

Revealing the Thermal Runaway Behavior of Lithium Iron Phosphate Power Batteries at Different States of Charge and Operating Environment

Tianyi Li^{1,*}, Yinghou Jiao^{2,*}

¹ College of Intelligent Systems Science and Engineering, Harbin Engineering University, Harbin 150001, P. R. China.

² School of Mechatronics Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China.

*E-mail: litianyi0830@163.com; jiaoyh@hit.edu.cn

Received: 6 July 2022 / Accepted: 15 August 2022 / Published: 10 September 2022

With the widespread use of Li-ion batteries, their safety issues have received increasing attention. Thermal abuse, electrical abuse, mechanical abuse, etc., can cause thermal runaway of batteries. Therefore, understanding Li-ion battery thermal runaway behavior and its suppression is of great practical significance. In this work, an experimental platform composed of a 202-Ah large-capacity lithium iron phosphate (LiFePO₄) single battery and a battery box is built. The thermal runaway behavior of the single battery under 100% state of charge (SOC) and 120% SOC (overcharge) is studied by side electric heating. Systematic studies are conducted to investigate the thermal runaway behavior of LiFePO₄ battery modules operating in different environments (open area and power battery box) and the suppression effect of spraying fire extinguishing media on thermal runaway. The results show that the decomposition of the solid electrolyte interphase (SEI) film in the battery is the key reason for thermal runaway, which is more intense in the overcharged state. To provide early warning of battery thermal runaway, it is suggested to collect the upper surface temperature of the battery in the battery management system. Moreover, the thermal runaway temperature of the Li-ion battery is lower in the power battery box than in the open area, but there is a risk of causing a chain reaction of the surrounding batteries. At this time, timely fire extinguishing agent spraying can effectively reduce the temperature of the thermal runaway battery and prevent the subsequent chain reaction. This study provides deep insight into the thermal runaway behavior of large-capacity LiFePO₄ batteries that work in practical situations.

Keywords: Li-ion battery, thermal runaway, overcharge, state of charge, operating environment

1. INTRODUCTION

Li-ion batteries have the advantages of high energy density, long cycle life, and no pollution to the environment, and they are widely used in electric vehicles, power storage stations and other fields[1,2]. However, the number of fire and explosion cases associated with Li-ion batteries has increased in recent years, which leads to increasing attention on the safe operation of Li-ion batteries.

Therefore, it is of great practical importance to study the characteristics of the thermal runaway behavior of Li-ion batteries to provide a reliable early warning scheme for the safe use of batteries.

In recent years, many researchers have conducted a series of studies on the mechanism of thermal runaway of Li-ion batteries, and the causes of thermal runaway of Li-ion batteries are summarized as thermal abuse[3,4], electrical abuse[5,6] and mechanical abuse[1,7]. When the Li-ion battery is affected by high temperature, SEI film decomposition will cause direct contact and redox reactions between the anode and the electrolyte[8]. As a result, flammable gas and a large amount of heat are released, which accelerate the melting of the separator and cause the short circuit of the battery[9,10]. Simultaneously, both cathode and anode violently react with the electrolyte, which increases the internal pressure of the battery. This phenomenon can cause severe thermal runaway of the battery, combustion and even explosion[11,12]. Lu.[13] reported that when thermal runaway occurred in Li-ion batteries, the temperature of the battery surface and the surrounding environment would significantly increase. At this time, the appearance of an open flame may cause a chain reaction in the adjacent battery and circuit inside the battery box. Wang.[14] showed that the ohmic heat[15] generated by the short circuit of cylindrical Li-ion batteries under mechanical abuse was the main cause of temperature rise in a short time. Yuan.[16] conducted an overcharge test on Li-ion batteries by continuously overcharging the Li-ion battery to a state of charge (SOC) of 200%. They found that the internal temperature of the battery rose to 235°C, and the battery was in a thermal runaway state, which finally caused combustion and explosion.

To date, the 18650 cylindrical battery is the most popular system to study the battery thermal runaway behavior. These studies on thermal runaway and its propagation are usually conducted in nonpractical scenarios. Additionally, few studies have focused on the thermal runaway behavior of Li-ion batteries in different operating environments. Moreover, most studies have been conducted on ternary Li-ion batteries[17,18], and thermal runaway studies on square-shaped batteries, especially large-capacity LiFePO₄ batteries, have rarely been reported. Herein, we construct an experimental platform containing a 202-Ah square-type LiFePO₄ single battery and a battery box to study the thermal runaway behavior of LiFePO₄ batteries in different operating environments and SOC states, which aims to provide experimental data and support for thermal runaway warning and its suppression.

2. EXPERIMENTAL

2.1 Experimental platform construction

The parameters of the LiFePO₄ battery in this experiment are shown in Table 1.

A single battery thermal runaway experimental setup with a LiFePO₄ battery box for electric buses and perfluorohexanone fire extinguishing devices was built as an experimental platform. The experimental platform also included a combustion chamber, a battery charging and discharging cabinet, a DAM-TC16-N thermocouple data acquisition device, a cloud thermal image type infrared thermal imager, and a high-speed camera.

Table 1. Basic parameters of the experimental battery

Parameters	Value/Composition
Geometric dimensions L × W × H (mm × mm × mm)	174 × 54 × 207
Rated voltage/V	3.2
Rated capacity/Ah	202
Electrolyte	LiPF ₆ , ethylene carbonate (EC), methylene carbonate (EMC), propylene carbonate (PC), vinylidene carbonate (VC)
Anode	Graphite
Cathode	LiFePO ₄

2.1.1 Single battery thermal runaway experimental device

Zhu.[19] showed that when the battery was heated at different positions to induce thermal runaway, the time of thermal runaway by side heating was earlier than that by bottom heating. To study the worst thermal runaway situation, experiments were conducted by side heating, and the experimental setup is shown in Figure 1. Two metal clamps were used to fix the LiFePO₄ battery, with a 900-W electric heating plate installed on one side of the battery. To minimize the effect of heat transfer between the heating plate, the battery and metal clamps, heat insulation panels were installed on the inner side of the fixtures on both sides. The experiments were performed in the combustion chamber.

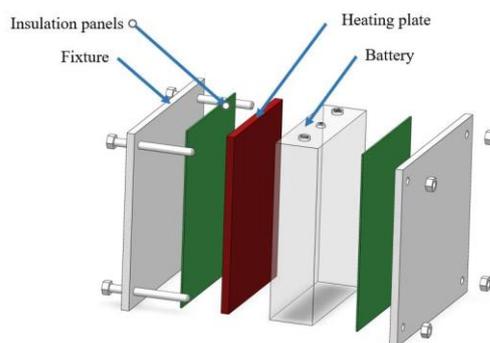


Figure 1. Diagram of the experimental device for the single LiFePO₄ battery thermal runaway experiment.

2.1.2 Li-ion battery box construction

A 1:1-scale battery simulation experimental box with a commercial electric bus battery box was constructed with a size of 1060 × 660 × 250 (mm). As shown in Figure 2, the experimental battery box included 9 large-capacity single batteries and 36 model batteries. Because the battery shell would expand during the process of thermal runaway, which could result in poor contact between temperature points and battery and consequently measurement errors, iron hoops were used to bundle 9 square aluminum

shell batteries together to reduce the effect of battery expansion. A 900-W electric heating plate was installed at the middle of the right side in the battery box, which could be externally controlled to open and close. In addition, the battery box was connected to the perfluorohexanone fire extinguishing device through a rubber hose, so that the battery thermal runaway could be suppressed through the fire extinguishing device when it occurred in the battery box.

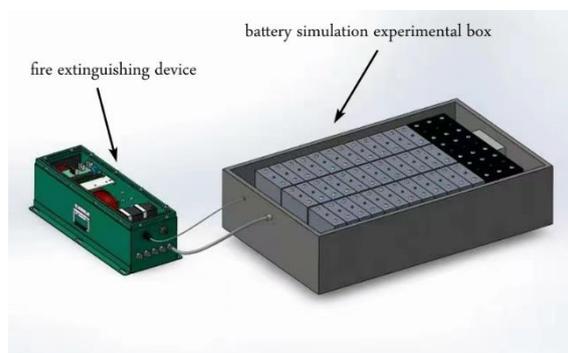


Figure 2. Diagram of the thermal runaway experimental setup of the LiFePO₄ module box.

2.2 Experimental protocol design

Three groups of LiFePO₄ battery thermal runaway experiments were designed. The experimental schemes and objectives are shown in Table 2.

Table 2. Experimental protocol and experimental purpose

Serial number	Experimental program	Purpose of the experiment
1	Heating the 202 Ah LiFePO ₄ single battery at 100% SOC in open area until the safety valve opens, recording the temperature change at each point of the single battery.	To determine the selection of thermal runaway temperature point of the battery
2	Heating the 202 Ah LiFePO ₄ single battery at overcharging state in open area until the safety valve opens, recording changes in critical temperature points.	To investigate the effect of overcharging on battery thermal runaway behavior
3	Heating the batteries in a standard battery box until the safety valve opens, and spraying perfluorohexanone to suppress thermal runaway, recording the temperature at each critical point.	To investigate the characteristics of thermal runaway in different operating environment and the suppression effect of fire extinguishing media on thermal runaway

3. RESULTS AND DISCUSSION

3.1 Thermal runaway experiments of a LiFePO₄ single battery under thermal abuse

The calorific value of the battery Q_{cell} is composed of the reaction heat Q_r , joule heat Q_j , polarization heat Q_p and side reaction heat Q_{side} [20]:

$$Q_{\text{cell}} = Q_r + Q_j + Q_p + Q_{\text{side}} \quad (1)$$

Q_{side} includes four different parts: SEI decomposition heat Q_{SEI} , reaction heat between anode and electrolyte Q_{an} , reaction heat between cathode and electrolyte Q_{ca} and electrolyte decomposition heat Q_{ele} . Q_{side} can be formulated as follows:

$$Q_{\text{cell}} \approx Q_{\text{side}} = Q_{\text{SEI}} + Q_{\text{an}} + Q_{\text{ca}} + Q_{\text{ele}} \quad (2)$$

$$\text{where } Q_{\text{an}} = H_{\text{an}} m_{\text{an}} R_{\text{an}} \quad (3)$$

$$R_{\text{an}} = A_{\text{an}} \exp\left(-\frac{E_{\text{a,an}}}{RT}\right) C_{\text{an}} \exp\left(-\frac{\delta_{\text{SEI}}}{\delta_{\text{SEI,ref}}}\right) \quad (4)$$

H_{an} , m_{an} , R_{an} , A_{an} and C_{an} correspond to the enthalpy of the chemical reaction of the anode, mass of the anode, anode decomposition reaction rate, anode reaction frequency factor, and concentration of lithium intercalated in the anode, respectively.

From Formulas (3) and (4), Q_{an} is clearly related to C_{an} and proportional to the SOC of the battery. Thus, the thermal runaway behavior is strongly related to the SOC of the Li-ion battery. It is also believed that the thermal runaway is more intense at 100% SOC[21], so LiFePO₄ batteries with an SOC of 100% were used for this group of experiments. The experimental Li-ion battery was first charged to 100% SOC at constant current and subsequently set aside for 1 h to reach a stable state. Afterwards, the battery was heated in the combustion chamber using an electric heating plate with a heating power of 900 W. To explore the law of temperature change in various parts of the battery, 7 temperature points (T1 ~ T7) were arranged at different places of the battery (Figure 3). The battery was heated until thermal runaway occurred. Then, the safety valve opened with a large amount of gas and smoke and an unobserved open flame. The temperature changes of T1~T7 were recorded as shown in Figure 4.

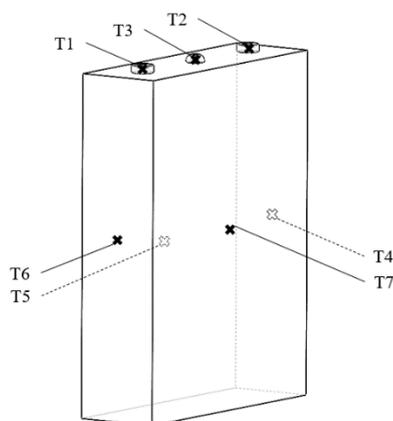


Figure 3. Diagram of the temperature point settings in the 100% SOC single LiFePO₄ battery thermal runaway experiment.

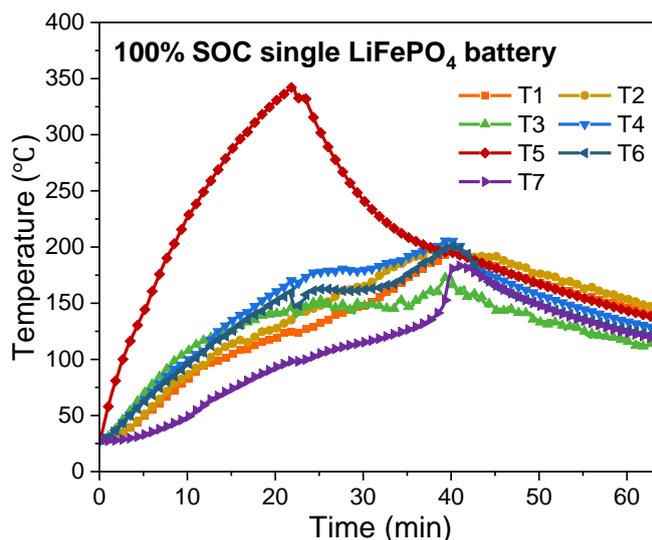


Figure 4. Temperature changes of 7 temperature points of 100% SOC single LiFePO₄ battery under thermal runaway condition.

To simulate the thermal runaway behavior under thermal abuse, an electric heating plate was used to heat the side of the LiFePO₄ battery. At the early stage of heating, in addition to the rapid increase in temperature of the heating surface (T5), the temperatures of the side of the heating surface T3, T4 and T6 simultaneously rose with good consistency. Because the heat was transferred upward and concentrated in the middle and upper parts of the battery, the temperature of the upper surface was slightly higher, and there was no significant difference between T4 and T6 on the anode and cathode sides. Meanwhile, because heat was also transferred from outside to inside, the temperatures of T1 and T2 at the anode and cathode tabs and T7 opposite the heating surface were significantly lower than those of T3, T4 and T6, and T7 was the lowest. When the temperature of the upper surface of battery T3 reached 80°C, the rate of change of T4 on the anode side slightly increased compared to T6 on the anode side. At this time, the SEI film inside the battery started to decompose, and the anode was no longer protected by the SEI film. Subsequently, after T3 reached 118°C and T4 reached 111°C, the heating rate of T4 further increased. This phenomenon arises from the anode and electrolyte reacting with each other, which releases a large amount of Q_{an} . The temperature on the anode side gradually exceeded the upper surface temperature. When the separator inside the battery melted, the cathode and electrolyte also started to react to generate Q_{ca} . As a result, the temperature of the cathode side (T6) gradually exceeded the upper surface temperature (T3). When the heat and gas production inside the battery accumulated, the safety valve opened at 23 min, and a large amount of gas and black smoke was emitted. Ten seconds before the safety valve opened, T4 reached a high temperature of 166°C. Because much heat was removed by a short period of gas eruption, T4 and T6 slightly decreased for a short time. Then, the heating device was immediately shut down. Due to the loss of the heat source, the heating surface temperature T5 gradually decreased, but the internal side reaction of the battery did not stop. As a result, thermal runaway further developed, and the battery temperature simultaneously increased. When complete thermal runaway occurred, the differences between T1, T2, T4, and T6 were very small, with

the highest temperature reaching 206°C. An increasing rate was found for temperature point T7 with a temperature rise to 39°C in 2 min and a temperature rise rate of 19.5°C/min. The electrolyte violently reacted and generated a large amount of Q_{ele} until the battery underwent thermal runaway. In the end, without an external heat source, thermal runaway slowly stopped, and all temperatures simultaneously dropped. Song et al.[22-25] have studied the thermal runaway behavior of ternary Li-ion batteries. Comparing the differences between ternary and lithium iron phosphate Li-ion batteries, it can be seen that the thermal runaway of ternary Li-ion batteries will go through four stages of bulging, smoking, spark injection and deflagration. Due to the high activity of ternary Li-ion batteries, battery expansion occurs at about 50°C, and the highest temperature during thermal runaway often reaches above 500°C. Unlike ternary Li-ion batteries that produce jet fire owing to thermal runaway, lithium iron phosphate Li-ion batteries show obvious difference. If there is no combustible material at the discharge port of lithium iron phosphate Li-ion batteries, there will not exist open flame. However, the gas production is significantly larger than that of ternary Li-ion batteries[14]. At the same time, the SEI film of the lithium iron phosphate Li-ion batteries decomposes at about 80°C, which is significantly higher than 50°C of ternary Li-ion batteries. The maximum temperature 206°C reached by thermal runaway of lithium iron phosphate Li-ion batteries is also far lower than 500°C of ternary Li-ion batteries, which demonstrates the better safety of lithium iron phosphate Li-ion batteries.

From the above analysis, SEI film decomposition will lead to direct contact between the anode and the electrolyte and cause a series of subsequent violent and irreversible side reactions. This results in the release of a large amount of heat and the thermal runaway of the battery. Richard et al.[26, 27] studied the thermal runaway behavior of small-capacity lithium manganate and lithium iron phosphate Li-ion batteries by using an accelerating rate calorimeter. They came to a similar conclusion that when the battery surface temperature exceeded 80°C, the decomposition of SEI film would cause the temperature rise rate to be greater than 1°C/s and the duration to exceed 3 s, indicating that the battery began to happen thermal runaway. Therefore, SEI film decomposition can be used as a key point to control the thermal runaway of the battery. The temperature changes of T1 ~ T7 in Figure 4 shows that before the SEI decomposition, the temperature on the side of the heated surface of the battery consistently increased except for T7. Because heat was mainly concentrated in the upper part of the battery, the upper surface temperature was higher. Considering the uncertainty of the heated surface in the actual situation and the margin of the battery management system alarm, an early warning can be made by measuring the battery surface temperature when it exceeds 80°C, and corresponding measures can be taken to ensure the safety of the battery. When the battery safety valve was opened due to thermal runaway, the temperature distribution at different parts inside the battery was uneven, and the temperature difference from T1 to T6 was 38°C. At this time, a large error could be made if the early warning was still made by measuring the battery temperature. Because a large amount of combustible gas and smoke will be released when thermal runaway occurs, the use of combustible gas detectors can be considered for effective warning. Yuan.[28] reached a similar conclusion in their study. By analyzing the differences in composition of gases released during thermal runaway of LiFePO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ -based batteries, they found that the main components of thermal runaway gases from LiFePO_4 batteries were H_2 , CO_2 , C_2H_2 , C_2H_4 and C_2H_6 , and CO had the lowest proportion among the thermal runaway gases from these three types of batteries. For the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery, the main

components of thermal runaway gases were CO_2 , H_2 and CH_4 . The content of CO and CH_4 was the highest in the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ batteries. Based on the above analysis, gas detection can be one of the main indicators of thermal runaway warning for Li-ion batteries. However, different combustible gas detectors should be selected according to the specific battery type. It is not advisable to use a single temperature detection or CO gas detector in the thermal runaway warning of Li-ion batteries.

3.2 Thermal runaway experiments of LiFePO_4 batteries under overcharging conditions

To investigate the effect of overcharging on the thermal runaway of the Li-ion battery, two 202-Ah batteries were charged to 100% SOC and subsequently set aside for 1 h to reach a stable condition. Then, they were put into the combustor and one of them was charged with a constant current of 202 A for 12 min to reach 120% SOC. Then, the Li-ion battery was heated using the device in Figure 1. The temperatures T1, T2 and T7 were collected from the cathode and anode tabs and the center position opposite to the heated surface, respectively, as shown in Figure 5. The temperature changes of T1, T2 and T7 of Li-ion batteries at 100% SOC and 120% SOC are shown in Figures 6(a) and 6(b).

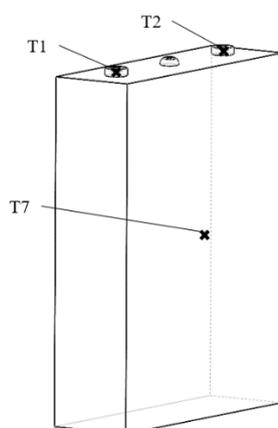


Figure 5. Diagram of the temperature point settings in the 100% SOC single- LiFePO_4 -battery thermal runaway experiment.

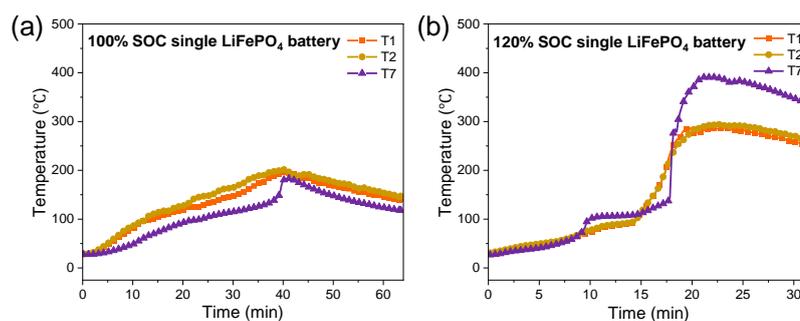


Figure 6. Temperature changes of a single LiFePO_4 battery under thermal runaway conditions with (a) 100% and (b) 120% SOC.

A significant difference in temperature change is observed by comparing Figures 6 (a) and (b). For the battery under 100% SOC, which was heated by using the side electric heating plate, due to the heat transfer from the outside to the inside, the temperature change was not uniform from the beginning. The temperature at the upper surface of the battery cathode and anode tabs was always higher than the temperature at the center position opposite to the heated surface. The highest temperature of the battery with thermal runaway was approximately 201°C. According to Formula (1), the battery heat Q_{cell} mainly came from the reaction heat Q_r , Joule heat Q_j and polarization heat Q_p . At an overcharge state of 120% SOC, heat was transferred from the inside to the outside, and the initial temperature rise rate was relatively uniform with better consistency. After 9 min of constant current overcharging, the temperature change rate of T7 suddenly increased, accompanied by SEI film decomposition and deterioration of the battery internal structure. The uniformity of the temperature became worse, and the time of SEI film decomposition was slightly lower than that of the battery under 100% SOC. However, due to the violent reaction of the electrolyte during thermal runaway, T7 reached a maximum of approximately 390°C, which is much higher than the highest temperature of 201°C under 100% SOC. The maximum temperature points of T1 (288°C) and T2 (296°C) were also much higher than those of T1 (197°C) and T2 (202°C) of the battery under 100% SOC, which indicates that the thermal runaway reaction was more severe in the overcharged LiFePO₄ batteries. Herein, we discussed the differences of thermal runaway of lithium iron phosphate Li-ion batteries under two states of 100% and 120% SOC using a constant current of 1 C. Homoplastically, Wang[29] studied thermal runaway behavior of lithium iron phosphate Li-ion batteries in the overcharge state by using two rates of 0.4 C and 0.5 C. Zuo[30] employed a constant current of 2 C and set a higher cut-off voltage to overcharge, which studied the changes of voltage and pressure of lithium manganese Li-ion batteries with time. These studies show that the thermal runaway reaction of Li-ion batteries is more severe under the overcharge state, and the higher overcharge rate means the earlier thermal runaway reaction[29].

3.3 LiFePO₄ power battery box thermal runaway experiment

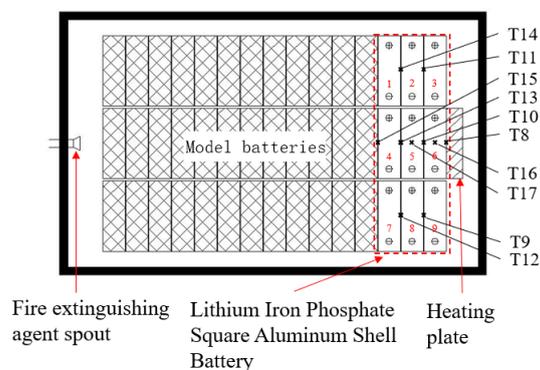


Figure 7. Diagram of the temperature point settings of the LiFePO₄ power battery box.

To study the thermal runaway of the LiFePO₄ battery module in the actual environment and the suppression effect of the fire extinguishing agent on the battery thermal runaway, the device in Figure 2 was used to heat the experimental battery until the safety valve was opened. Then, the heating device

was immediately turned off, and the battery was ignited by using an external open flame 3 min later. A perfluorohexanone fire extinguishing agent of 1.8 kg was sprayed to suppress thermal runaway. The temperature point setting in the power battery box is shown in Figure 7, and the experimental observation is shown in Figure 8. Thermal runaway temperature changes of batteries in different operating environments and battery box temperature field changes were recorded, as shown in Figures 9 and 10, respectively.



Figure 8. Power battery box thermal runaway suppression experiment. (a) Before thermal runaway. (b) When thermal runaway occurs. (c) Open flame ignition experiment. (d) After the fire extinguishing agent has been sprayed.

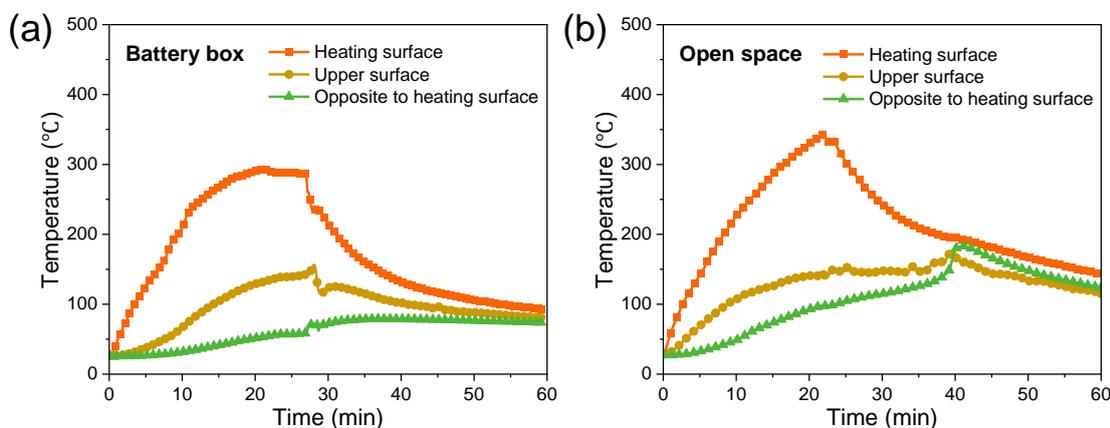


Figure 9. Comparison of thermal runaway temperature changes of the battery in (a) the battery box and (b) open space.

Figure 8 shows that the safety valve opened after heating for 27 min by an electric heating plate. Black smoke appeared on the observation window of the battery box, while a large amount of white gas overflowed from the vent, at which time the temperature of the upper surface of the battery in the battery box was 143°C and the temperature of the opposite center point was 59°C (Figure 9a). For the single LiFePO₄ battery in open space, the corresponding temperatures were 148°C and 110°C, respectively (Figure 9b). In the experiment performed in the open area, the produced gas was quickly ejected from the battery from the safety valve, and most of the ejected high-temperature electrolyte was splashed into the surrounding environment, with less splashing on the upper surface of the battery. In the module battery box, the produced gas remained in the box due to the obstruction of the module box. In this case, the high-temperature electrolyte mostly splashed down on the upper surface of the battery module due to the shielding of the module box upper cover. Although these factors increased the temperature in the

battery, the O₂ content was lower in the battery box than in the open area. Therefore, the side reactions inside the battery were suppressed. Compared with the temperature opposite to the heating surface of the battery in the open area (99°C), the temperature in the battery box was 71°C. Simultaneously, the temperature opposite to the heating surface in the battery box was significantly lower than that of a single battery in open space because the heat of the thermally runaway battery was transferred to the surrounding batteries in the battery box. However, if thermal runaway is not controlled in time, heat transfer may initiate a chain reaction and make the battery box combust or explode. This experiment studied the thermal runaway behavior and temperature change differences of a 202Ah large-capacity lithium iron phosphate battery in the battery box of electric bus and in the open space state. Wang.[31] studied the changes of thermal runaway heat and mass loss of the battery in the lithium iron phosphate battery box for energy storage. Wang.[32] studied the thermal runaway behavior of ternary Li-ion battery modules. The above research shows that the module box increases the heat transferred by the thermal runaway battery to other safety batteries through high temperature gas production and electrolytes. The temperature that can be reached by the upper surface of the battery in the module box is higher than that of the corresponding measuring point in the open space experiment, and the heat transferred to the surrounding is also higher than that of the open space, which leads to greater safety risks.

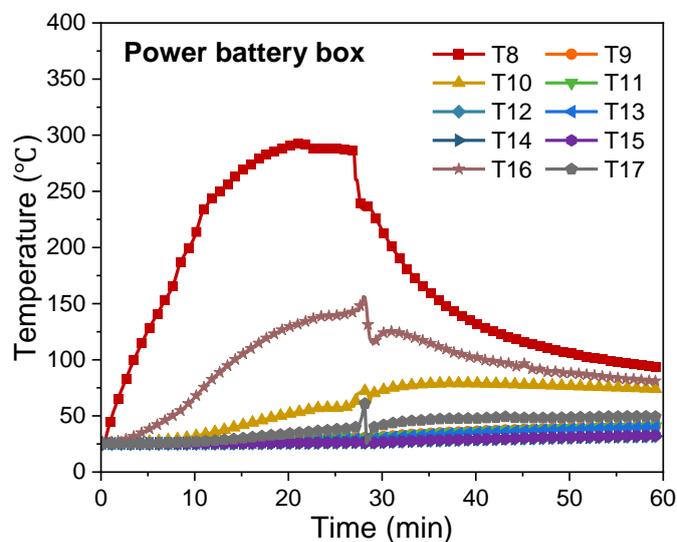


Figure 10. Temperature changes of the power battery box after thermal runaway and spraying the fire extinguishing agent.

After the safety valve had been opened for 3 min, the thermal runaway gas was ignited to produce an open flame using alcohol cotton balls. Figures 8 and 10 show that although the LiFePO₄ battery thermal runaway did not directly produce a jet fire, the large amount of combustible gas ejected into the open flame caused combustion or even explosion. After 1.8 kg perfluorohexanone fire extinguishing agent had been sprayed to suppress thermal runaway, the open fire was completely extinguished after 40 s. The highest temperature of the thermal runaway battery was 156°C, which is much lower than the highest temperature (206°C) of the thermal runaway battery without spraying fire extinguishing agent. The battery temperature followed a linear declining trend. Reignition of the battery was attempted after 30 min, but no reignition phenomenon was found, which indicates that the impregnation effect of fire

extinguishing media can effectively inhibit the thermal runaway of LiFePO₄ batteries. In addition to the thermal runaway battery, the maximum temperature of the other batteries did not exceed the safety temperature of 80°C. This result suggests that when thermal runaway occurs for a single LiFePO₄ battery in the power battery box, timely spraying of fire extinguishing media can suppress the thermal runaway of the battery and prevent possible chain reactions of surrounding batteries to ensure battery system safety. In this study, environmental-friendly perfluorohexanone fire extinguishing agent was employed to extinguish fire. Moreover, many researchers[33-36] studied the inhibitory effects of H₂O, CO₂, perfluorohexanone, heptafluoropropane, ABC dry powder and other fire extinguishing agents on the thermal runaway of Li-ion batteries. The inhibitory effects are shown in Table 3.

Table 3. Comparisons of fire extinguishing process for various fire extinguishing agents[32-35]

Fire extinguishing agents	CO ₂	H ₂ O	ABC dry powder	Heptafluoropropane	Perfluorohexanone
Whether or not to put out fire	Yes	Yes	Yes	Yes	Yes
Release time/s	13	13	9	13	10
Response time/s	1	2	3	1	2
Whether or not to reignite	Yes	No	No	No	No

The results show that in the absence of fire extinguishing agents, all Li-ion batteries suffer from thermal runaway, while only liquid fire extinguishing agents of 500 mL can effectively suppress the spread of fire[37]. Except for the re-ignition for CO₂ fire extinguishing agent, other fire extinguishing agents can effectively inhibit the thermal runaway of Li-ion batteries. It is noteworthy that heptafluoropropane and perfluorohexanone do not pollute the protected battery and electrical parts, and have low toxicity and strong insulation. Hence, heptafluoropropane and perfluorohexanone are ideal media for thermal runaway suppression of Li-ion batteries.

4. CONCLUSIONS

By electrically heating and overcharging 202 Ah LiFePO₄ batteries to a thermal runaway state, the temperature changes of batteries in the open area and power battery box were studied, and the following conclusions are drawn:

(1) Using a side heating method to simulate thermal runaway under thermal abuse of Li-ion batteries, a poor uniformity of temperature change inside the battery was observed. The temperature at the side of the heating surface was much higher than that at the position opposite to the heating surface and the tabs. The upper surface temperature of the battery in the battery management system should be collected.

(2) The anode SEI film decomposition in the LiFePO₄ battery is the key point to control the battery thermal runaway. After SEI film decomposition, the anode is no longer protected, and the battery thermal runaway becomes irreversible. A safety warning should be performed at 80°C, which is the key temperature point of battery SEI film decomposition.

(3) In the overcharge mode of 120% SOC, the temperature rise of the Li-ion battery shows good consistency at the beginning, while the thermal runaway is more intense in the later stage. Moreover, 120% SOC has a higher maximum thermal runaway temperature than 100% SOC.

(4) The thermal runaway temperature of the LiFePO₄ battery is lower in a power battery box than in an open area because of heat dissipation and heat transfer. Nevertheless, there is a risk of causing chain reactions to the surrounding batteries. At this time, timely fire extinguishing agent release can effectively reduce the thermal runaway temperature and prevent chain reactions. The perfluorohexanone fire extinguishing agent can effectively inhibit the thermal runaway behavior of Li-ion batteries, and there is no re-ignition phenomenon, revealing the superior inhibitory effect.

ACKNOWLEDGMENT

This work was supported by the Taizhou city of Jiangsu province Science and Technology Incubation Fund (TF201906).

References

1. Y. Jin, Z. Zheng, D. Wei, X. Jiang, H. Lu, L. Sun, F. Tao, D. Guo, Y. Liu, J. Gao and Y. Cui, *Joule*, 4 (2020) 1714.
2. H. Wang, Z. Du, L. Liu, Z. Zhang, J. Hao, Q. Wang and S. Wang, *Fire Technology*, 56 (2020) 2427.
3. D. Ren, X. Feng, L. Liu, H. Hsu, L. Lu, L. Wang, X. He and M. Ouyang, *Energy Storage Materials*, 34 (2020) 563.
4. C.F. Lopez, J.A. Jeevarajan and P.P. Mukherjee, *J. Electrochem. Soc.*, 162 (2015) 2163.
5. L.S. Guo, Z.R. Wang, J.H. Wang, Q.K. Luo and J.J. Liu, *Journal of Loss Prevention in the Process Industries*, 49 (2017) 953.
6. A.W. Golubkov, S. Scheikl, R. Planteu, G. Voitic, H. Wiltsche, C. Stangl, G. Fauler, A. Thaler and V. Hacker, *RSC Advances*, 5 (2015) 57171.
7. X. Feng, D. Ren, X. He and M. Ouyang, *Joule*, 4 (2020) 743.
8. Q. Wang, B. Mao, S.I. Stoliarov and J. Sun, *Prog. Energy Combust. Sci.*, 73 (2019) 95.
9. O. Mathieu, C.M. Grégoire, M.A. Turner, D.J. Mohr, S.A. Alturaifi, J.C. Thomas and E.L. Petersen, *Energy & Fuels*, 36 (2022) 3247.
10. T. Li and Y. Jiao, *Energy Storage Science and Technology*, (2022) 1.
11. P. Jindal and J. Bhattacharya, *J. Electrochem. Soc.*, 166 (2019) 2165.
12. J. Ye, H. Chen, Q. Wang, P. Huang, J. Sun and S. Lo, *Applied Energy*, 182 (2016) 464.
13. L. Lu, X. Han, J. Li, J. Hua and M. Ouyang, *J. Power Sources*, 226 (2013) 272.

14. L. Yiding, W. Wenwei, L. Cheng, Y. Xiaoguang and Z. Fenghao, *Journal of Cleaner Production*, 277 (2020) 124094.
15. S. Du, Y. Lai, L. Ai, L. Ai, Y. Cheng, Y. Tang and M. Jia, *Appl. Therm. Eng.*, 121 (2017) 501.
16. Q. Yuan, F. Zhao, W. Wang, Y. Zhao, Z. Liang and D. Yan, *Electrochim. Acta.*, 178 (2015) 682.
17. C. Dai, *Int. J. Electrochem. Sci.*, (2019) 3363.
18. X. Feng, M. Fang, X. He, M. Ouyang, L. Lu, H. Wang and M. Zhang, *J. Power Sources*, 255 (2014) 294.
19. H. Zhu, C Wu, T. Zhou and J. Deng, *Energy Storage Science and Technology*, 11 (2022) 201.
20. D. Ren, X. Feng, L. Lu, M. Ouyang, S. Zheng, J. Li and X. He, *J. Power Sources*, 364 (2017) 328.
21. D. Sturk, L. Hoffmann and A.A. Tidblad, *Traffic Inj. Prev.*, 16 (2015) 159.
22. X. Song, Y.Z. Gong, X.K. Ping, J. Sun, X.T. Chen and Y.H. He, *Journal of Energy Storage*, 46 (2022) 103829.
23. L.H. Jiang, Z.M. Luo, T.Q. Wu, L.Y. Shao, J.H. Sun, C.Q. Liu, G.H. Li, K.N. Cao, and Q.S. Wang, *Journal of The Electrochemical Society*, 166 (2019) 1055.
24. Y.H. Liu, H.C. Niu, Z. Li, J. Liu, C.S. Xu and X.Y. Huang, *Process Safety and Environmental Protection*, 155 (2021) 486.
25. H. Huang, L. Zhang, Y.F. Zhang, Z.L. Zhang and L.Y. Cao, *Fire Science and Technology*, 38 (2019) 1108.
26. M.N. Richard and J.R. Dahn, *J. Electrochem. Soc.*, 146 (1999) 2068.
27. H.B. Dong, X.L. Xian, J.Q. Ma and C.Y. Yi, *Fire Science and Technology*, 41 (2022) 21.
28. L. Yuan, T. Dubaniewicz, I. Zlochower, R. Thomas and N. Rayyan, *Process Safety and Environmental Protection*, 144 (2020) 186.
29. H.R. Wang, *Zhengzhou university*, (2021) 003170.
30. P. Zhuo, Y.L. Zhu, C. QI, C.J. Wang and F. Gao, *Energy Storage Science and Technology*, 11 (2022) 2471.
31. T.H. Wang, H.J. Zhai, P. Qin, J.Y. Wu, F.Y. Tian, P.Y. Guo and Q.S. Wang, *Fire Safety Science*, 37 (2022) 25.
32. H.B. Wang, Y. Li, Q.A. Wang, Z.M. Du and X.N. Feng, *Chinese Journal of Engineering*, 43 (2021) 663.
33. L. Zhang, H. Huang, Y.F. Zhang and L.Y. Cao, 2018 Proceedings of the China Fire Protection Association Science and Technology Annual Conference, (2018) 246.
34. D.X. Yu, Y. Li, S.Y. Zhang, Y.L. Du and H.B. Dong, *Chinese Journal of Power Sources*, 43 (2019) 60.
35. Y.J. Liu, Q.L. Duan, K. Li, H.D. Chen and Q.S. Wang, *Energy Storage Science and Technology*, 7 (2018) 1105.
36. J. Zhang, J.Y. Li, M.J. Zhang, Y.H. Tian, H. Han, K. Yang and M.S. Chi, *Fire Science and Technology*, 39 (2020) 1168
37. D.X. Yu, Y. Li, S.Y. Zhang, Y.L. Du, H.B. Dong, X. Liu and G. Han, *Fire Science and Technology*, 36 (2017) 1731.