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Study of thermal runaway and the combustion behavior of lithium-ion batteries overcharged with high current rates

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A R T I C L E I N F O

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A B S T R A C T

Overcharged lithium-ion batteries can experience thermal runaway that can cause spontaneous combustion or an explosion. By measuring the heat release rate, surface temperature, flame temperature, positive and negative electrode temperature and mass loss of 18650 NCM lithium-ion battery, the combustion and explosion characteristics of lithium-ion battery under different current rates were analyzed. The results show that the 18650 lithium-ion battery undergoes two thermal runaway behaviors when overcharge at a high current rate. The first thermal runaway leads to a continuous explosion reaction, while the second thermal runaway has a combustion and explosion reaction that is more violent than the first thermal runaway. As the current rate increases from 1 C to 3 C, the time for the first thermal runaway to occur decreases from 1554 to 360 s, the time for the second thermal runaway to occur decreases from 2515 to 522 s, and the explosive response becomes more violent.

1. Introduction

Mankind's excessive dependence on fossil fuels has brought about a series of problems and caused the consequences of the continuous depletion of traditional energy sources. As a typical new energy source, lithium-ion batteries have many advantages, such as high energy density, low pollution, stable voltage, and long service life, and they are widely used in electronic equipment and electric vehicles [1,2]. However, fires and explosions associated with lithium-ion batteries occur frequently and cause significant damage to life and property. Many accidents with lithium-ion batteries occur under conditions of mechanical, electrical, or thermal abuse [3–7]. Such misuse is highly likely to trigger an internal short circuit (ISC). Overcharging is one of the most serious safety issues with lithium-ion batteries because during overcharging, the battery is filled with too much energy [8]. Overcharging occurs when a battery reaches its maximum voltage or state of charge (SOC) limit and a charging current continues to pass through the battery [9]. When a battery is overcharged for a long time, lithium dendrites form inside the battery [10,11], which may penetrate the separator and cause an ISC. When a large area of an ISC is formed inside the battery, the energy stored in the battery will be released at a high speed, thereby rapidly increasing the internal temperature and potentially causing thermal runaway. When the battery enters a thermal runaway state, it may discharge particles as well as flammable and toxic gases, which can form jets of flame. Therefore, it is necessary to study the combustion and thermal runaway caused by the misuse of lithium-ion battery electrical appliances.

Belov and Yang [12] conducted overcharge experiments on lithium cobalt oxide batteries through different current rates and studied the failure mechanism of lithium cobalt oxide batteries during overcharge. The results show that when the battery works in the overcharged state, the heat generated is not equal to the heat dissipation, and the heat out of control will occur. The high overcharging rate shows short responding time for the cell thermal runaway and large amount of heat generation. Lebkowski et al. [13] proposed that when the power battery is applied to the vehicle, there is a risk of overcharge in the case of failure of the charger and battery management system. Overcharge will lead to battery temperature rise, fire and even explosion. Hofmann et al. [14] tested the battery overcharge on the shelf of fume hood and acceleration calorimeter. Their results showed that decompression during a thermal runaway accident can prevent explosion of the battery and fires caused by the electrolyte. Yuan et al. [15] studied the behavior of a 32Ah

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prismatic lithium-ion battery undergoing overcharging by monitoring the internal and external temperature changes of the battery. Their results showed that the internal temperature of the battery could reach 235 °C before ignition, which was nearly 140 °C higher than the external temperature of the battery. Ye et al. [16] studied the dynamic thermal behavior of the overcharge process under adiabatic conditions by combining a multichannel battery cycler and an accelerating rate calorimeter. The results showed that overcharge in the constant current–constant potential–constant current mode was more dangerous than in the constant current mode. Ren et al. [8] evaluated the overcharging performance of a commercial pouch lithium-ion battery using a $Li_y(NiCoMn)_{1/3}O_2$-$Li_yMn_2O_4$ composite cathode and a graphite anode, and considered the effects of charging current, limiting plate, and heat dissipation. The results showed that rupture of the pouch and melting of the separator during overcharging were two key factors that caused thermal runaway. Huang et al. [17] used prismatic and pouch-type lithium-ion batteries with the same capacity and chemical composition to study experimentally the internal failure mechanism and related external characteristics during the overcharge process. The entire overcharge process was divided into five stages. The results showed that compared to the prismatic battery in the first through the third stages, the pouch-type battery had better thermal behavior and overcharge resistance.

Although many studies have been conducted to investigate the thermal runaway behavior caused by overcharge of lithium-ion batteries. However, there is still a lack of detailed analysis of the thermal runaway behavior of overcharged small NCM lithium-ion batteries with high charging rate. This article conducted an experimental study on the combustion and explosion behavior caused by thermal runaway of NCM18650 lithium-ion batteries overcharged with a high current rate. The temperature, heat release rate (HRR), and mass loss and of the 18650 lithium-ion battery were measured with a cone calorimeter during the combustion process. Also, the thermal runaway process of the lithium-ion battery was recorded with both infrared and visible light cameras. The thermal runaway characteristics of the overcharged lithium-ion batteries and the influence of different current rates on their thermal runaway behavior were analyzed.

2. Experiment

2.1. Experimental samples

We use 18650 type NCM523 lithium-ion batteries in the experiments. The battery diameter is 18 mm, the length is 65 mm, the capacity of each battery is 2.6 Ah, the rated voltage of the battery is 3.7 V, and the voltage range is 2.75–4.2 V. The battery is composed of a positive electrode, a negative electrode, a positive collector, a negative collector, an electrolyte, and a separator. The electrolyte consists of lithium hexafluorophosphate dissolved in dimethyl carbonate and vinyl carbonate solvents. The main function of the separator is to separate the positive and negative electrodes to prevent ISC in the electrochemical battery [18]. The positive collector is aluminum foil, and the negative collector is copper foil. The positive material of the battery is a ternary material (consisting of Ni, Co, and Mn (NCM)), the negative material is graphite, and the electrolyte is an organic solvent containing Li^+, which plays a role in transferring charge between the positive and negative electrodes of the battery. In the NCM battery, Co stabilizes the layered structure of the material and improves the cycle and multiplication performance of the material, Mn reduces material cost and improves material safety and structural stability, and Ni increases the energy density of the material, but also increases the potential for the cathode structure to have thermal problems [19–21].

2.2. Experimental apparatus and process

As shown in Fig. 1, the cone calorimeter experiment was performed according to the procedure in the ISO 5660-1 standard. The charging device was fixed above the sample box by a wire, and the lithium-ion battery was placed horizontally in the charging device. Thermocouples TC1 and TC2 were arranged at the positive and negative electrodes, respectively, of the battery to measure their temperature, as shown in Fig. 1. An additional 5 thermocouples, labeled TC3–TC7, were arranged at 0, 50, 100, 150, and 200 mm from the positive surface of the battery to measure the surface temperature and flame temperature of the battery. Before the experiment, the cone calorimeter was calibrated according to the procedure in the ISO 5660-1 standard, and the lithium-ion battery was overcharged to thermal runaway. The combustion products were collected by a gas hood and transported away through an exhaust system. An O_2 analyzer was used to measure O_2 consumption to calculate the HRR, and the fan flow rate was set to 24 L / s. The combustion

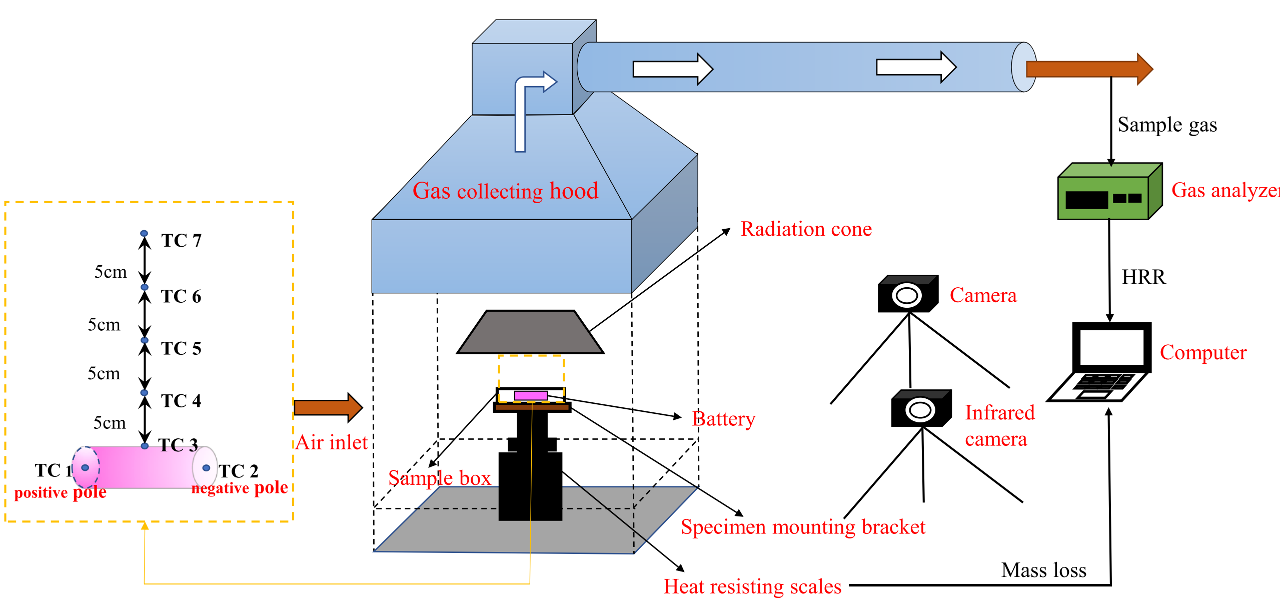


Fig. 1. Diagram of the experimental system containing the cone calorimeter, including the positioning of the thermocouples relative to the battery.

process of the lithium-ion battery was recorded with both infrared and visible light cameras. The ambient temperature was ~298.15 K under natural ventilation. In the experiment, the samples were weighed with heat-resistant scales. The lithium-ion battery was connected to the charging device for constant current charging, and the lithium-ion battery was overcharged at 1 C, 2 C, and 3 C current rates to thermal runaway. During the experiment, the following parameters were measured: HRR, mass loss, battery surface temperature, battery flame temperature, battery positive and negative electrode temperature, and battery voltage. The cells were stripped of plastic packaging prior to testing.

3. Results and discussion

3.1. . Combustion process

In this test, the thermal runaway reaction of lithium-ion battery was severe and there were two thermal runaway behaviors. Fig. 2 shows the thermal runaway process of an 18650 lithium-ion battery overcharged at a 2 C current rate. The combustion process was divided into four stages. In the first stage, there was smoldering without flames. In the second stage, the safety valve ruptured and the gas in the battery was discharged. About 2–3 s later, the battery exploded for the first time, ejecting blue-violet and yellow-white sparks, and then a small flame was ejected from the positive electrode of the battery. Milliseconds later, a continuous explosion sound was emitted, and a small number of large white and yellow-white luminous particles and a large number of small particle sparks were ejected, accompanied by a small flame. After 13 s, the spark ejection ended and the flame gradually disappeared. In the third stage, a violent explosion occurred, and a large number of sparks were ejected. As the spark jet was about to end, the flame began to burn violently. In the fourth stage, the flame height decreased and the flame gradually extinguished.

The sparks ejected from the first thermal runaway of the lithium-ion batteries were blue-violet and yellow-white incandescent particles, which were ejected from the battery due to high pressure when thermal runaway occurred in the battery. The color of sparks depended not only on their temperature, but also on their chemical composition [22].

Fig. 2. Experimental phenomena of an overcharged battery with a 2 C current rate.

Blue-violet sparks and yellow-white sparks came from copper in the copper current collector and aluminum in the aluminum current collector, respectively. The degradation of copper produced blue sparks. The observed blue-violet sparks may have been caused by the high temperature. The blue sparks gradually evolved into blue-violet sparks under the influence of the red heat. It can be seen from Fig. 2 that the range and intensity of the second thermal runaway spark injection was much larger than the first thermal runaway. The thermal runaway flame was mainly caused by the spark ignition after the release of the combustible gas. The sparks in the first thermal runaway stage were continuously generated, so the flame combustion time could not be precisely determined, but it could be confirmed that the flame must occur after the spark jet. In the second thermal runaway, the sparks were denser and mainly concentrated in the beginning period, such that the flame dominated after the spark injection ended.

Fig. 3 shows the thermal runaway process of an 18,650 lithium-ion battery overcharged at 1 C, 2 C and 3 C current rates. The combustion and explosion behavior of 1 C and 3 C is similar to that of 2 C, and they also experienced two thermal runaway behaviors. It can be seen from the figure that when the first thermal runaway flame burns, the flame shape was vertical bar type and concentrated on the positive electrode of the battery, mainly because the amount of combustible gas generated in the first thermal runaway was less and mainly concentrated on the positive electrode. Therefore, the purpose of monitoring and preventing battery combustion and explosion can be achieved by installing a sensor on the positive electrode. The second thermal runaway flame was lotus shaped, and the flame burned above the whole battery. Due to the occurrence of the second thermal runaway, a large number of combustible gases and sparks were generated, and the combustible gases were ignited by sparks to form a violent combustion flame. Because a large amount of Joule heat is generated when charging lithium-ion batteries with high current rate. The internal of ternary lithium-ion battery is a non-uniform system. The generation of a large amount of Joule heat in a short time will promote the accumulation of heat at special locations. High current rate overcharge also produces more polarization heat. The heat accumulation promotes the occurrence of the first thermal runaway. The first thermal runaway causes the release of some gases, but the high current rate overcharge causes the temperature to rise

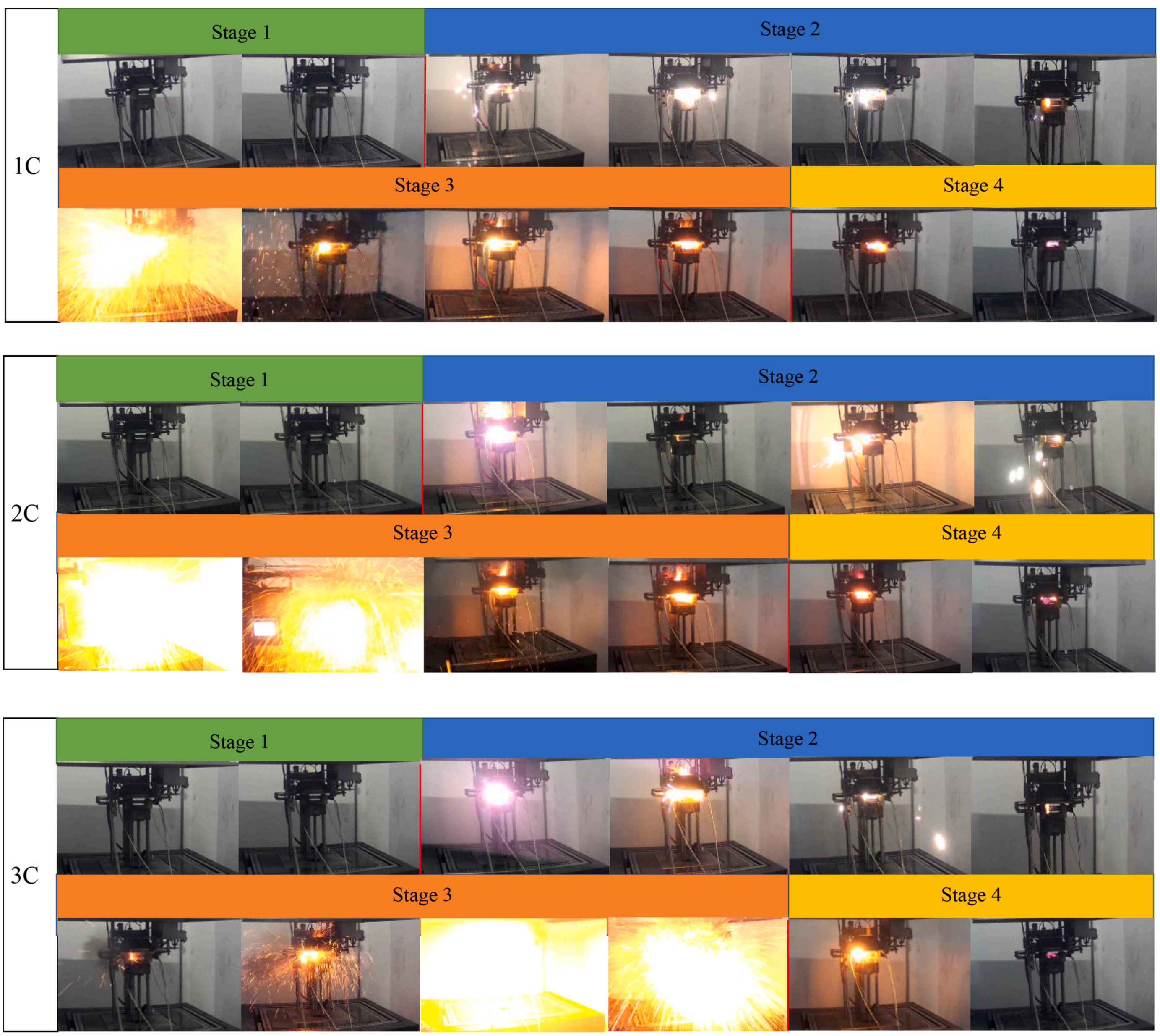


Fig. 3. Experimental phenomena of an overcharged battery with 1 C, 2 C and 3 C current rates.

continuously, the internal reaction of the battery intensifies, and finally the internal short circuit occurs, resulting in the second thermal runaway.

However, even if the initial conditions are the same, there are often slight differences in the thickness of the diaphragm, the thickness of the shell and the proportion of the internal electrolyte of the lithium-ion battery. When the battery is thermally out of control, non-standard failure mechanisms such as bottom cracking or side cracking may occur, and the completion of the decomposition reaction of the lithium-ion battery will also affect the final reaction of the battery. Therefore, other forms of thermal out of control reactions may also occur in the lithium-ion battery [23].

3.2. Analysis of two thermal runaway mechanism

Fig. 4 shows the infrared and visible light images of the lithium-ion battery overcharged to thermal runaway at the 1 C current rate. The battery shown in Fig. 4(a) was in the smoldering stage, and the battery temperature increased continuously. As shown in Fig. 4(b), when the safety valve ruptured gas was quickly ejected from the battery, and the gas volume slowly increased. Subsequently, there was a loud bang, followed by a continuous rumbling, accompanied by large, luminescent particles ejected from the lithium-ion battery, and sparks and flames ejected from the battery cathode. As shown in Fig. 4(d), the flame went out, the battery no longer released gas, and the battery temperature continued to rise. At 2179 s, the gas leaked slowly from the positive electrode of the battery, and the gas leak rate became faster and faster. Seconds later, an electric spark was ejected from the battery and a flame began to burn. The flame continued to burn for 10 s and then went out. The battery temperature slowly decreased, but there was still smoke coming out of the battery.

The cause of the two thermal runaways is related to gas generated in the battery. The gas generated during thermal runaway has three main sources: (1) O_2 produced by the decomposition of solid electrolyte interphase layer and the NCM material at high temperature [24] and CO_2 produced by the mixed reaction of by-products and electrolyte [25]; (2) CO_2 released by the reaction of lithium embedded in the graphite anode and the electrolyte at high temperature [26]; (3) HF, CO_2, and C_2H_4 generated by the decomposition of the electrolyte at high temperature [26,27]. When charging a lithium-ion battery, the charge transfer causes a potential difference to occur inside the battery, resulting in an increase in voltage. The inside of the battery is a nonuniform system, with some locations having a large potential difference and other locations having a small potential difference, which causes an increase in internal resistance and thus an increase in heat production. When charging with a high current rate, the heat is much larger in some locations than in other locations, and overcharging with a high current rate also generates a lot of polarization heat. Polarization heat and local heat causes serious decomposition of the electrolyte, the internal reaction rate of the battery is accelerated, a large amount of gas is generated, and thermal runaway occurs. The multiple successive explosions during the first thermal runaway may be due to heat accumulation at multiple points within the battery. After the first thermal runaway is completed, further charging increases the resistance of the positive electrode. Due to Joule heating, the battery temperature rises, and the electrolyte reacts with the highly oxidized positive electrode, destroying the positive electrode structure and further heating the battery. The rapid exothermic reaction between the positive electrode and the electrolyte triggers a reaction between the overcharged negative electrode (deposited lithium) and the electrolyte, resulting in a large amount of gas [27] that eventually leads to a second thermal runaway.

3.3. Heat release rate

The heat released by the burning of a material per unit time is measured by HRR. According to Thornton's principle, HRR can be determined using Eq. (1):

$$\dot{q} = E\left(\dot{m}^{0}_{o_2} - \dot{m}_{o_2}\right) \tag{1}$$

where $\dot{q}$ is the HRR, $\dot{m}^{0}_{o_2}$ is the mass flow rate of O_2 in the inlet, $\dot{m}_{O_2}$ is the mass flow rate of O_2 in the exhaust (kg / s), and $E = 13.1$ ($\pm$ 5%) MJ kg^{-1} is the energy released by O_2 per mass unit consumed by a given fuel.

Fig. 5(a) shows the HRR curve of lithium-ion battery overcharged at 3 C current rate, which can be divided into four stages. In the first stage, the HRR value approaches 0 due to the lack of flame. In the second stage, the first thermal runaway occurred. Due to the combustion of the flame, the heat release rate increased to 0.45 kw. In the third stage, the second thermal runaway occurred. Due to the violent combustion of the flame, the heat release rate increased sharply to 4.27 kw. In the fourth stage, the flame goes out gradually, and the HRR value approaches 0. Fig. 5(b) shows the HRR curves of lithium-ion batteries overcharged at 1 C, 2 C and 3 C current rates. The experimental results show that overcharge can cause two thermal runaway behaviors of lithium-ion batteries. When the current rate is 1 C, the peak HRR of the first and second thermal runaways are 0.28 and 3.20 kW, respectively. When the current rate is 2 C, the peak HRR of the two thermal runaways are 0.39 and 3.85 kW, respectively. When the current rate is 3 C, the peak HRR of the two thermal runaways are 0.45 and 4.27 kW, respectively. The second thermal runaway HRR peak is much larger than the first thermal runaway HRR peak, so it can be judged that the second thermal runaway flame combustion is more intense than the first one. The intensity of flame combustion is related to the amount of combustible gas released. Because the heat source of the first thermal runaway is mainly polarization heat and local heat generation, the gas production reaction is less. When the second heat production is out of control, the temperature of the battery rises sharply, the chemical reaction in the battery is violent, the amount of gas production increases, and the combustion reaction becomes more intense. With the current rate from 1 C to 3 C, The HRR peaks of the first thermal runaway and the second thermal runaway increase gradually. Higher current rate can accelerate the chemical reaction inside the battery, promote the accumulation of heat, increase the ignition risk, and lead to violent combustion and explosion reaction.

3.4. Temperature

3.4.1. Surface temperature

The temperature change of the battery surface and flame is considered to be an important parameter to describe the thermal runaway and combustion characteristics of a battery. For lithium-ion batteries overcharged at a current rate of 3 C, as shown in Fig. 6, in the first stage before the battery reaches the first thermal runaway, the surface temperature changes relatively smoothly, and the temperature shows a steady and slow rising trend, mainly due to the internal heat of the battery The accumulation of heat has little effect on the surface temperature of the battery. In the second stage, the range of the temperature curve change increases, the temperature rises faster, and the internal exothermic reaction rate of the battery is faster, reacting more quickly and releasing more heat [28]. In the third stage, the temperature increases sharply until it reaches a peak, indicating the second thermal runaway. A large amount of heat accumulates inside the battery, leading to severe combustion and explosions. In the fourth stage, the temperature shows a downward trend.

Fig. 7 shows the temperature change curve of the battery center surface when the battery is thermal runaway due to being overcharged at the three current rates. At current rates of 1 C, 2 C and 3 C, the duration of the first stage was 1554, 476 and 360 s, respectively, decreasing as the current rate increased. The duration of the second phase of the battery was 961, 308 and 162 s, respectively, which also decreased as the current rate increased. According to Joule's law, the rate of ohmic heat generation is proportional to the square of the current

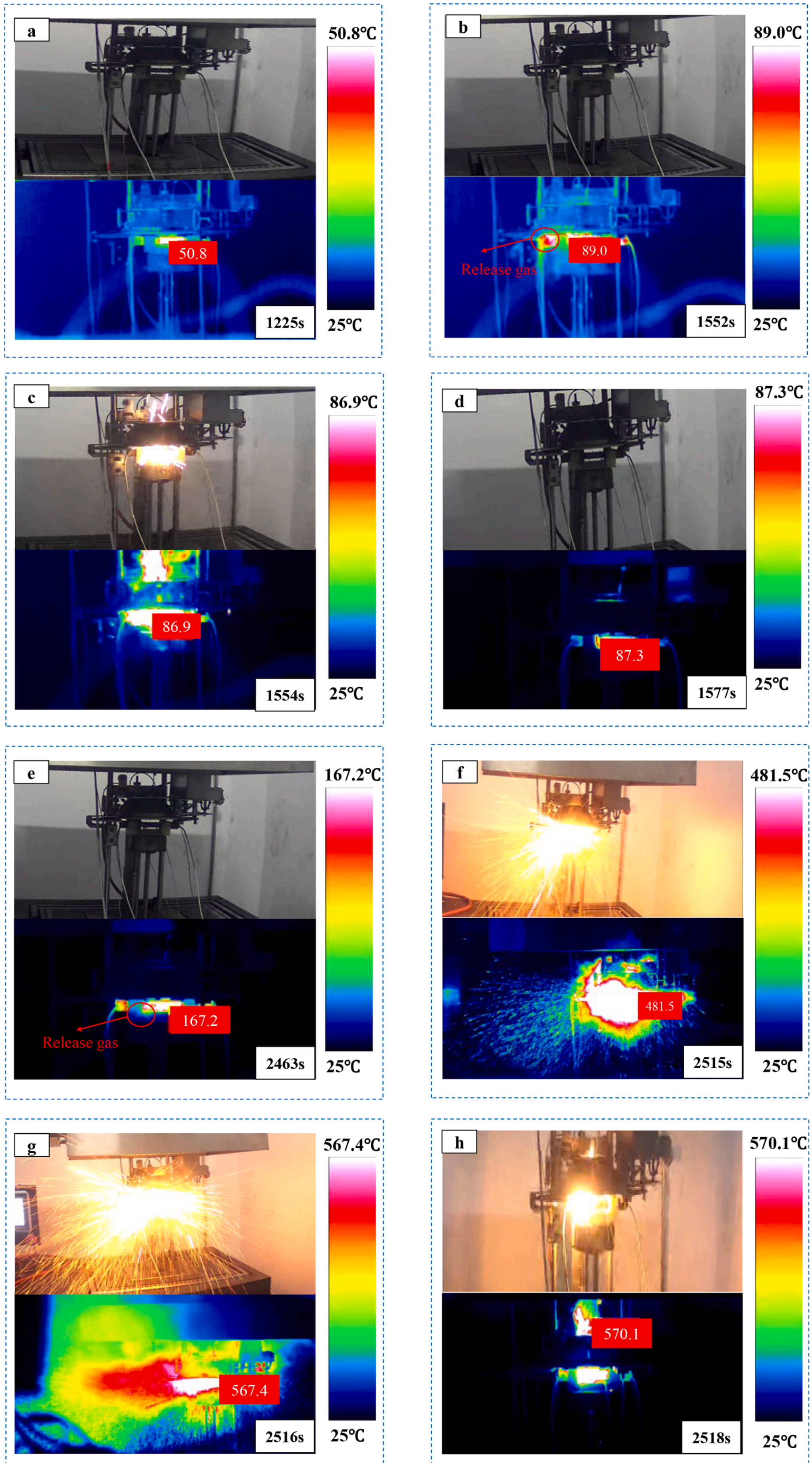
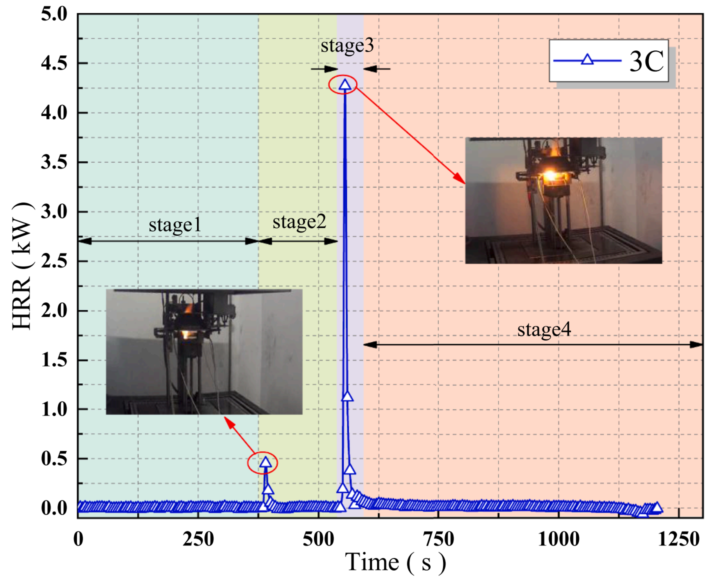
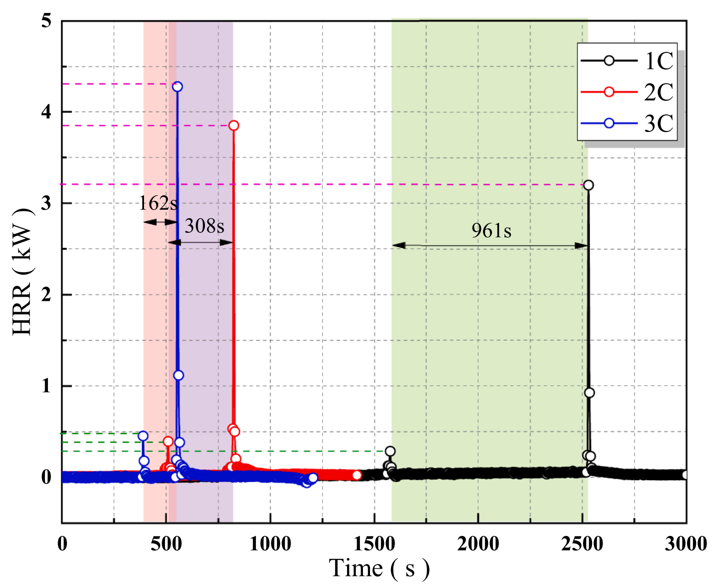


Fig. 4. Visible light and infrared images of a battery overcharged at a 1 C current rate.



(a) Heat release rate (HRR) of lithium-ion batteries overcharged at a 3 C current rate.



(b) Heat release rate (HRR) of lithium-ion batteries overcharged at 1 C, 2 C and 3 C current rates.

Fig. 5. Heat release rate (HRR) of lithium-ion batteries overcharged at different current rates.

rate [29]. As the current rate increased from 1 C to 3 C, the rate of ohmic heat generation became faster, and therefore the time needed for thermal runaway to occur decreased. As the current rate increases from 1 C to 3 C, the peak temperature and the temperature change rate of the second stage increase significantly. For high current rate, the internal heat of the battery accumulates rapidly and the surface temperature increases rapidly. For low current rate, the internal reaction of the battery is slow and the surface temperature rises slowly.

3.4.2. *Flame temperature at different locations*

Fig. 8 shows the flame temperature of the battery overcharged at a 3 C current rate, measured at locations defined in Fig. 1. At TC3 the surface temperature of the battery is much higher than the temperature at other TC locations. The change of the TC3 temperature mainly depends on the change of internal heat of the battery, and the internal temperature shows an upward trend when the battery is charged. In the first stage, the temperature at TC4, a point 5 cm from the battery, is almost the same, and there is no obvious change. Because there is no flame, less gas is released and the gas is mainly concentrated near the safety valve. It is difficult for thermocouples to determine the gas temperature more than 5 cm from the center of the battery. After 360 s, the first thermal runaway occurs, and the temperature of the 5 measuring points increases slightly, mainly due to the electric spark injection, the release of gas, and the heat generated by the flame combustion. The temperature changes at the 3 points above 5 cm are more obvious. The temperature of the 3 measuring points above 5 cm are reduced and stabilized. The temperature at TC4 is higher than the temperature above 10 cm in the third stage. This may be due to the fact that TC4 is located closer to the battery and is affected by heat radiation, and the temperature is slightly higher than the temperature at other points. The temperatures at points TC3–TC7 rise sharply at 522 s, when the second thermal runaway occurs. At 538 s, the temperature at TC3 reaches a peak of 788.55 K, at 536 s the temperature at TC4 reaches a peak of 579.75 K, and at 526 s, the temperature at TC5 reaches its peak of 491.35 K. At 534 s, the

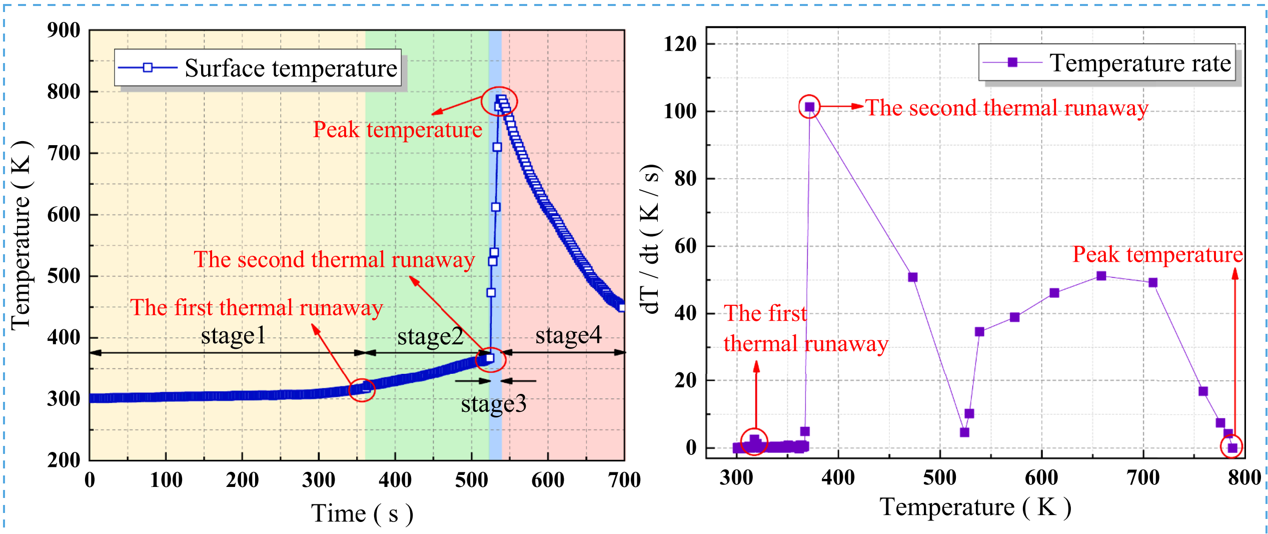


Fig. 6. Surface temperature and temperature rate of a battery overcharged at a 3 C current rate.

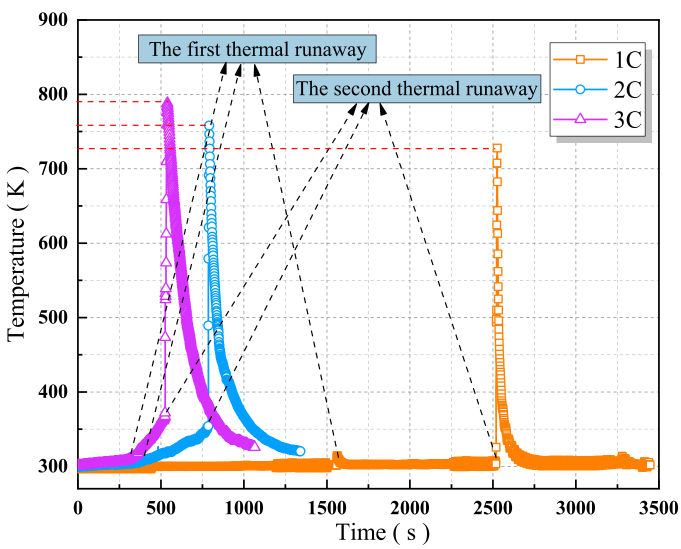


Fig. 7. The center surface temperature of lithium-ion batteries overcharged at different current rates.

temperature at TC6 reaches a peak of 355.65 K, and at 534 s, the temperature at TC7 reaches a peak of 356.75 K. The peak temperature of the center surface of the battery is much higher than the temperature of other points. When each measurement point reaches its peak, electric sparks are no longer present. When TC5 reaches the peak temperature, the flame burns most intensely, and there is no flame in the area 15 cm above battery. The TC5 position is the point where the flame can be captured and the farthest from the flame center among the five thermocouples. The flame height of TC6 and TC7 is less than 15 cm, so the peak temperature of TC6 and TC7 may be the temperature of flue gas. When TC4 reaches the peak temperature, TC4 is the position where the flame can be captured by the five thermocouples and is the furthest away from the flame center. At 538 s, the flame goes out and TC3 reaches the peak temperature. At this time, the surface of the battery appears purple-red. The peak temperature of TC3 mainly depends on the exothermic reaction inside the battery. As shown in Fig. 9, the batteries with current rates of 1 C and 2 C have a similar change law as the battery with current rate of 3 C, and the temperature at TC3 is higher than that at other measuring points. When the current rate is 1 C, the temperature difference is small, mainly because the battery current rate is low, the heat accumulation rate is slow, the battery temperature change is not obvious, when there is no thermal runaway, the battery surface temperature and flame temperature are low.

3.4.3. Positive and negative electrode temperature

Fig. 10 shows the temperature curves of the positive and negative electrodes of the lithium-ion battery overcharged at a 3 C current rate. In the first stage, the temperature of the positive and negative electrodes increased steadily [30–32]. At 1554 s, the first thermal runaway occurred, and sparks and flames appeared. Because the range of sparks and flames was small and concentrated near the positive electrode, the temperature of the positive electrode increased and a small peak appeared, but the temperature of the negative electrode did not fluctuate significantly. The temperature of the positive and negative electrodes began to drop at 2179 and 2236 s, respectively. At 2179 s, the sound of safety valve cracking was heard, the gas and heat are ejected together, and the positive and negative temperatures decreased. As shown in Fig. 4 (e), the infrared image shows that the battery released gas at 2463 s. Although the gas release took away part of the heat, the thermocouples on the surface of the positive and negative electrodes of the battery were closer to the battery due to the weakening caused by the expansion and heating of the battery. Therefore, the temperature of the positive and negative electrodes of the battery showed an upward trend. At 2515 s, the thermal runaway occurred. The temperature of the positive and negative electrodes of the battery increased sharply and reached peak values of 699.05 and 705.75 K at 2520 and 2524 s, respectively. After reaching the peak value, the temperature of both electrodes began to show a downward trend.

3.5. Mass loss

The mass loss was analyzed with a heat-resistant balance. The initial mass, which included the charging device and thermocouple, was measured and then subtracted from all subsequent measurements to determine the mass loss. For the thermal damage caused by overcharge, the mass loss process could be roughly divided into four stages. The first stage consisted of mass loss due to the expansion of the battery and the gas release caused by the rupture of the safety valve. The second stage encompassed the large number of internal materials of the battery that were sprayed out in the form of sparks and luminescent particles during the first thermal runaway. In the third stage were the internal materials of the battery that were sprayed out in the form of sparks during the second thermal runaway. The fourth and final stage was the end of the

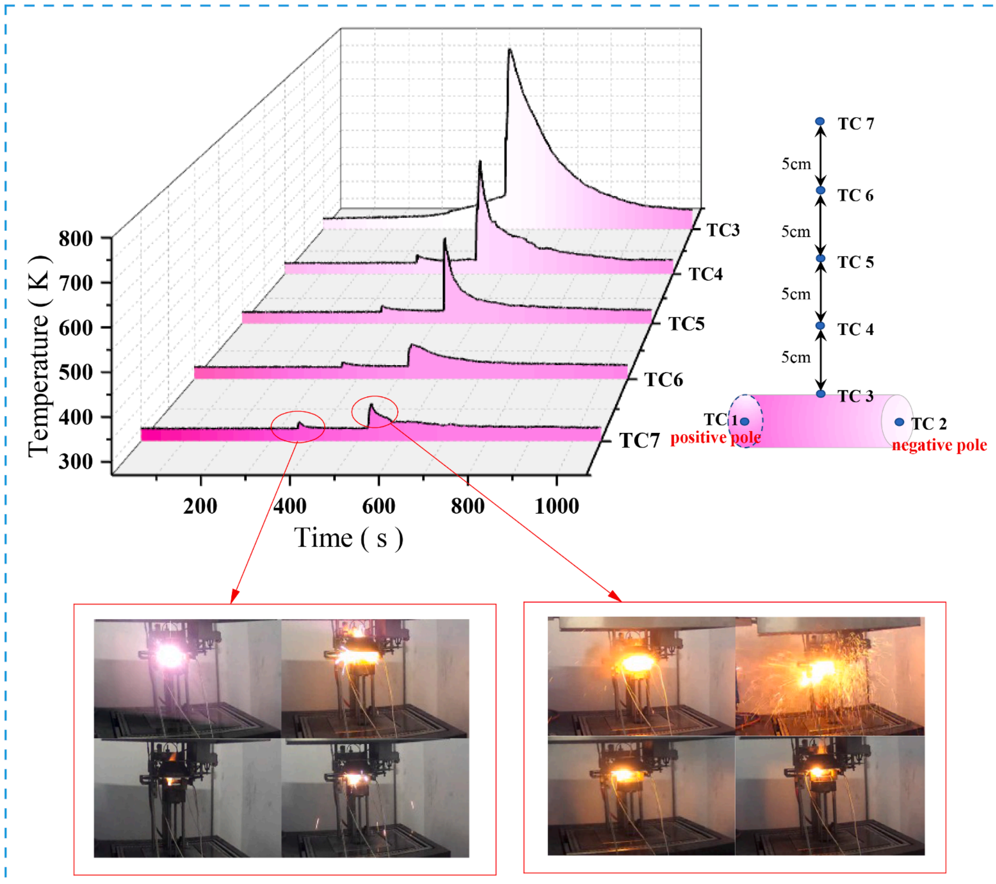


Fig. 8. Flame temperatures at different locations of a battery overcharged at a 3 C current rate.

reaction.

As shown in Fig. 11, the mass loss of the lithium-ion battery that was overcharged at a 1 C current rate continued to decline in the first stage, which could have been due to the vaporization of the electrolyte inside the battery resulting in gas generation and a small amount of gas release from the battery. At 1554 s, the battery experienced its first thermal runaway. The battery had a violent explosion reaction and its mass increased sharply. Subsequently, the internal materials of the battery were sprayed in the form of electric sparks and large luminous particles, and the mass of the battery continued to decline. At 2515 s, the second thermal runaway occurred. Due to violent reactions such as battery explosion, the mass increased sharply and then decreased suddenly. Most of the mass loss occurred in the second thermal runaway stage. In the final stage, because most combustible gases had been consumed, the mass was close to a constant. The mass loss spike was generated by rebounding force (F_{rb}) at the beginning of ejection [2]. As shown in Fig. 11, the mass loss spike of the two thermal runaways was 0.21 and 1.23 g respectively. The rebounding force of the second thermal runaway was greater than that of the first thermal runaway. Therefore, the explosion reaction of the second thermal runaway was more violent than that of the first thermal runaway. The mass loss in the first thermal runaway was much less than that in the second thermal runaway. The mass loss was mainly due to gas injection and electric spark injection. Fig. 11 shows that the amount of electric spark injection in the first thermal runaway was much less than that in the second thermal runaway.

Fig. 12 shows the mass loss curve of the battery when the battery was overcharged at three different current rates. With the current rate from 1 C to 3 C, the mass loss spike of the first thermal runaway were 0.21, 16.26 and 24.23 g, respectively, and the mass loss spike of the second thermal runaway were 1.23, 33.57 and 48.25 g, respectively. The rebounding force was directly proportional to the current rate. Compared with the battery with a small current rate, the battery with a large current rate was easier to spray, and the two thermal runaway matches this law. As the current rate increased, the explosive reaction of the battery became more and more intense, the heat generation rate increased, and the heat accumulation accelerated. The electrolyte inside the battery decomposed. The reactions of the liquid, the negative electrode, and the electrolyte were all stronger. A large amount of gas accumulated, causing the explosive reaction to become more violent. The gas production volume of the second thermal runaway was greater than that of the first thermal runaway, so the second thermal runaway explosion reaction was more violent than the first one. With the current rate from 1 C to 3 C, the total mass loss values are 24.27, 29.83 and 32.69 g. In these experiments, the higher the input current rate, the greater the mass loss of lithium-ion battery.

4. Conclusions

This study used a cone calorimeter to analyze the thermal runaway behavior of 2.6 Ah 18650 NCM lithium-ion batteries. The HRR, surface temperature, flame temperature, positive and negative electrode temperature, and mass loss were measured. This article also used both an infrared and a visible light camera to record the process of thermal runaway of the lithium-ion batteries. Current rates of 1 C, 2 C, and 3 C were used to overcharge the lithium-ion batteries for testing. We drew the following specific conclusions:

(1) In this study, the lithium-ion battery has two thermal runaway behaviors when it is overcharged with a high current rate. The main reason is that the lithium-ion battery has two internal heat accumulations under the condition of high current rate overcharge,

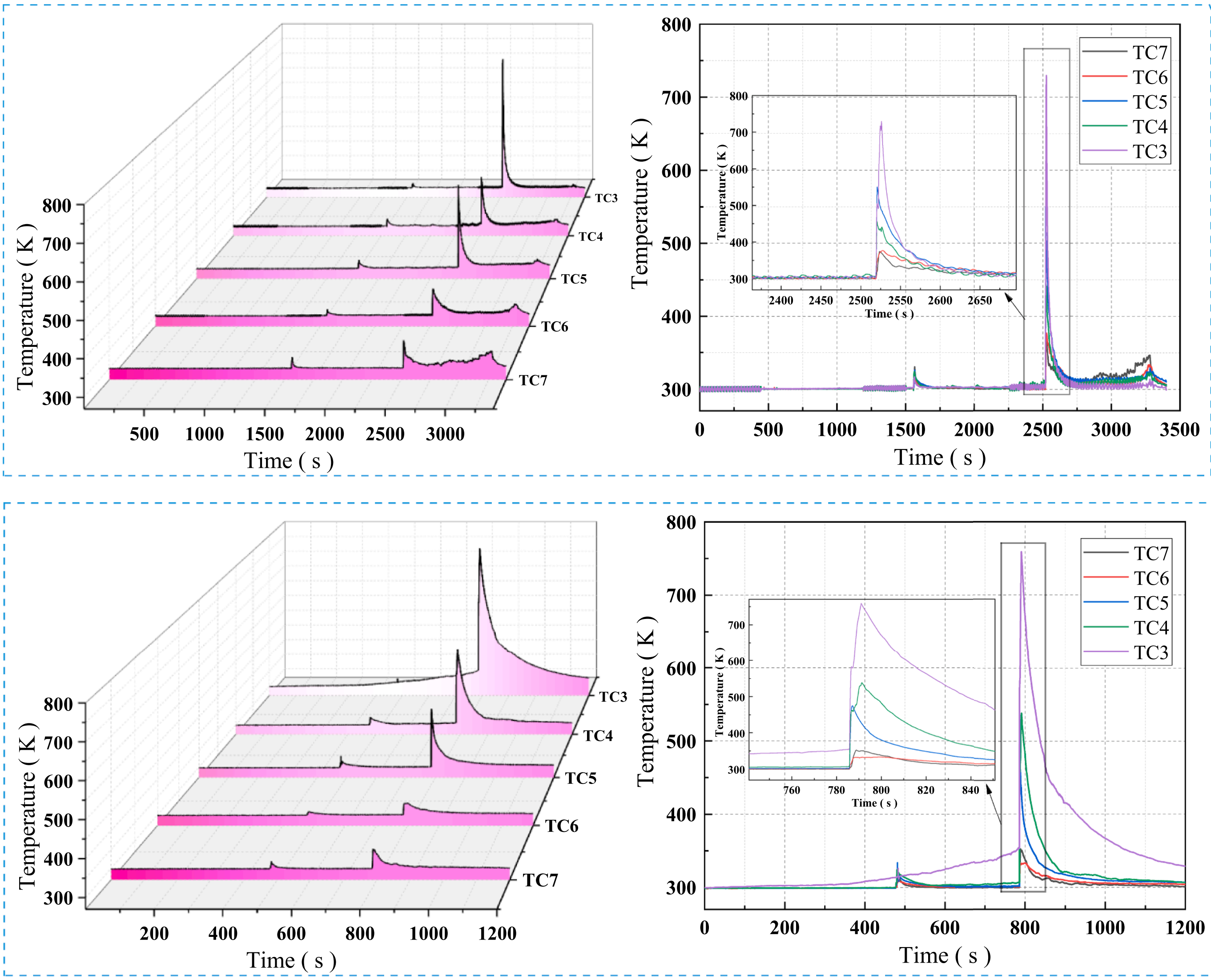


Fig. 9. Flame temperatures at different locations of a battery overcharged at 1 C, 2 C current rates.

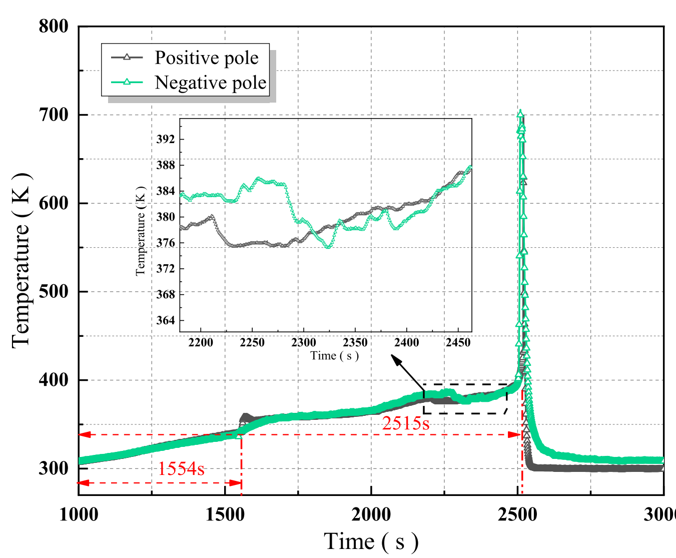


Fig. 10. Temperature of the positive and negative electrode of a battery overcharged at a 1 C current rate.

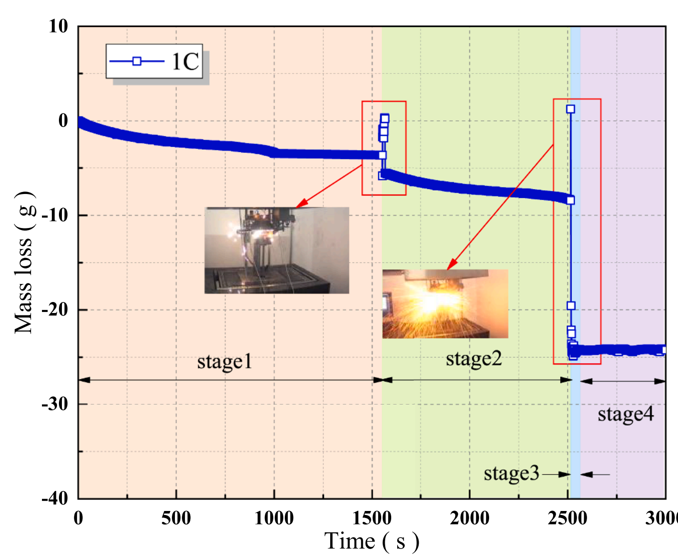


Fig. 11. Mass loss of a battery overcharged at a 1 C current rate.

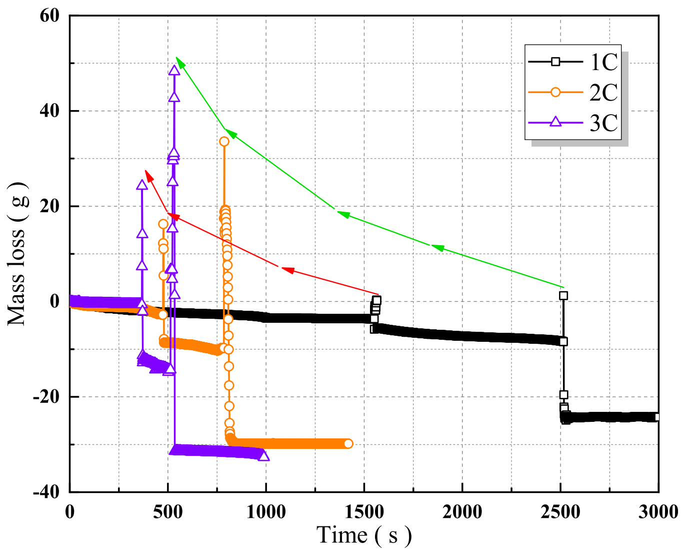


Fig. 12. Mass loss of batteries overcharged with different current rates.

resulting in two gas accumulations, which causes two thermal runaways.

(2) In the first thermal runaway, a continuous explosion occurs and sprays large luminous particles and electric sparks. In the second thermal runaway, the range of spark injection is larger and the number of sparks is larger. Because there were a number of spark ejections during the first thermal runaway, the time point of flame burning is not fixed, while the second thermal runaway spark injection is concentrated in the beginning period of thermal runaway, and the flame slowly dominates at the end of the spark injection. When the current rate is 1 C, the HRR peaks of the first and second thermal runaways are 0.28 and 3.20 kW, and the mass loss spike are 0.21 and 1.23 g, respectively. The flame combustion and explosion reaction of the second thermal runaway is more violent than the first thermal runaway, and this is also true for the current rates of 2 C and 3 C.

(3) As the current rate increases from 1 C to 3 C, the time for the first thermal runaway is reduced from 1554 to 360 s, the time for the second thermal runaway is reduced from 2515 to 522 s, and the duration of the thermal runaways increases. The mass loss spike for the first thermal runaway increases from 0.21 to 24.23 g, the mass loss spike for the second thermal runaway increases from 1.23 to 48.25 g, and the explosive reaction increases in intensity.

In this study, the lithium-ion battery was overcharged at high current rate, and two different thermal runaways occurred, and the thermal runaway reaction had certain regularity. However, as the thermal runaway reaction of lithium-ion batteries is highly uncertain, the same initial conditions may lead to different reaction results. Due to the differences in the internal materials and structures of lithium-ion batteries, the thermal runaway reaction of lithium-ion batteries is uncertain.

Data availability statement

Some or all data, models, or code generated or used during the study are available from the corresponding author by request.

CRediT authorship contribution statement

Zhen Liu: Conceptualization, Methodology. **Xinrong Guo:** Data curation, Software, Writing – original draft. **Na Meng:** Visualization, Investigation. **Zhanglong Yu:** Supervision, Validation. **He Yang:** Software, Writing – review & editing.

Declaration of Competing Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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Further reading

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