

Article

An Experimental Study on the Thermal Runaway Propagation of Cycling Aged Lithium-Ion Battery Modules

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Abstract: The primary concerns for individuals using lithium-ion batteries (LIBs) are aging and thermal runaway (TR). This paper focuses on the thermal runaway propagation (TRP) of cycling aged LIB modules. The impacts of state of charge (SOC), state of health, and cyclic aging temperature on TRP in LIB modules are investigated. The analysis includes parameters such as temperature, voltage, and mass of the modules during TRP. It was found that as SOC increases, the maximum increase in temperature and maximum temperature rate of the modules increased, as did the total mass loss and smoke emissions. The average heat transfer between adjacent cells was higher for the lower SOC. Cycle aging reduces the thermal stability of LIBs, leading to a lower maximum temperature and maximum temperature rate, as well as a larger mass loss compared with fresh battery modules. Regarding aging temperature, low-temperature aging reduces the total duration of TRP compared with room temperature, but it increases the maximum temperature rate and causes greater mass loss. Aging also increases the average heat transfer between adjacent cells.

Keywords: lithium-ion battery; thermal runaway propagation; state of charge; state of health; thermal safety



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1. Introduction

Lithium-ion batteries (LIBs) are widely used in electronics, energy storage power stations, and automobiles as a new energy source due to their high energy density and low environmental impact [1]. However, concerns about LIBs have persisted due to frequent thermal runaway (TR) accidents and the degradation of battery life. Currently, the problem of thermal runaway in aging battery modules is not well understood. To address this issue, it is crucial to investigate the TR behavior of aging lithium-ion batteries.

Serious incidents concerning fire and explosions in LIBs often originate from the TR of a single battery. Therefore, researchers have extensively investigated the TR of single batteries [2,3]. In practical applications, energy storage systems typically consist of multiple LIBs. Once TR occurs in one cell, the heat is transferred to neighboring cells, triggering TR in those cells as well, and resulting in the release of additional heat. This cascading effect of TR can have severe and potentially catastrophic consequences. Consequently, there has been a growing focus on investigating the thermal runaway propagation (TRP) in LIBs.

State of charge (SOC) and state of health (SOH) are two parameters for LIBs that have garnered significant attention. Different SOC values indicate the amount of energy stored in a battery at a given moment, with only a shift in stored energy and electrode potential occurring inside the battery [4]. SOH represents the amount of energy that a cell can store after a certain period of use. LIBs experience aging when in storage, or due to working conditions; this is known as calendar aging and cyclic ageing, respectively. During the aging process, various side reactions occur inside the battery, including the loss of active materials and lithium ions [4,5]. In practice, batteries may be stored and operated at varying temperatures, and temperature has a significant effect on the internal reactions of

the battery, resulting in various aging effects [6,7]. These side reactions alter the internal structure and properties of the battery, resulting in distinct behaviors during TR.

Many studies have investigated the impact of SOC and SOH on the TRP of battery modules. Huang et al. [8] investigated the TR behavior of large LIBs with different SOC and discovered a positive correlation between SOC and TRP speed. Wang et al. [9] conducted a study on the TRP behavior of LFP battery modules and additionally investigated the propagation law of a double-layered cell module. The authors observed that TR was more likely to propagate in a single-layer module. Fang et al. [10] investigated the impact of different SOC and spacing distances on the TRP of two vertically aligned 18,650 cells, and determined the critical SOC and spacing required for TR to occur. Liu et al. [11] investigated the impact of environmental pressure and SOC on the TRP of 18,650 LIBs, and they discovered that the TRP rate decreased as SOC and environmental pressure decreased. Wang et al. [12] investigated the factors that influence the TR of 18,650 batteries, and they discovered that TRP was affected by different arrangement modes, connection modes, and SOC, whereas cyclic aging had negligible impact on the propagation process.

A number of studies have been performed on the TR of aging batteries. Ren et al. [13], Kong et al. [14], and Cai et al. [15] investigated the thermal runaway characteristics of aged LIBs at various temperatures. The former two focus on the effect of charging and discharging rates on TR behavior, whereas the latter examines the impact of changes in the internal structure of aging batteries on TR. Friesen et al. [6] examined the impact of low-temperature cycling and the charging state on the TR of 18,650 LIBs induced by mechanical abuse testing. Liu et al. [16] investigated the impact of non-uniform aging on TR, and they observed that TR is more likely to occur following aging. Additionally, low SOC is more susceptible to the effects of non-uniform plating compared with high SOC. In contrast, Essl et al. [17] examined the thermal response, exhaust emissions, and exhaust composition following cyclic aging at various temperatures. The results revealed a reduced hazard level in the aging battery, characterized by lower maximum temperature, gas production, CO content in the exhaust, and reduced mass loss compared with fresh batteries. Doose et al. [4] proposed that decreasing SOC and SOH can mitigate the severity of TR, with the storage capacity of lithium ions playing a crucial role in determining the extent of the TR reaction. Wang et al. [12] investigated the impact of aging on TRP in battery modules. The results indicated that aging could accelerate propagation, leading to reduced mass loss, whereas its effect on heat transfer was negligible.

Unlike previous studies that focus on cyclically aging single batteries, the novelty of this paper concerns the investigation of the TRP characteristics of cyclic aging battery modules. By collecting data such as temperature, voltage, mass, and flue gas, and by analyzing the TRP speed and heat transfer, the influence of SOC, SOH, and aging temperature on TRP of battery modules is comprehensively researched. Numerous efforts have been dedicated to enhancing the safety of LIBs [18–20] and advancing battery management systems [21–24]. The research presented in this paper can serve as a valuable reference for mitigating thermal runaway incidents and improving safety measures.

2. Experimental

2.1. Battery Information

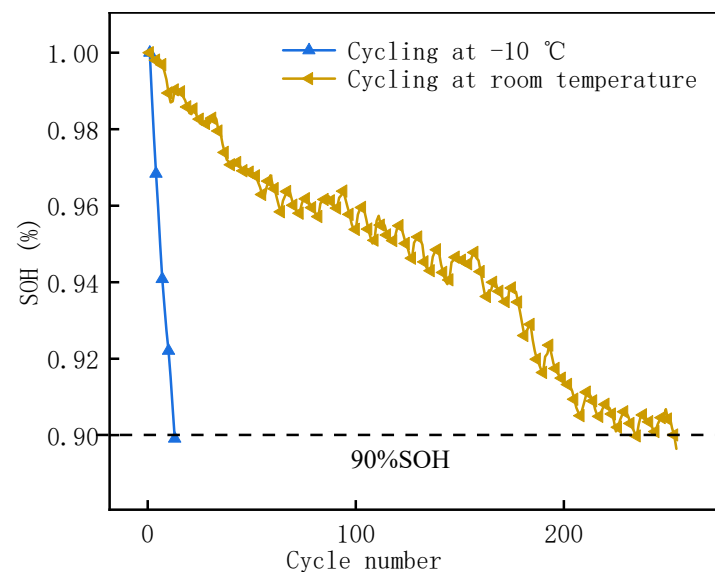
In this experiment, we utilized the Sanyo 103450P prismatic lithium-ion battery (Sanyo, Osaka, Japan), which is widely employed in financial and medical devices, as well as portable power supplies. The battery core was composed of a LiCO_2 cathode, graphite anode, and polyester film, while the shell was made of aluminum-nickel alloy. The battery had dimensions of 34 mm × 10 mm × 50 mm, and it was equipped with a thermal fuse at the negative end to prevent internal short-circuits resulting from excessive temperature or currents. It also comprised a rupture disc to discharge gas in cases of high pressure. Table 1 provides other basic parameters.

Table 1. The physical parameters of Sanyo 103450P.

Parameters	Value
Nominal capacity	1880 mAh
Nominal voltage	3.70 V
End voltage	2.75 V
Charge voltage	4.20 V
Weight	40 g

Prior to the experiment, the battery underwent cycling using the Neware CT-4008Tn-5V6A-S1-F. The aging process involved the following steps. The batteries were placed at room temperature (RT, 10–20 °C) or in low-temperature test chambers set to −10 °C. Once the battery temperature equilibrated with the ambient temperature, the battery was charged to a cut-off voltage of 4.2 V, at a 1 C rate, using the constant current and constant voltage method (CV-CC); then, it was discharged to 2.75 V at the same rate, using the constant current method (CC). This constituted a single cycle. The discharge capacity of the first cycle was labeled as the initial capacity, denoted as C_0 , and the discharge capacity of the last cycle was labeled as C_1 . The SOH of a battery was defined based on its capacity [25], and expressed as the percentage of C_1 to C_0 . The SOH of a battery can be calculated using Equation (1). Once the SOH of a battery reached 90%, the current charging device would automatically stop working. Figure 1 shows the capacity of the degraded cells under different cycle conditions. The batteries that cycled at −10 °C exhibited rapid degradation and reached 90% SOH after only 12 cycles, whereas the batteries cycled at RT exhibited a better performance, with the cycle numbers reaching 250 cycles. This is because a low temperature increases the internal resistance of the battery, reduces the battery capacity, and accelerates aging [14,15]. Subsequently, the cycled battery was allowed to stabilize at RT for 30 min, then, it was charged to either 50% SOC or 100% SOC as a backup. All experiments were repeated twice to ensure the reliability of the results.

$$\text{SOH} = \frac{C_1}{C_0} \times 100\% \quad (1)$$

**Figure 1.** Capacity of the degraded cells under different cycle conditions.

2.2. Apparatus and Experimental Setup

All tests were conducted in a laboratory chamber, as depicted in Figure 2. This study conducted nine sets of experiments under various conditions to investigate how the SOC,

SOH, and aging temperature influence the TRP properties of the battery module. The nine sets of experiments are displayed in Table 2. The TR mode is shown in Figure 2. Each battery module comprised four horizontally arranged cells, with no electrical connection between them. A heating block with a power of 100 W was in direct contact with the initial battery. The heating block stopped working once the initial battery began to undergo TR. Mica plates of dimensions 50 mm × 34 mm × 3 mm were arranged around the heating block and battery module to reduce heat exchange with the surroundings during TRP. The entire battery module heating unit was clamped with a stainless-steel plate clamp and placed in the laboratory chamber. An electronic balance was used to measure the mass change of the cell module during the TRP. Additionally, a lifting platform was placed between the battery module and the electronic balance to prevent extreme temperature damage. The experiment was monitored and recorded with a SONY camera, and gas emissions from the battery module during TR were pumped into a Testo 330 gas analyzer for testing. During TRP, the central temperature of each cell was measured using K-type thermocouples which have diameters of 0.5 cm, a measuring temperature range of 0–1300 °C, a measurement accuracy of 0.5 °C, and an acquisition frequency of 1 Hz. The positions of the thermocouples are shown in Figure 2, where T_{i-l} and T_{i-r} represent the left and right surface temperatures of a single cell, and i represents the battery sequence ($i \in \{1,2,3,4\}$). Furthermore, to measure the voltage change of each individual battery, a nickel strip was welded to both terminals of the battery, and then connected to a data acquisition device (ICPCON I-7019) that transmitted the temperature and voltage data to a computer.

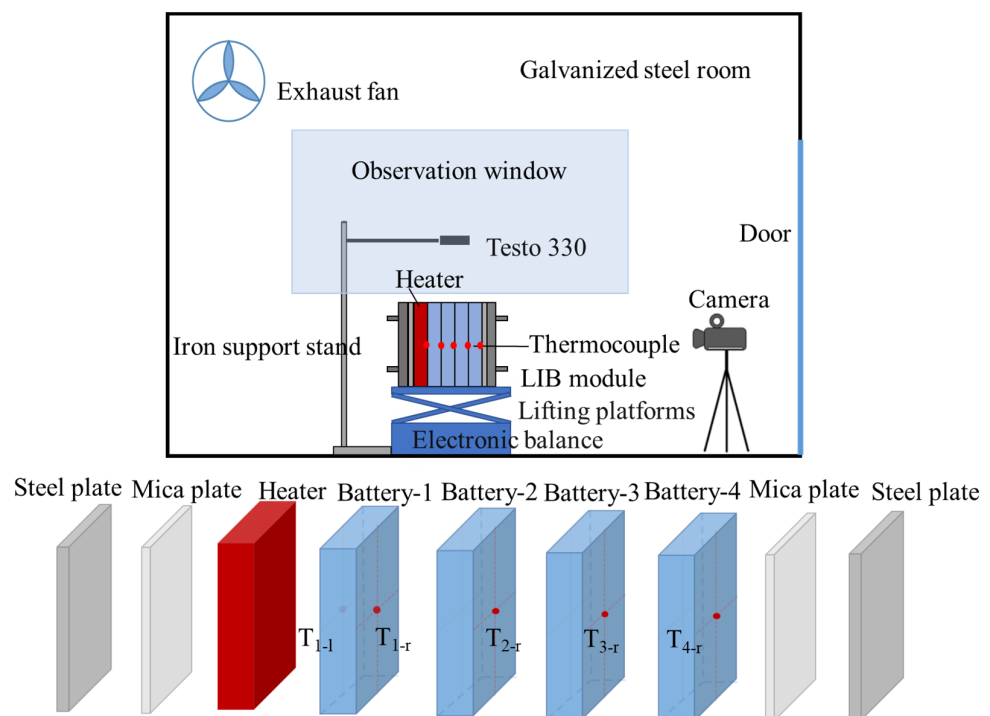


Figure 2. The TR propagation platform.

Table 2. Experimental design.

Test	Temperature (°C)	State of Health (%)	State of Charge (%)
1	RT	100	100
2	RT	100	50
3	RT	100	0
4	RT	90	100

Table 2. Cont.

Test	Temperature (°C)	State of Health (%)	State of Charge (%)
5	RT	90	50
6	RT	90	0
7	−10	90	100
8	−10	90	50
9	−10	90	0

3. Results and Discussion

3.1. Thermal Runaway of LIB Modules with Different SOC_s

3.1.1. Characteristics of Thermal Runaway Propagation with Different SOC_s

Previous studies [10] have commonly identified the following three stages in battery TR. Stage I involves the continuous heating of Bat1, leading to a side reaction [8] and accumulation of gas inside the battery. After a period of time, the safety valve opens to release gas due to the extreme temperature and pressure [26]. During Stage II, the cell's internal reaction intensifies, with TR reaching its most intense state, generating abundant sparks and smoke. During Stage III, TR ends and burning gradually subsides. Figure 3 depicts the TRP process for a fresh battery module with SOC_s of 100%, 50%, and 0%, in accordance with the TR stages described above. In the 100% SOC case, TR occurs in the first battery of the group, as indicated by I–III, which correspond with the three stages described above. Subsequently, the TR propagated with other batteries, and the three stages were repeated. The TRP process for the battery module with 50% and 0% SOC was the same, but the response of low-SOC was more moderate and the TRP time was longer than for high-SOC. Bat1 in the 0% SOC module did not exhibit burning after smoke emissions, and there were no clear indications of TRP.

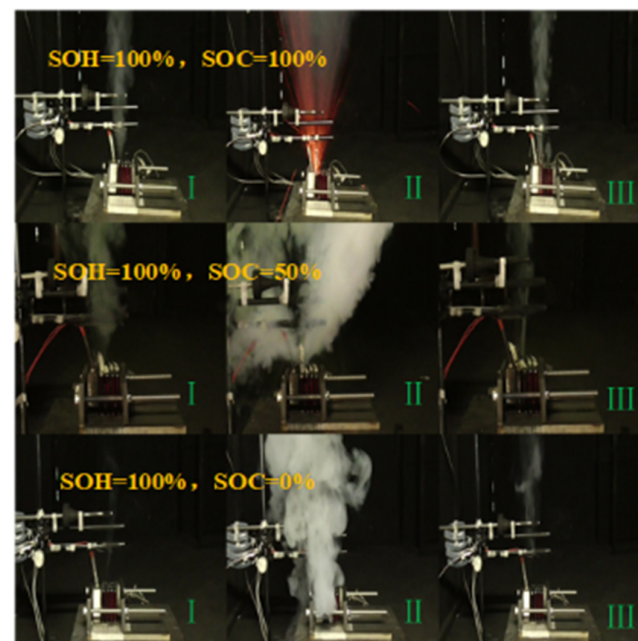


Figure 3. Thermal runaway propagation process of fresh LIBs: Stage I, Stage II, Stage III.

3.1.2. Temperature and Voltage

Figure 4 displays the temperature and voltage curves for the different SOC_s. At 100% SOC, all four cells exhibited TR, as shown in Figure 4a. As the battery temperature increased, the voltage of Bat1 dropped sharply at 406 s due to slight damage in the internal diaphragm, which resulted in a slight short circuit when the positive and negative electrodes contacted each other [8]. It is also possible that the gas produced by the side-reaction within the cell

increased the pressure within the cell and caused the current to be interrupted [15]. In this paper, the temperature of the right surface of the battery (T_{i-r}) was used to represent the temperature of the battery. The battery i safety valve opening time is marked $SV\ i$ in the temperature variation curves. At 713 s, the increase in the temperature rate and temperature curve of Bat1 was sharp, indicating that Bat1 entered the TR state. At 717 s, T_{1-r} dropped due to the smoke that was emitted from the opening of the battery safety valve, which took away a significant amount of heat [9,10]. The temperature curve then surged again at 743 s. This was caused by the large amount of heat released when Bat2 entered TR, which reheated Bat1. At this point, the inner diaphragm of Bat1 broke completely, the voltage dropped to 0 V, and Bat1's TR ended. Similarly to Bat1's temperature curve, Bat2 experienced a short temperature drop which was then heated by Bat3's TR, and repeated in subsequent experiments; it is not described further here. Bat3 and Bat4 entered the TR successively as the voltage decreased.

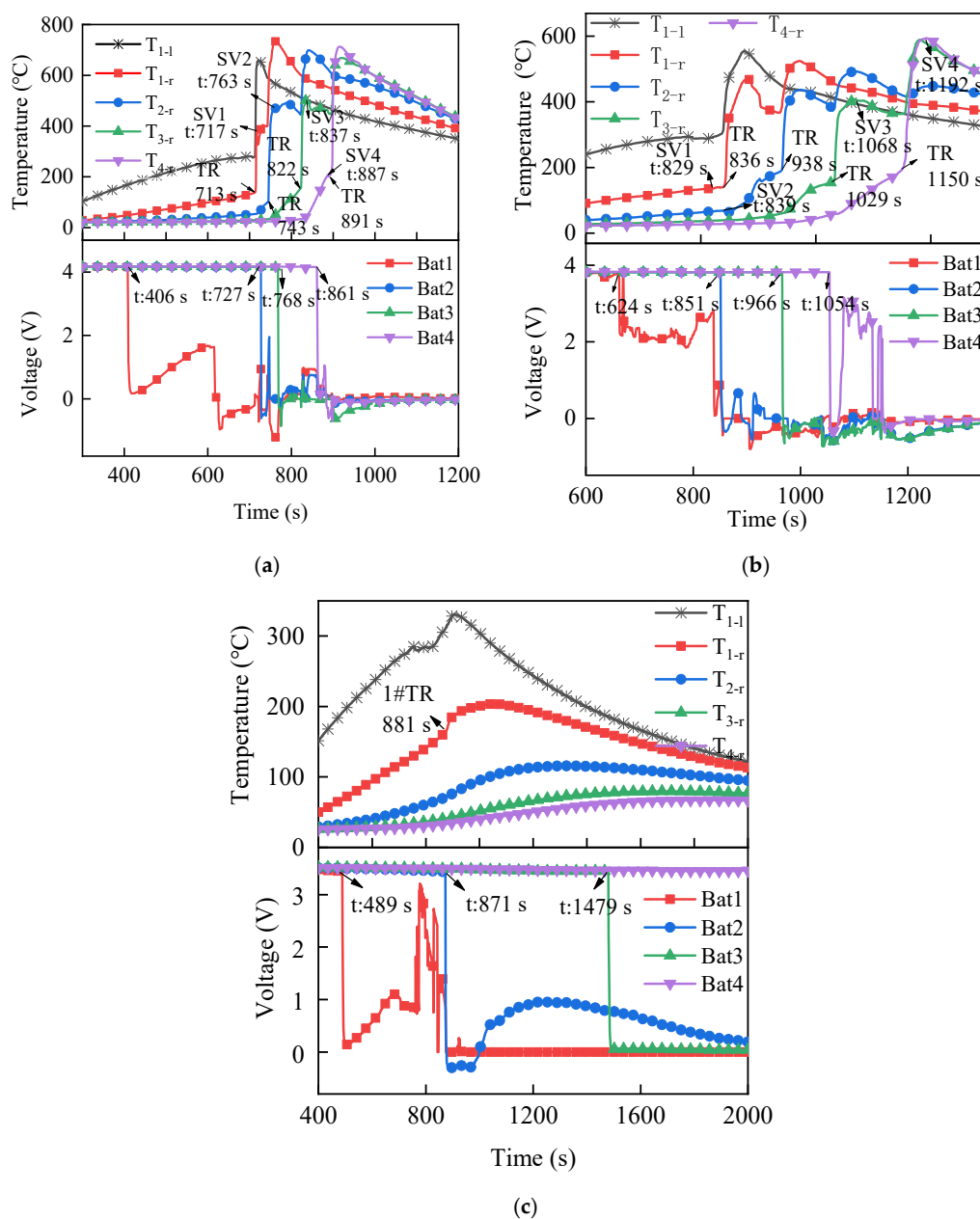


Figure 4. Temperature and voltage of 100% SOH battery modules during thermal runaway propagation: (a) 100% SOC, (b) 50% SOC, and (c) 0% SOC.

The temperature curve of 50% SOC is similar to that of 100% SOC, but milder. The TR of the battery module with 0% SOC is not evident. Only Bat1 experienced TR, whereas Bat2 and Bat3 only exhibited internal short-circuits without a violent reaction. This is because as SOC decreases, the reduction of lithium ions in the anode and the negligible amount of oxygen released by the cathode material cannot react further with the electrolyte and anode during TR; this shows a strong dependence on the lithium state of the anode [27]. Figure 5 illustrates the maximum temperatures of three battery modules during TR. The maximum temperature that can be reached with 100% SOC is above 600 °C, with Bat2 even reaching 733 °C. The battery module temperature at 50% SOC was lower than that at 100% SOC, reaching about 500 °C, whereas the maximum temperature at 0% SOC was only 330 °C. It is likely that the higher electrochemical energy content of a larger capacity cell translates into more heat, leading to higher temperatures during thermal runaway [28].

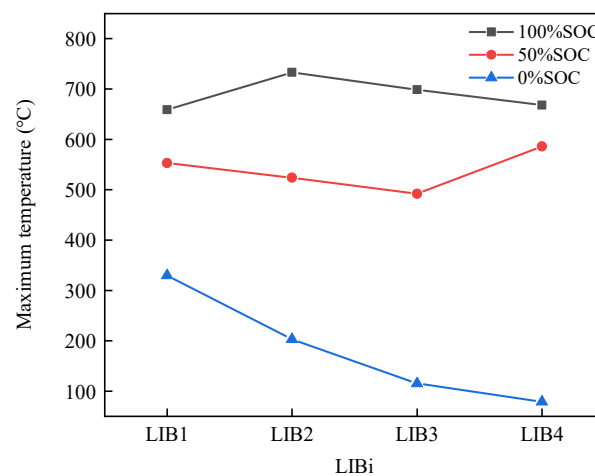


Figure 5. The maximum temperature of fresh battery modules during thermal runaway propagation.

To better understand the influence of SOC on the TRP of the battery module, we calculated the increase in temperature rate at different SOC levels using the temperature curve of the battery surface, based on Equation (2), as follows:

$$\frac{dT_i}{dt} \approx \frac{T_{i,t+1} - T_{i,t}}{\Delta t} \quad (2)$$

where $\frac{dT_i}{dt}$ represents the increase in temperature rate of battery i , and $T_{i,t}$ and $T_{i,t+1}$ represent the temperature of battery i at t s and $t + 1$ s, respectively.

The increase in temperature rate curve is presented in Figure 6. The $i\#$ ($i=1,2,3,4$) corresponds to the battery number i . In this paper, the TR time is defined as the starting moment when the increase in temperature rate is constant and greater than 1 °C/s, in accordance with previous studies [9]. From the figure, it is evident that all cells at 100% SOC and 50% SOC experience TR. In Figure 6a, the rapid increase in the temperature rate of LIBs is attributed to the uncontrollable exothermic reaction of the internal materials when the battery is overheated, coupled with slow heat dissipation. The increase in temperature rate of the battery module at 100% SOC exceeded 90 °C/s, whereas at 50% SOC, it was lower, but still reached nearly 30 °C/s. Only the increase in temperature rate of Bat1 at 0% SOC exceeded 1 °C/s. The increase in temperature rate increased as the SOC increased. This is because a higher SOC results in more oxygen being released due to electrode decomposition. The released oxygen then reacted with the electrolyte, generating additional heat. As a result, the heat release became faster and more intense, leading to a more pronounced and violent thermal response [29]. Additionally, Figure 7 displays the TR onset time of the battery module at three different SOC levels. The time for TR occurrence was delayed with decreasing SOC, confirming that cells with lower SOC levels are more internally stable and need

to absorb additional heat to induce TR. Moreover, the higher the SOC, the shorter the TRP time of the battery module and the faster the propagation speed.

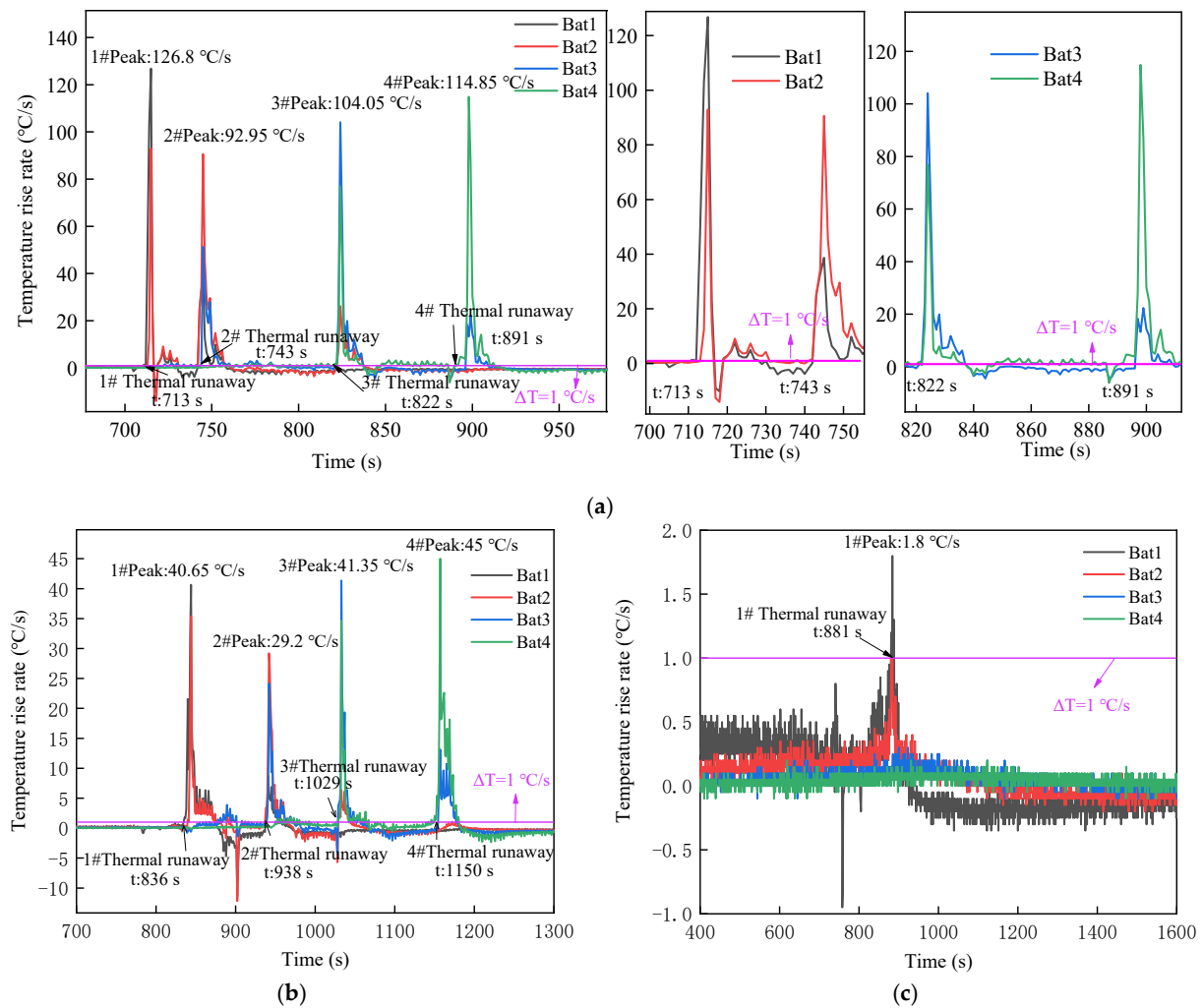


Figure 6. Increase in temperature rate of 100% SOH battery modules during thermal runaway propagation: (a) 100% SOC, (b) 50% SOC, and (c) 0% SOC.

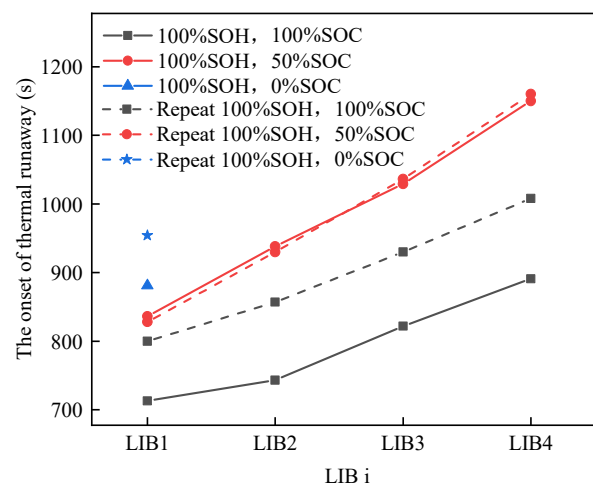


Figure 7. The onset of thermal runaway.

3.1.3. Mass Change

Figure 8 presents the mass change curves of the fresh cell modules for the three different SOC levels during TR. The module at 0% SOC experienced a total mass loss of 3.4 g. At 50% SOC, the curve exhibits a total mass loss of 25.3 g, as characterized by four distinct downward trends that align with the TR of four individual cells. As the TR propagated, the mass loss of Bat2- and Bat4 gradually increased, except for Bat1. This is because Bat1 was heated by the heating block, and the gas exited the safety valve slowly. Bat2 was violently heated by the burning Bat1, resulting in a shorter gas release. The gradual increase in mass loss of Bat3 and Bat4 was due to the fact that Bat1 and Bat2 already vented, and they had more space to expand and release more gas [30]. The 100% SOC battery module experienced a total mass loss of 45 g, with a single cell losing the most mass. The figure illustrates that the battery experienced greater mass loss as the SOC increased. This can be attributed to the higher energy stored in the electrode at higher SOC levels, resulting in more intense reactions with the electrolyte, and consequently, leading to a greater mass loss. In the future, it might be possible to design a quality detection device that can detect the TR of batteries in order to mitigate potential casualties.

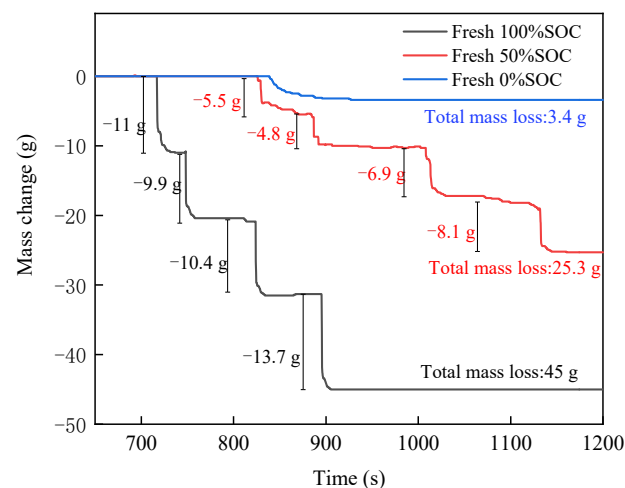
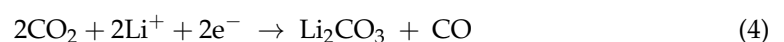
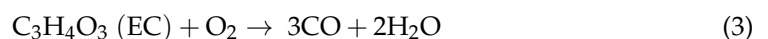


Figure 8. Mass change of fresh LIBs at different SOC levels.

3.1.4. CO Emission

During the TR of LIB modules, an amount of smoke is produced. Previous studies have identified that the gases emitted during TR mainly consist of CO_2 , CO , H_2 , C_2H_4 , CH_4 , C_2H_6 , and C_3H_6 [31]. Some of these gases can be toxic to humans. For instance, CO , which is a major concern, can originate from the following two sources [27]: incomplete combustion of the carbonate solvent and a REDOX reaction between lithium ion and CO_2 , as shown in the following reaction equations.



In this experiment, the emission from the LIB modules during TR was monitored using a professional flue gas analyzer (Testo, West Chester, PA, USA, 330-1 LL). Figure 9 shows the CO emission results for three SOC battery modules with 100% SOH. As the SOC increased, the duration of time where gases were emitted decreased, confirming that a higher SOC results in a faster TRP. The maximum CO emissions for 100% SOC, 50% SOC, and 0% SOC can reach 3229 ppm, 597 ppm, and 96 ppm, respectively. The SOC can affect CO emission during TR, and as SOC increased, CO emissions also increased, which is consistent with previous research findings [32]. Moreover, CO is a flammable and explosive gas, and when its concentration is too high, it may cause secondary burning. Le Chatelier's

principle (L-C), shown in Equation (5), was widely used to calculate the flammability limit of gases, where L_{mix} represents the flammability limit of a mixture, L_i is the flammability limit of gas i , and x_i is the quantity of combustible gas. There was a positive correlation between the SOC and the release of CO, as shown in Equation (5). The higher the SOC, the greater the amount of CO released, and consequently, the higher the risk of explosion. This serves as a valuable reference for safety management practices. For instance, the timing and duration of ventilation, as well as the quantity of inert gas injection, can be determined to effectively mitigate the toxic effects of gases [26].

$$L_{mix} = \left[\sum_{i=1}^n \frac{x_i}{L_i} \right] - 1 \times 100\% \quad (5)$$

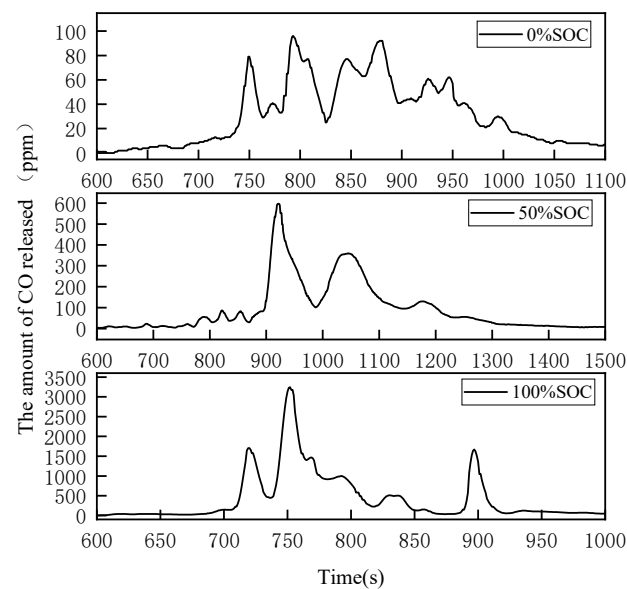


Figure 9. CO emissions of fresh LIBs at different SOC levels.

3.2. Thermal Runaway of LIB Modules with Different SOHs

3.2.1. Characteristics of Thermal Runaway Propagation in Aging Batteries

Figure 10 compares the TRP situation of the cell modules at 100% SOH and 90% SOH after being aged with RT. As shown in the figure, the cell that underwent RT aging continued to follow the three stages of the TRP process (Section 3.1.1). Based on the pictures captured by the camera, differences can be observed with the fresh battery module. Firstly, when the SOC was 100%, the fresh module's Bat1 emitted thick, long-lasting smoke before ejecting sparks, whereas Bat1 aged at RT emitted a faint smoke before burning violently, which is barely visible. Additionally, when the TR propagated to other batteries, the smoke emitted by the battery module after RT aging was thicker and more intense than the fresh battery. At 50% SOC, the exhaust smoke emitted from the fresh battery module's Bat1 was initially weak, but the emissions were more violent with broader radiation when the safety valve was opened. However, the exhaust smoke of the aged Bat1 was slightly stronger than that of the fresh battery module in the early stages, and the smoke was stronger after the safety valve was opened, albeit lighter than that of the fresh battery. The fresh Bat2 did not release gas violently immediately after the safety valve opened. However, the exhaust behavior of Bat2 became violent as time passed, while the aging Bat2 immediately released a large amount of gas after the safety valve opened. The fresh battery module's Bat3 emitted smoke for a slightly longer period of time after the safety valve was opened, compared with the aged battery module's Bat3; the aged battery module's Bat4 opened the safety valve more rapidly. At 0% SOC, at first, both modules' Bat1 released gas slowly. The difference between them is that the fresh battery module did not eject gas violently, and the

entire process was relatively quiet. After aging, the safety valve could be heard popping, and the smoke was more intense. The aging Bat2 also exhibited jet-like behavior, but it was less pronounced, whereas the fresh cell's Bat2 did not exhibit jet-like behavior.

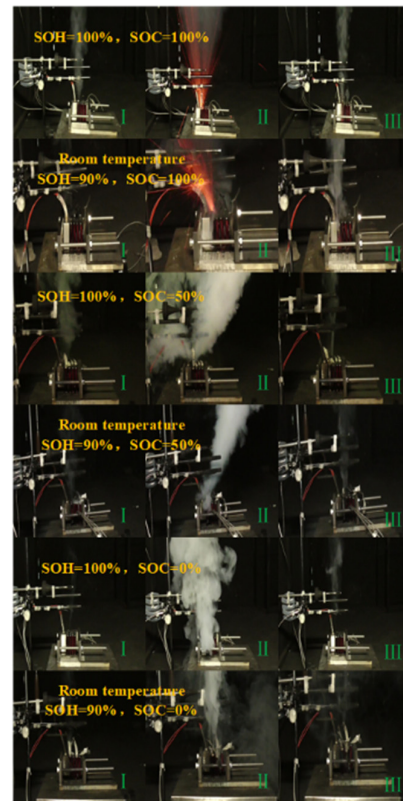


Figure 10. Thermal runaway behavior after aging at room temperature: Stage I, Stage II, Stage III.

3.2.2. Temperature and Voltage

Figure 11 displays the temperature and voltage curves of the TRP process with three different SOC after RT aging. The curves are identical to those of fresh cells, which undergo processes such as voltage drop, safety valve opening, TR intensification, and TRP. Generally, after aging, TR continues to adhere to the rule established in Section 3.2.1: the greater the SOC, the more heat released.

Table 3 summarizes the maximum increase in temperature rate of the three different SOC after cyclic aging, in accordance with Equation (1). Figure 12 compares the key time points of TR before and after aging, in order to compare the impact of cyclic aging on the TRP of LIB modules. The thermal runaway onset times (t_{TR}) of Bat1–Bat4 after aging with different SOC are as follows: for 100% SOC, they are 669 s, 687 s, 789 s, and 897 s, respectively; for 50% SOC, they are 700 s, 802 s, 890 s, and 990 s, respectively; and for 0% SOC, it is 795 s. Comparing the fresh battery modules, the aging battery module's TR start time is advanced; this is consistent with previous studies [15]. As the structure of the negative electrode changes during battery charging and discharging cycles due to the insertion and disinsertion of lithium ions, the solid electrolyte interface (SEI) film on the negative electrode's surface ruptures. Once the SEI film is ruptured, the negative electrode reacts with the electrolyte to form a new SEI film, and this process is repeated, which causes SEI instability and poor thermal stability [33]. For 100% SOC, the increase in temperature rate after aging is lower than that of the non-aging battery module. This can be attributed to the aging battery's reduced internal capacity, as well as the consumption of positive and negative electrode materials and lithium ions during the cyclic aging process. These factors collectively contribute to a reduction in the severity of TR. However, for 50% and 0% SOC, the increase in temperature rate was larger than that of the non-aging battery modules,

because the aging battery accumulated heat during the early stages, then experienced a violent burst during TR.

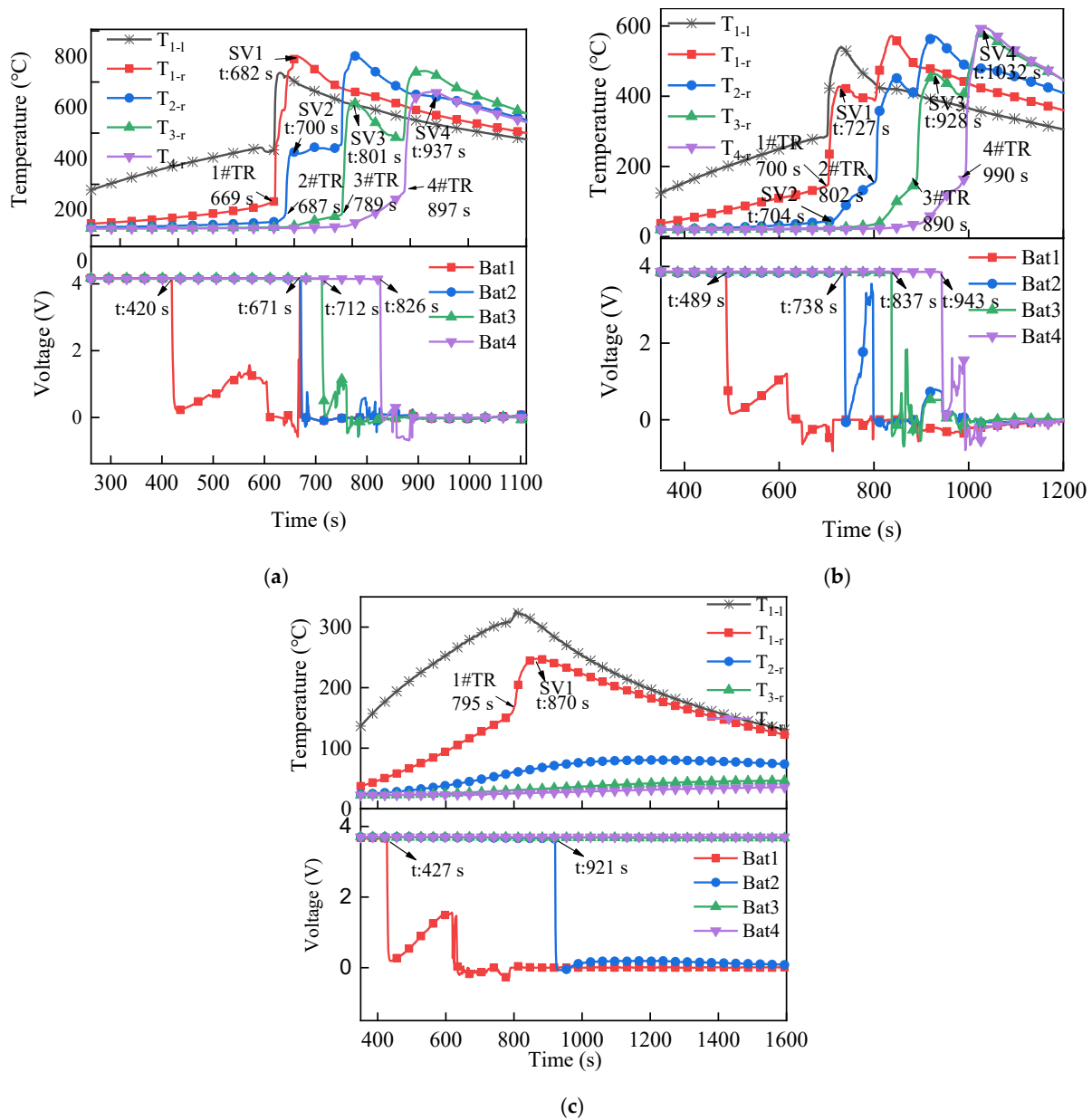


Figure 11. Temperature and voltage of battery modules aged with RT during thermal runaway propagation: (a) 100% SOC, (b) 50% SOC, and (c) 0% SOC.

Table 3. Comparison of maximum increase in temperature rates of battery modules before and after aging at room temperature.

Test	Bat1	Bat2	Bat3	Bat4
100% SOH, 100% SOC	126.8 °C/s	92.95 °C/s	104.05 °C/s	114.85 °C/s
90% SOH, 100% SOC	116.5 °C/s	55.8 °C/s	69.35 °C/s	61.8 °C/s
100% SOH, 50% SOC	40.65 °C/s	29.2 °C/s	41.35 °C/s	45 °C/s
90% SOH, 50% SOC	32.75 °C/s	49.4 °C/s	53.75 °C/s	68.05 °C/s
100% SOH, 0% SOC	1.8 °C/s	-	-	-
90% SOH, 0% SOC	4.3 °C/s	-	-	-

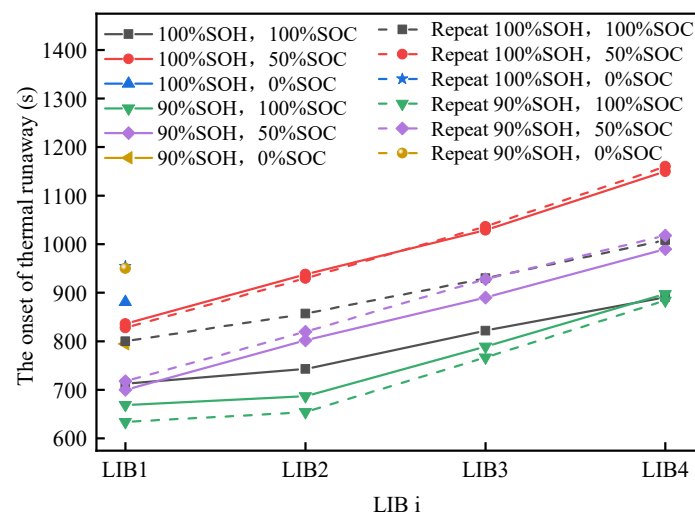


Figure 12. The effect of aging on the occurrence time of thermal runaway.

3.2.3. Mass Change

Figure 13 displays the mass change curve of the RT aged battery modules. Compared with the fresh modules, the aging battery module experienced greater mass loss. This may be because the SEI was repeatedly generated and broken by cyclic aging with RT, which caused part of the mass loss. Moreover, the electrode structure was damaged due to the frequent insertion and deintercalation of lithium ions in the electrode, resulting in more mass loss when TR occurred. Furthermore, during the TR of the aging battery modules, the mass loss among individual cells was irregular, unlike the consistent pattern observed in fresh battery modules. This may be due to changes in the internal structure of the battery and the number of active substances after aging, which affect the injection effect of the battery and cause the regular pattern of mass change to disappear.

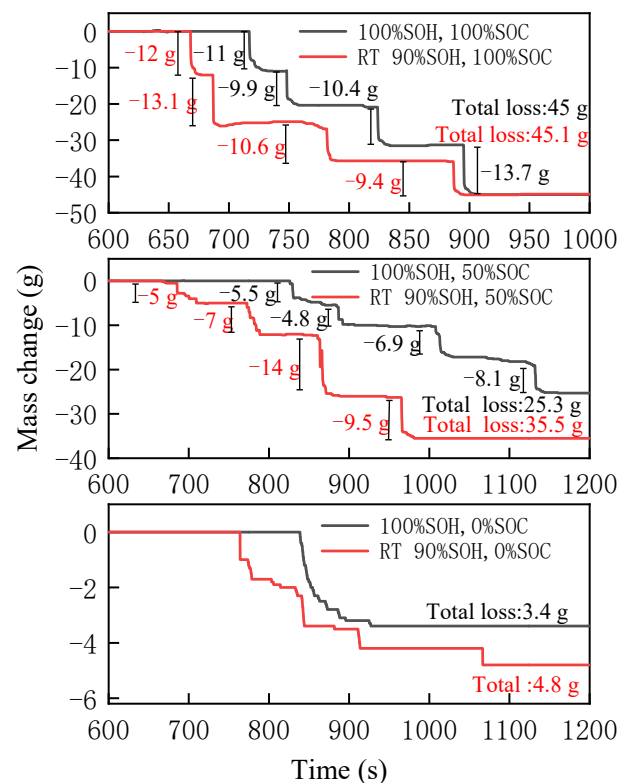


Figure 13. Mass change comparison before and after aging at room temperature.

3.3. Thermal Runaway of LIB Modules with Different Aging Temperatures

3.3.1. Characteristics of Thermal Runaway Propagation in Aging Batteries

Figure 14 shows the characteristics of the battery modules after low temperature aging ($-10\text{ }^{\circ}\text{C}$) during TR. To investigate the effect of aging temperature on TRP, the performance of the battery module during TR was determined by comparing RT aging and low temperature aging. First, when the SOC was 100%, the TR of the battery module aged at $-10\text{ }^{\circ}\text{C}$ occurred later than that of the battery module aged with RT. Second, when batteries exhibited TR, the reaction of the battery aged with RT was more intense. An apparent pillar of fire was observed and a large number of sparks were emitted. In contrast, the battery aged at $-10\text{ }^{\circ}\text{C}$ did not exhibit an obvious pillar of fire when it exhibited TR. Finally, based on the video recording, the battery module aged at $-10\text{ }^{\circ}\text{C}$ completed TRP faster than that aged with RT. When the SOC was 50%, the TR of the battery module after low temperature aging was also slower than that of the battery module aged with RT, but it also ended earlier. In addition, it was observed that the safety valve of RT aged cells gradually opened as the smoke increased. In contrast, the Bat2–Bat4 in the battery module that aged at $-10\text{ }^{\circ}\text{C}$ suddenly opened the safety valve before gas release. When the SOC was 0%, the TR intensity was lower than 50% SOH. In the battery module aged at $-10\text{ }^{\circ}\text{C}$, Bat1 opened the safety valve before the gas release, whereas in the battery module aged with RT, Bat1 opened the safety valve after the gas release. Within a few seconds after the safety valve was opened, the gas gradually dissipated, and TR ended.

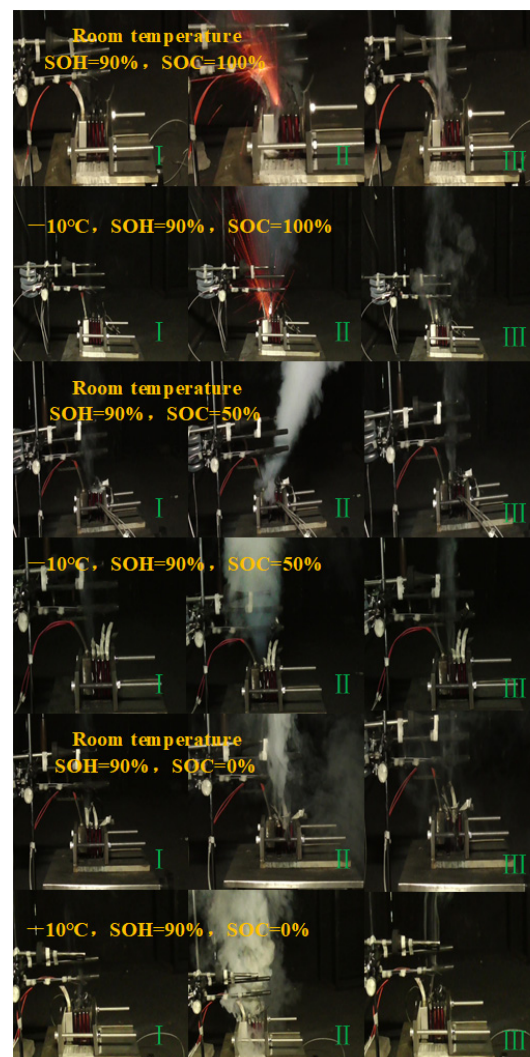


Figure 14. TR behavior of battery modules aged at $-10\text{ }^{\circ}\text{C}$: Stage I, Stage II, Stage III.

3.3.2. Temperature and Voltage

Figure 15 illustrates the temperature and voltage curves of the battery module after low-temperature aging for three different SOC levels. The battery module exhibited a similar behavior to the previous sets in TR. The temperature slowly increased, along with the heating block, followed by a temporary voltage drop. Subsequently, the safety valve was opened, and the battery entered a stage of vigorous heat release, causing a complete voltage drop to 0 V. After TR, the battery temperature gradually decreased. With the 0% SOC level, only Bat1 and Bat2 were short-circuited, indicating that the thermal runaway did not propagate to others.

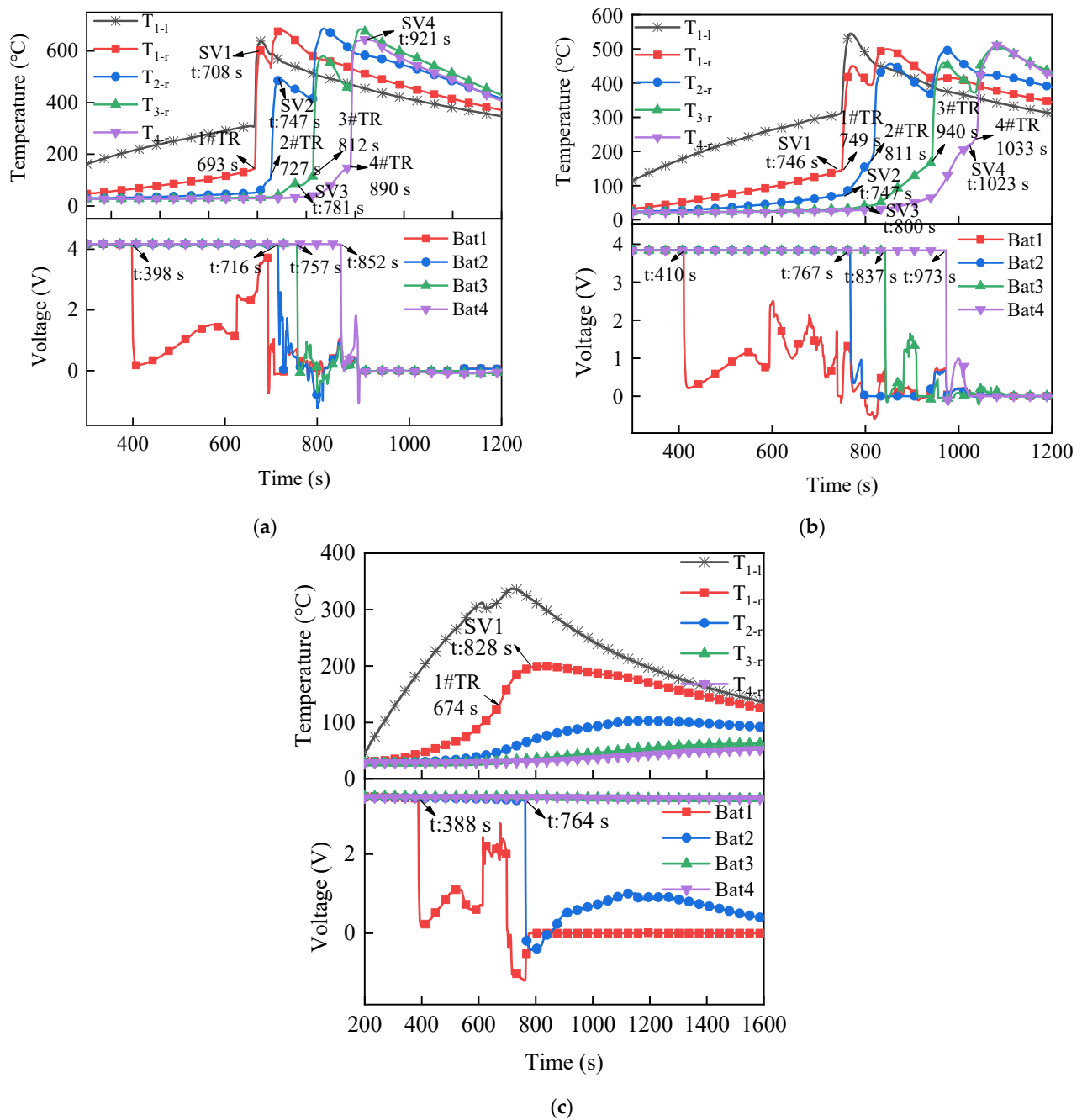


Figure 15. Temperature and voltage change of battery modules aged at -10°C : (a) 100% SOC, (b) 50% SOC, and (c) 0% SOC.

Table 4 shows the maximum increase in temperature rate of batteries under TR after low-temperature and RT aging. Figure 16 illustrates the influence of different aging temperatures on the required time of TRP. Moreover, 0% SOH is not discussed since it does not have thermal runaway propagation. The total times for the TRP of the battery module at 100% SOC and 50% SOC are 197 s and 284 s, respectively. These times are lower than those observed under RT aging, which are 228 s for 100% SOC and 290 s for 50% SOC. This is because after low-temperature aging, the numerous lithium ions in the anode form lithium dendrites that are more prone to reacting with the electrolyte than graphite, resulting in poor thermal stability and a higher likelihood of TR [28]. Furthermore, when the SOC is 100%, the increase in temperature rates after low-temperature aging were 164.3 °C/s, 51.6 °C/s, 83.9 °C/s, and 103.15 °C/s, respectively, which are mostly greater than that of the battery after RT aging; these results are the same as those in Cai et al. [15]. Nevertheless, when the SOC is 50% and 0%, the battery module aged under RT conditions experienced a higher increase in temperature rate, compared with the battery module aged under low-temperature conditions. These can be attributed to the incomplete detachment of the safety valve during the thermal runaway process, which trapped hot gas within the battery and impeded heat dissipation. In contrast, the battery module aging at a low temperature opened the safety valve prior to gas emission, facilitating efficient heat dissipation.

Table 4. The maximum increase in temperature rate of the battery modules aging with RT or −10 °C.

Test	Bat1	Bat2	Bat3	Bat4
RT, 100% SOC	116.5 °C/s	55.8 °C/s	69.35 °C/s	61.8 °C/s
−10 °C, 100% SOC	164.3 °C/s	51.6 °C/s	83.9 °C/s	103.15 °C/s
RT, 50% SOC	32.75 °C/s	49.4 °C/s	53.75 °C/s	68.05 °C/s
−10 °C, 50% SOC	39.55 °C/s	25.9 °C/s	28.95 °C/s	27.1 °C/s
RT, 0% SOC	4.3 °C/s	-	-	-
−10 °C, 0% SOC	1.9 °C/s	-	-	-

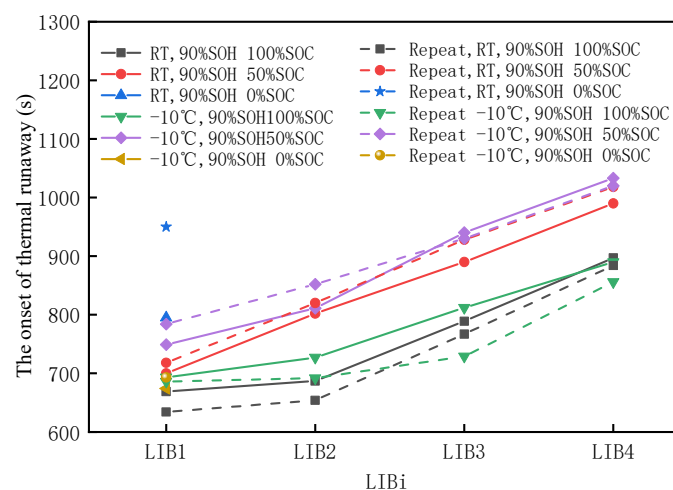


Figure 16. The effect of aging temperature on the occurrence time of thermal runaway.

3.3.3. Mass Change

Figure 17 shows the mass change of the battery module after being aged at room temperature and −10 °C during TRP. At 100% SOC, the mass loss of individual cells after low-temperature aging was higher than that after RT aging. This phenomenon can be observed in the recorded video, where the gas injection was more intense and accompanied by a prominent fire column after low-temperature aging. Consistent with previous studies, this phenomenon can be attributed to the high surface area of the lithium anode, which promotes the formation of a number of SEI layers on the surface of the lithium metal. These

SEI layers subsequently undergo decomposition. Additionally, the structural changes resulting from the reduction of lithium content in the cathode contributed to the increased mass loss observed [6]. At 50% SOC, the mass loss of TR after RT and low-temperature aging was 35.5 g and 20.5 g, respectively. This was because of an early rupture in the safety valve of the low-temperature aging battery module, which led to a minor internal pressure loss of the battery and an inability to eject excess gas. At 0% SOC, the loss of TR after low-temperature aging was also lower than that after RT aging, due to the same reason mentioned above.

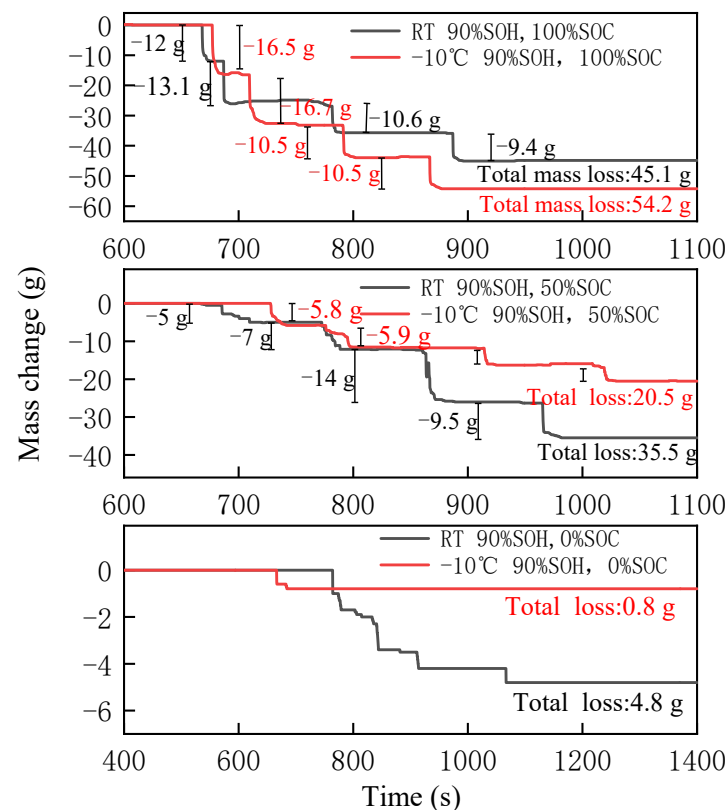


Figure 17. Mass change of the battery module at different temperatures.

From the above analysis, it can be concluded that the TR intensity of LIBs will increase after low temperature aging, which has also been confirmed by others [6,15]. In real life, when using electric vehicles in winter, or in cold countries in Europe, it is necessary to take some precautions in order to avoid the impact of low temperatures on the safe use of batteries. In recent years, various battery preheating technologies have been developed. Luo [34] designed a cPCM that can heat battery modules at 13.4 °C/min and provide a comfortable environment of 20–55 °C for the battery at extreme temperatures of −40 to +50 °C. Jiang [35] proposed a novel self-heating method by applying a discharge current on the AC current. This method enabled the battery module to reach a temperature range of −20.8 °C to 2.1 °C within 600 s, with an internal temperature difference of less than 1.6 °C. Importantly, this heating process does not cause a significant loss of lithium ions or a reduction in battery life.

3.4. Analysis of Heat Transfer

In real-life, LIBs accidents frequently result from the TR of an individual battery. To improve our understanding of the TRP in LIBs, researchers have also studied heat transfer between cells. Studies have demonstrated that in an open environment, flame radiation contributes only a little to the overall heat transfer. The primary mode of heat transfer for the battery involves contact between battery shells [36]. The heat transfer analysis

in this paper was carried out under ideal conditions. It is believed that the temperature distribution within a single battery follows a linear relationship, and the core temperature can be determined by averaging T_{i-l} and T_{i-r} . According to the calculation methods used in previous studies [27], the heat flow transferred from bat_i to bat_{i+1} can be expressed by Equation (6), with $R_{bat-bat}$ representing the thermal resistance between bat_{i+1} and bat_i , which can be evaluated using Equation (7). $Q_{i \rightarrow (i+1)}(t)$ is the heat transfer from bat_i to bat_{i+1} at time t , calculated using Equation (8).

$$q_i(t) = \frac{T_i(t) - T_{(i+1)}(t)}{R_{bat-bat}} \{i \in 1, 2, 3, 4\} \quad (6)$$

$$R_{bat-bat} = \frac{\delta}{\lambda_z} \quad (7)$$

$$Q_{i \rightarrow (i+1)}(t) = A \times \int_{t_{TR,i}}^{t_{TR,(i+1)}} q_i(t) dt, i \in \{1, 2, 3, 4\} \quad (8)$$

In this study, the heat transfer distance (δ) represents the distance between adjacent battery centers, which was 0.01 m. The thermal conductivity of the battery (λ_z) was $3.4 \text{ Wm}^{-1}\text{k}^{-1}$. The area (A) through which the heat flowed was 0.0017 m^2 in this paper. Figure 18 presents the heat transfer calculations for the 100% SOC and 50% SOC battery modules, as no TRP was observed in the 0% SOC battery module. The heat transfer between adjacent batteries was found to be less than 25 kJ. Table 5 presents the average value of heat transfer between adjacent cells. The results indicate that both the 50% SOC battery module (after aging at room temperature and -10°C) as well as the fresh 50% SOC battery module exhibit higher average heat transfer compared with a 100% SOC battery module under the same working conditions. This finding suggests that a battery module with high SOC has lower thermal stability and requires less heat absorption to trigger TR. In addition, aging increases the average heat transfer between the same SOC battery modules. However, it was observed that the average heat transfer between 50% SOC battery modules aged at -10°C is lower than the average heat transfer under the other two conditions. This difference can be speculated to be caused by the combination of aging and low capacity.

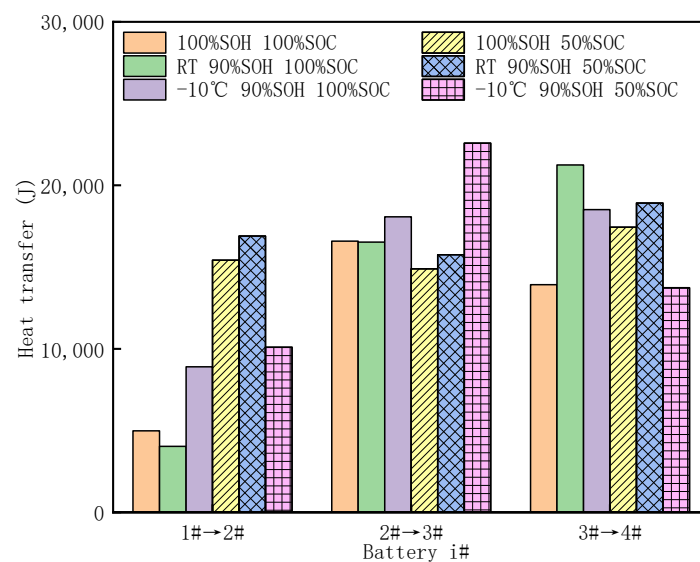


Figure 18. Heat transfer between LIBs.

Table 5. The average heat transfer between adjacent cells of different battery modules.

Battery Type	$Q_{\text{average}}(\text{J})$
100% SOH, 100% SOC	11828
100% SOH, 50% SOC	15916
RT, 90% SOH, 100% SOC	13934
RT, 90% SOH, 50% SOC	17187
−10 °C, 90% SOH, 100% SOC	15159
−10 °C, 90% SOH, 50% SOC	15471

4. Conclusions

In this study, we explored, in detail, the TR characteristics of the battery modules with varying SOC, SOH, aging temperatures and its propagation. We obtained critical parameters such as temperature, voltage, mass, and flue gas during the TRP. The experimental results led us to draw the following conclusions:

1. Increasing the SOC of the battery module leads to a more severe TR, as evidenced by earlier TR start times, accelerated TRP, increased temperature and temperature rates, greater mass loss, and higher CO emissions. These factors contribute to the increased harm caused by TR.
2. Compared with the fresh battery modules, the room-temperature aged battery modules were less thermally stable and lost more mass.
3. Compared with room temperature aging, the thermal stability of the battery modules was worse after low temperature aging, which was reflected in a faster propagation rate, higher increase in temperature rate, and greater mass loss.
4. The heat transfer between adjacent cells was less than 25 kJ. Thermal runaway propagation between cells with higher SOC requires less heat at the same SOH, and the average heat transfer between adjacent cells increased with the aging degree.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author/authors. The data are not publicly available due to privacy restrictions.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

LIBs	lithium ion batteries
TR	thermal runaway
TRP	thermal runaway propagation
SOC	state of charge
SOH	state of health
SEI	solid electrolyte interface
CSBC	copper slug battery calorimetry
RT	room temperature
CV-CC	constant current and constant voltage
CC	constant current
SV	safety valve

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