and repaired upon Li anode, leading to the continuous accumulation of thermally unstable SEI resulting in potential safety risks at elevated temperature.43–45 Meanwhile, Li dendrites can increase the specific surface area of Li anode and intensify the serious exothermic reactions between Li metal and other cell components, such as SEI, electrolytes (non-aqueous and solid-state electrolytes), and cathodes.46–49 Beside these, thermal decomposition and combustion of electrolytes themselves can also aggravate the safety risks.50 However, the detailed reactions sequence and heat contribution during thermal runaway of high-energy-density LMBs in working conditions are still tightly sealed to researchers. Therefore, it is of great importance to understand the safety characteristics and the roots of working LMBs based on the practically adopted cell patterns, such as pouch cells.

In this contribution, the thermal runaway features of the 3.26 Ah Li | LiNi0.5Co0.2Mn0.3O2 (NCM523) pouch cells with 1.0 M lithium hexafluorophosphate (LiPF6) ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte were comprehensively investigated during their whole life cycle. Combined with the exothermal, morphological, and compositional characterizations of the cycled Li, the trigger for thermal runaway of the cycled cell is considered as the exothermal reactions between the large amounts of inorganic SEI and LiPF6 salts, while the reactions between Li metal and electrolytes lead to the final occurrence of thermal runaway. Compared with the activated cell, the self-heating and triggering temperature of the cycled cells are significantly reduced from 112.2°C to 72.7°C and from 215.3°C to 88.2°C, respectively. The pristine cells would not undergo thermal runaway until 300°C. These results illustrate the thermal runaway feature of LMBs quantitatively and clearly explain the origin of thermal runaway.

2 | RESULTS AND DISCUSSION

The adopted Li | NCM523 pouch cell consists of the NCM523 cathode (4.0 mA cm⁻²), Li metal anode (50 μm), and routine ester electrolyte (1.0 M LiPF6 EC/DEC (1:1 by vol.)). The polypropylene/polyethylene/polypropylene (PP/PE/PP) separator is employed in the pouch cell (Figures S1 and S2). The assembled Li | NCM523 cells are cycled at 0.03 C (1.0 C = 180 mA g⁻¹) for the first two cycles and then at 0.1 C for long cycling (Figure S3A). The discharge capacity of the first cycle is 3.26 Ah and the energy density of the cell is 343 Wh kg⁻¹ (Figure 1A, the calculation method in Table S1). After 13 cycles, the discharge capacity of the cell declines significantly due to the rapid depletion of the active Li and the accumulation of dead Li and SEI in the working cell, accompanied with an increasing polarization voltage and a rapid decay in the Coulomb efficiency (CE, Figure S3B).51–53

EV-ARC is a frequently adopted instrument to obtain the thermal safety performance of cells working at an adiabatic test environment (Figure S4).54 In the heating stage, the EV-ARC works in a heat–wait–seek mode. When the battery self-heating temperature rate reaches...
0.02°C min⁻¹, it will change into a self-heating stage, at which the critical temperature is defined as $T_1$. When the battery self-heating temperature rate achieves 1°C s⁻¹ (defined as $T_2$), the temperature rises rapidly in a thermal runaway stage. The maximum temperature reached by the cell after thermal runaway is $T_3$. In general, the lower $T_1$ and $T_2$ are the easier to trigger thermal runaway, and the higher $T_3$ suggests more exothermic heat produced during thermal runaway.

### 2.1 Thermal runaway feature of the cycled cell

The thermal runaway feature of 20-cycled Li | NCM523 cell at 100% state-of-charge (SOC) was characterized by EV-ARC. Only a few residues remain of the pouch cell after thermal runaway (Figure 1B). The thermal runaway of the cell is initiated at 72.7°C ($T_1$) and then triggered at 88.2°C ($T_2$) after 1.38 h (Figure 1C). The cell reaches a maximum temperature of 407.4°C ($T_3$). During thermal runaway, the pouch bag ruptures and the residual electrode materials are ejected, leading to a low $T_3$. A stable voltage curve is observed until the temperature rise rate reaches 1°C s⁻¹, suggesting that the internal short-circuits appear later than $T_2$ (Figure 1D) and internal short-circuit is not the cause for thermal runaway. The EV-ARC results exhibit that LMBs have a larger risk of thermal runaway than LIBs.

The cell components and mixtures were characterized by DSC to assess the origin of thermal runaway. The DSC and EV-ARC results do not match exactly due to their different working mechanisms, but are somewhat instructive and complementary to each other. The DSC curve of NCM523 and electrolyte has an exothermic peak at 283.5°C, attributed to thermal-induced oxygen reaction with electrolyte (Figure 2A). The cathode cannot contribute to the heat release before thermal runaway temperature ($T_2$). The heat contribution of Li metal anode is also analyzed. There is an exothermic peak locating at 143.7°C in the DSC curve of cycled Li with an onset temperature of 89°C (Figure 2B), indicating that cycled Li anode can contribute to initiate the thermal runaway. The exothermic reactions between Li metal and electrolyte (128.1 and 158.0°C) can further increase the temperature to $T_2$, leading to thermal runaway. The exothermic peak of anode and cathode reaction (234.5°C) leads to further heat generation and brings the battery temperature to $T_3$ rapidly.

The DSC results of the cell compositions, together with
EV-ARC results, reveal that the exothermic reactions containing cycled Li are the causes for the cell thermal runaway: Li anode itself contributes to the self-heating feature of the pouch cells ($T_1$), the reactions between Li metal anode and the electrolyte lead to the occurrence of thermal runaway ($T_2$), and exothermic reactions in the pouch cells including cathode, anode, and electrolyte result in the highest temperature ($T_3$) during thermal runaway. Cycled Li is further characterized to probe the reason of the exothermic reaction ($T_1$). By comparing the images of cycled Li and pristine Li, the cycled anode contains numerous dendritic dead Li after cycling and some even adheres to the separator (Figure 3A). The powdery and porous structure has a very high specific surface area, which rendering high reactivity toward other cell components.60 Meanwhile, the X-ray photoelectron spectroscopy (XPS) spectra confirm that cycled Li is composed mainly of plenty of LiPF$_6$ decompositions, inorganic components, organic components, and some amounts of metallic Li (Figure 3B, Figure S5).61,62 It is worth noting that both Li$_2$CO$_3$ and Li$_2$O are the main components of the inorganic SEI. 63,64

Based on the chemical compositions, LiPF$_6$ and inorganic products of SEI were tested by DSC. The reaction at 77°C (near $T_1$) of LiPF$_6$ and Li$_2$O contributes to self-heating of the cell (Figure 3C, Figure S6A). Furthermore, the exothermic peak at 143°C of LiPF$_6$ and Li$_2$CO$_3$ is consistent with the occurrence of an exothermic peak for cycled Li, causing the temperature of the cell to rise continuously, triggering thermal runaway. These exothermic reactions are due to the reaction of PF$_5$ (LiPF$_6$ decomposition) with Li$_2$O and Li$_2$CO$_3$.65,66 By contrast, the reaction of residual Li and the inorganic SEI compositions does not result in an exothermic peak of cycled Li at 143.7°C (Figure S6B). These conclusions are also confirmed by Li | NCM523 cell with 1.0 M LiTFSI EC/DEC electrolyte (Figure 3D, Figure S7) and Si/C anode with 1.0 M LiPF$_6$ EC/DEC electrolyte (Figure S8). Therefore, the reaction between the LiPF$_6$ and inorganic SEI results in the initial exotherm ($T_1$).

According to the above discussions, the thermal runaway mechanism of the Li | NCM523 cell with 1.0 M LiPF$_6$ EC/DEC after cycling is proposed (Figure 4). When the cell temperature increases under abuse conditions, the LiPF$_6$ decompositions (PF$_5$) will react with Li$_2$O and Li$_2$CO$_3$ in the SEI on the dendritic Li to produce mild heat, while the organic components of SEI are unstable and can transform into inorganic compounds.43 Then, the cell begins to self-heating ($T_1$) and its temperature rises gradually. During this process, the SEI is gradually consumed, exposing fresh dendritic Li to react with the electrolyte and forming new SEI. The reaction continues to release heat and raises the temperature of the cell, which in turn causes the Li and electrolytes to react more vigorously. Eventually, the cell temperature rate reaches 1°C s$^{-1}$ ($T_2$), resulting in thermal runaway.

As temperature increases sharply, the separator collapses and the voltage starts to drop. The large-scale internal short circuit generates joule heat. Next, the NCM523 cathode releases oxygen. The reactive oxygen reacts exothermically with the organic solvent (EC and DEC) in the electrolyte. Furthermore, the oxygen diffusing into the anode also reacts exothermically with the Li metal.67 All these reactions result in the highest temperature during thermal runaway. The volatilization of the electrolytes and the gas generated by these reactions cause the cell to bulge and rupture.
**FIGURE 3** Characterizations on cycled Li metal anode. (A) Scanning electron microscopy (SEM) images of pristine Li and cycled Li, the optical images of cycled Li electrode and separator in the pouch cell. The scale bar in the optical photo is 1 cm. (B) The O 1s X-ray photoelectron spectroscopy (XPS) spectra of cycled Li. (C) differential scanning calorimetry (DSC) profiles of LiPF$_6$ with Li$_2$O and Li$_2$CO$_3$. (D) DSC profiles of cycled Li (cycled in 1.0 M LiTFSI EC/DEC) and the mixtures of LiTFSI and Li$_2$CO$_3$.

**FIGURE 4** Thermal runaway map of the chain reactions for the current lithium metal batteries (LMBs).

2.2 Thermal runaway feature during whole life cycle

Both the pristine (0% SOC without cycling) and activated cell (100% SOC only charged once) were also examined by EV-ARC to achieve a better understanding on the thermal stability in the whole life cycle of Li | NCM523 batteries. The activated cell exhibits a self-heating temperature at 112.2°C, and thermal runaway occurs at 215.3°C with a maximum temperature of 1148.4°C (Figure 5A,B). Due to
The strong exothermic reactions during thermal runaway, only a small amount of the pouch bag remains (Figure 5C). The difference in \( T_3 \) between cycled cell and activated cell is that activated cell has a fully charged capacity of 3.26 Ah, while cycled cell just has a fully charged capacity of only 0.2 Ah. The reduced energy reduces the maximum temperature of the cell.\(^{56}\) On the other hand, the cycled cell with numerous dendrites, SEI, and dead Li produces enough gas to get the electrode material out at elevated temperature, leading to the incomplete combustion reaction after \( T_2 \) and the final lower \( T_3 \). It is different from an activated cell. The trigger for \( T_1 \) and \( T_2 \) of activated cell is due to the highly reactive dendritic Li on the anode surface after the initial charge (Figures S9 and 10). For a pristine cell, there is no thermal runaway. The temperature of \( T_1 \) is 176.1\(^\circ\)C without \( T_2 \) (Figure 5D,E). It only occurs with eruptions of flammable electrolytes (Figure 5F, Movies S1). The pristine cell with a high \( T_1 \) exhibits good thermal stability due to the Li anode without dendrite.

The thermal behaviors in the whole life cycle of Li | NCM523 pouch cells were comprehensively investigated by comparing the key parameters extracted from the EV-ARC test results (Table 1). The pristine cell exhibits superior thermal stability without thermal runaway, because all electrode materials, especially Li foil, are fresh. After the first charging, Li\(^{+}\) from the cathode is deposited as dendrites. Dendrites can increase the content of SEI on the anode and largely strengthens the exothermic reactions related to the Li anode. Consequently, the temperature of \( T_1 \) is reduced from 176.1\(^\circ\)C to 112.2\(^\circ\)C. After 20 cycles, large amounts of dendrites accumulate on the anode and the SEI on the surface of the Li anode increases substantially after rupture and regeneration, bringing the temperature of \( T_1 \) down to 72.7\(^\circ\)C and decreasing \( T_2 \) from 215.3\(^\circ\)C to 88.2\(^\circ\)C.

Besides the reduction in the \( T_1 \) and \( T_2 \) temperature, dendrites on the anode also lead to the reduction in the interval time between these characteristic temperatures. The parameter of \( \Delta t \) (the interval time from \( T_1 \) to \( T_2 \)) is introduced to evaluate the escape time during thermal runaway.\(^{68}\) The \( \Delta t \) of the cycled cell (1.38 h) is much less than 13.99 h of an activated cell, suggesting its greater risk during thermal runaway, which agrees with the conclusions drawn from the parameters of \( T_1 \) and \( T_2 \). Therefore, the thermal stability of Li | M523 batteries severely drops with the accumulation of dendrites on the anode. If the Li anode can be stably deposited and stripped without dendrites, the safety of LMBs can be improved similar to that

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**Table 1** Key parameters extracted from the EV-ARC results of the whole life cycle of Li | NCM523 pouch cell

| States       | \( T_1 \) (\(^\circ\)C) | \( T_2 \) (\(^\circ\)C) | \( T_3 \) (\(^\circ\)C) | \( \Delta t \) (h) |
|--------------|----------------|----------------|----------------|----------------|
| Pristine cell| 176.1          | /              | /              | /              |
| Activated cell| 112.2          | 215.3          | 1148.4         | 13.99          |
| Cycled cell  | 72.7           | 88.2           | 407.4          | 1.38           |

*Note:* Due to the large amount of gas generated during thermal runaway, the cell components rush out of the cells, leading to the incomplete reactions of electrode materials.

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of LIBs due to the reduced reactivity of fresh Li metal and the liquid electrolyte (Figure S11). Besides suppressing dendrite growth, enhancing the thermal stability of electrolytes against Li metal can also largely improve the safety of LMBs, such as fire-resistant solvents and Li salts of liquid electrolytes and solid-state electrolytes.

3 | CONCLUSION

The thermal behaviors of a high-energy-density (343 Wh kg$^{-1}$) 3.26 Ah Li | NCM523 pouch cell with 1.0 M LiPF$_6$ EC/DEC over its whole life cycle are explored. The thermal stability of the cell is found to decrease as the number of cycles increases with the accumulation of dendrites on the anode. For pristine cells without thermal runaway, the high $T_1$ of 176.1°C shows that the excellent thermal stability is due to the fresh electrode materials, especially Li metal. Thermal runaway is triggered in the activated cell after the initial charge with the decrease in $T_1$ to 112.2°C. After 20 cycles, the thermal stability of the cycled cell decreases sharply. It is attributed to the generation of the larger amount of SEI and dendritic Li at the anode, leading to the reduction of $T_1$ to 72.7°C and $T_2$ from 215.3 to 88.2°C. Thermal runaway is triggered by the reaction of Li with the electrolyte. The reaction of the anode and cathode and the burning of the electrolyte result in an elevated cell temperature of $T_3$. This work reveals the thermal runaway features of the Li metal pouch cell over whole life cycle for the first time. It is critically important to suppress dendrite growth and reduce the reaction activity of Li metal anode and electrolyte, especially at high temperature. An optimized electrolyte is highly expected that can alleviate the dendritic problem and increase the $T_2$ temperature for a practical Li metal battery. This work can present deep understandings on thermal runaway mechanisms of LMBs and can shed fresh lights on the development of safe LMBs.

4 | EXPERIMENTAL

4.1 | Cell fabrication

The 3.26 Ah Li | LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NCM523) pouch cell was assembled with NCM523 (4.0 mAh cm$^{-2}$, 96 wt% active material, 2 wt% conductive additive, and 2 wt% binder), Li foils (50 μm, 99.9%, China Energy Lithium Co., Ltd.) on the Cu, routine ester electrolytes of LiPF$_6$ in EC/DEC (8.0 g, 1.0 M, 1:1 by volume ration; Beijing Chemical Industry Group). To assemble a pouch cell, 14 cathode sheets and 15 anode sheets were stacked layer-by-layer with PP/PE/PP separators (Celgard 2325, 25 μm). The 1.0 Ah Li | NCM523 pouch cell with LiTFSI in EC/DEC (4.0 g, 1.0 M, 1:1 by volume ration) was made of 4 cathode sheets and 5 anode sheets. All pouch cells were assembled in dry room with a dew-point temperature of −40°C. The pouch cells were tested in a voltage range of 2.8−4.3 V at 0.03 C for first two cycles then at 0.1 C.

The Si/C composite anode was ball-milled with Si powder (100−200 nm, Aladdin), Super P conductive carbon black, and polyvinylidene fluoride binder (PVDF) at a weight ratio of 6:3:1 in N-methyl pyrrolidone solvent (Lizhiyuan Battery Materials Co., Ltd.) to form a homogeneous slurry. The slurry was directly coated on a Cu current collector and then dried at 60°C for 12 h. The Si/C electrode was poused disks with a diameter of 13.0 mm. The loading was ~1.5 mg cm$^{-2}$. The cell with Si/C was made of Li (600 μm), PP, and LiPF$_6$ in EC/DEC (50 μl, 1.0 M, 1:1 by volume ratio). The cell was assembled in 2025-type coin cell, and tested from 0.01 to 1.5 V at 1 C (1 C = 2887 mAh g$^{-1}$). All cells were monitored in the galvanostatic mode in a Land CT2001 multichannel battery tester. Both coin and pouch cells were measured at room temperature (25°C) and without additional stress.

4.2 | Materials characterization

The morphologies of Li electrodes were observed by a JSM 7401F (JEOL Ltd., Tokyo, Japan) scanning electron microscopy (SEM) operated at 3.0 kV. XPS experiments were employed on scanning X-ray microprobe (Thermo Fisher Scientific, ESCALAB Xi+) operated at 15 kV, with monochromated Al Kα radiation. Ar$^+$ sputtering rate for the XPS depth-profiling calibrated on SiO$_2$ surface was ~30 nm min$^{-1}$, and the sputtering time was 6 min.

The thermal runaway tests of pouch cells were employed in the EV-ARC system that was produced by Thermal Hazard Technology. K-type thermocouples inserted in the cell to monitor the internal temperature. The cell voltage was recorded using a data logger by Hitachi. Here, a typical heat−wait−seek mode was adopted for testing from 40°C to 300°C. The temperature setting for each step was 5°C. The wait time and seek time were set as 30 and 20 min, respectively. The characteristic temperatures ($T_1$, $T_2$, and $T_3$) were extracted based on the data analysis. The thermal stability of cell materials was also tested under Ar atmosphere in a Simultaneous Thermal Analyzer (STGA/DSC1/1600LF, METTLER): heating rate was 10°C min$^{-1}$; the temperature was raised from 30°C to 300°C. The tested materials were placed in sealed crucibles by DSC press. The heat flow of the mixture was calculated based on the sum of the masses of the components.
ACKNOWLEDGEMENTS

Beijing Municipal Natural Science Foundation (Z200011), National Key Research and Development Program (2021YFB2500300), National Natural Science Foundation of China (22179070, 22075029, U1932220), the “Shuimu Tsinghua Scholar Program of Tsinghua University”, and Mercedes-Benz AG. Xiang-Qun Xu and Xin-Bing Cheng contributed equally to this work.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION
Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: Xu X-Q, Cheng X-B, Jiang F-N, et al. Dendrite-accelerated thermal runaway mechanisms of lithium metal pouch batteries. SusMat. 2022;2:435–444. https://doi.org/10.1002/sus2.74