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Fire behaviors study on 18650 batteries pack using a cone-calorimeter

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Abstract

To investigate the effects of different state of charges (SOCs), external heating powers and charging/discharging treatment on the fire behaviors of 18650 batteries pack, three groups of abuse experiments were conducted with the help of a cone-calorimeter. The fire hazards of batteries pack were characterized by measuring the flame photographs, battery surface temperature, ignition time, thermal runaway time, heat release rate and radiative heat flux. According to the results, it is found that the fire behaviors of batteries pack will appear in advance and behave more violent with the increase in SOC. Additionally, the higher heating power will exacerbate the fire hazards of batteries pack by increasing the surface temperature rise rate, the total heat released and the total heat flux of pack leading to an earlier thermal runaway and more rigorous consequence. Finally, the pack with discharging/charging treatment has a much lower heat released compared to the pack without any treatment due to the incomplete burning and incomplete release of energy. Besides, their fire behaviors also exhibit earlier and severer.

Keywords Batteries pack · Fire behaviors · SOC · Heating power · Charge/discharge · Heat release rate

Introduction

With the layouts of governments all over the world on new energy industry, the lithium-ion battery gets a more and more extensive application, such as charge-pals, laptops, mobile phones, and electronic vehicles (EVs). And LIBs continue to thrive rapidly for a long time due to the demands of energy and its own advantages such as high energy density, zero pollution during using, stable performances and long-life cycles [1, 2]. However, risks also arise at the meantime that the fire and explosion accidents of LIBs often occurred because of their sensitivity to high temperature, overcharging and collision. And, the accidents can be found in many fields, from new energy vehicles, to mobile phones and the battery manufactures such as a fire that occurred in a Tesla Model S charging at a Tesla Supercharger in Shanghai as a result of battery problem on March 4, 2017, when an iPhone 7 took fire in Australia resulting in the devastation of a car and the explosion on the workshop of a battery manufacture in Qidong caused twenty people to be dead or wounded. Therefore, it is necessary to conduct a further study on the fire behaviors of LIBs to have a better understanding on the safety of them.

In most instances, researchers have paid a lot of attentions to the thermal characteristics of LIB [3–12]. Ribière et al. investigated the fire-induced hazards of LIBs by fire calorimetry and analyzed the toxicity of gases generated including CO, CO_2, SO_2 and HF. Fredrik et al. took six abuse tests on lithium-iron phosphate cells to research the inhibiting effect of water mist application on the generation of HF. Sun et al. performed combustion experiments to analyze the toxicity of combustion products of LIB and investigated the relationship between the concentration of toxic products and the battery capacity. Ouyang et al. conducted a series of thermal failure researches to explore the thermal failure propagation of battery pack. An obvious domino effect in the thermal failure propagation of battery pack was found, and the effects of SOC, the number of heaters, failure location and pack size on failure propagation were also discussed. Besides, to investigate the effectiveness of depressurization on the fire suppression of LIBs, Fu et al. took an

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experimental and theoretical study on the ignition and combustion characteristics of LIBs using a low-pressure tank. Results showed that with the reduction in pressure, LIBs exhibited a lower fire risk. They also proposed 30 kPa was the critical pressure for the ignition of LIB under 50 kW m^{-2} radiation heat flux. In addition, there were many papers that researched the effects of SOC on the thermal behaviors of single LIB [13–17]. Wang et al. investigated the combustion behaviors of lithium-iron phosphate cells with 50% and 100% SOC in ISO-9705 combustion room. Andrey et al. measured the thermal runaway characteristics of commercial LIB in destructive thermal ramp experiments to explore how SOC affected the severity of thermal runaway behaviors and the generation of gases such as CO, H_2 and CO_2. Finally, large quantities of works are related to the temperature variations of LIB during charging or discharging [18–24]. Yan et al. investigated the thermal performances of phase-change-materials-based battery management system in cycling. Wu et al. had a comparison analysis on the thermal runaway of LIB under internal heating mode and external heating mode with the help of ARC. Liu et al. conducted experiments to study the thermal runaway process of LIB during charging and discharging under different rates. Besides, Kim et al. presented a method for modeling the thermal behavior of a LIB during charge by measuring the heat release rate and temperature distributions of battery. However, it is easy to find that many batteries used around us were united as packs such as charge-pals, flashlights and electronic toys. But, few researches have been performed to explore the fire behaviors of packs and the studies about batteries packs with different SOCs still haven't been reported. What's more, many accidents of batteries packs took place when they were in the state of charging or discharging, whereas scarce work focused on the fire behaviors of packs under charging/discharging conditions. Finally, differences in the fire behaviors of packs under different external heating powers were seldom concerned.

In order to fill in the gap, this paper researched the fire behaviors of batteries pack containing three cells, and the influence of SOC, charging/discharging treatment and external heating power on the fire behaviors were also explored. Specific information including flame photographs, battery surface temperature, ignition time, thermal runaway time, heat release rate (HRR) and radiative heat flux was measured and analyzed to provide necessary basic data for the safety management of batteries pack.

Experiment

Battery samples

The batteries used in current study are cylindrical SAMSUNG 18650 with a diameter of 18 mm and a height of 65 mm. Its nominal capacity is 1300 mAh using lithium nickel manganese cobalt oxide (NMC) as the cathode and graphite as the anode. Besides, its cut-off voltage for charge and discharge is 4.2 V and 2.5 V, respectively. Before tests, the original energy stored in batteries was released by discharging with a CC (constant current) of 2600 mA until the voltage decreased to 2.5 V, and then the batteries would be charged by the same CC to the fixed SOCs. Hereafter, the batteries would be placed still for 24 h to ensure the batteries remained stable before tests. The schematic diagram of batteries pack used in test is shown in Fig. 1.

Apparatuses and experimental design

As shown in Fig. 2, experiments were carried out in a well-ventilated cone chamber with a dimension of 1.2 m × 1.2 m × 1.2 m. The battery was placed upon a supporting mesh made of iron wire. The electric heater with a power range from 0 kW to 2 kW was positioned below the mesh with a distance of 1 cm away from the battery. A K-type thermocouple with a diameter of 1 mm

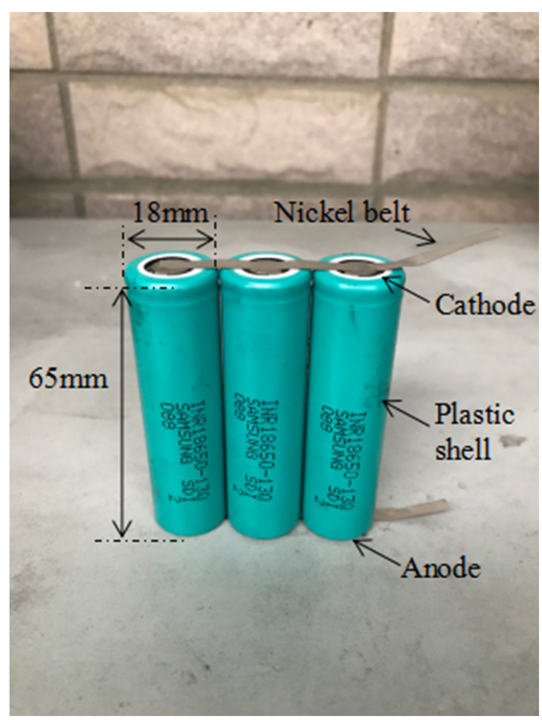

Fig. 1 Schematic diagram of batteries pack

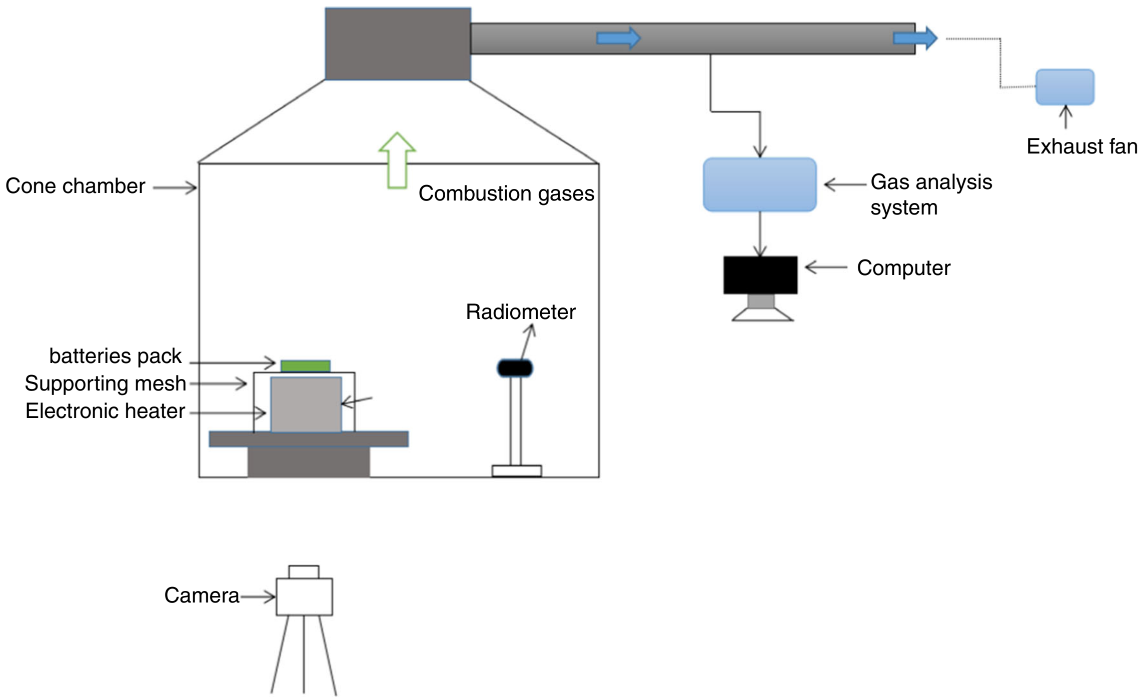

Fig. 2 Simplified experimental setup

was attached to the mid of battery to measure its surface temperature, and the temperature was recorded at the data acquisition equipment (NI cDAQ-9174) by a computer. Cycling battery was achieved by a charge/discharge cycle equipment (NEWARE CT-3008) with a voltage range from 0 V to 5 V. A camera (SONY XPS160) with 25 fps was employed to record the tests. Besides, the concentrations of O_2, CO_2 and CO were obtained by the Servomex 4100 gas analyzer and then used to calculate the variations of HRR based on the oxygen consumption principle. Finally, a radiometer sensor (TS-10C) with 0.2 μV W^{-1} m^2 resolution and 50 mV measurement range was positioned 25 cm horizontally away from the battery to measure the heat flux of fire and it was placed facing the safety vent so that the greatest heat flux could be required when LIBs took fires.

Three groups of experiments were carried out to explore the influence of SOC, charging/discharging treatment and external heating power on the fire behaviors of batteries pack.

Group 1: Four tests of packs with different SOCs (25%, 50%, 75% and 100%) were conducted to explore the effects of SOC on the fire behaviors of packs.

Group 2: Two tests of packs (75% SOC) under the effect of heater with a power of 1.0 kW and 1.5 kW, respectively, were conducted to explore the influence of heating power on the fire behaviors of packs by comparing with the 75% SOC pack heated by a 2.0 kW power in Group 1.

Group 3: Two tests of packs (75% SOC) with charging treatment and discharging treatment were conducted to explore how they affected the fire behaviors of packs by comparing with the same SOC pack but without any treatment in Group 1. And the experimental configurations are listed in Table 1.

Results and discussions

The effects of SOC

There has always been a big concern to estimate the SOC for all energy storage devices. SOC estimation with high accuracy not only gives us information about remaining useful energy, but also it evaluates the reliability of batteries. The batteries packs used in the electronic products

Table 1 The experimental configurations

Group	Test no.	SOC/%	Treatment	Heating power/kW
1	1	25	–	2.0
	2	50	–	2.0
	3	75	–	2.0
	4	100	–	2.0
2	1	75	–	1.0
	2	75	–	1.5
3	1	75	Charge	2.0
	2	75	Discharge	2.0

around us have different SOCs during using which causes quite different fire behaviors of packs if heated. Therefore, it is necessary to have an experimental study of the SOC effects on the packs fire behaviors. SOC can be defined accordingly based on capacity obtained during charge expressed as follows [25]:

$$\mathrm{SOC} = \frac{\int i\mathrm{d}t}{C_\mathrm{n}} \tag{1}$$

where i is the battery current; C_n is the nominal capacity; t is time.

Several typical moments during the burning process of packs under the effect of a 2 kW power electric heater are shown in Fig. 3. Similar to the fire behavior of single battery reported before [7, 13, 26], the burning process of batteries pack can also be divided into five stages: (a) heating stage, (b) safety vent cracking, (c) ignition, (d) violent ejection and combustion, (e) flame abatement. During the heating stage, the pack remained stable with little change except parts of plastic shell melted. With the continuously rise in temperature, the quantities of gases inside battery became larger and larger causing the rapid growth of internal pressure until the cracking of safety vent which was used to protect battery. Hereafter, there would have some amounts of gases released and then the gases were ignited. The flame would last until the violent ejection with plenty of flammable gases liberated. And then, a stable combustion could be observed. Except for the pack with 25% SOC, it would not have the violent ejection process but replaced by a stable and enduring combustion process after the safety vent cracking and the ignition. With the depletion of the combustibles, the fire abated and extinguished.

Fig. 3 Combustion phenomena of packs in tests: **a** 25% SOC; **b** 50% SOC; **c** 75% SOC; **d** 100% SOC

Comparing the fire behaviors of packs with different SOCs, it can be found that the pack with higher SOC appears earlier safety vent cracking, ignition and ejection. What's more, the severity of ejection and combustion behaviors would deepen with the increase in SOC. It reveals that the pack with higher SOC possesses a more serious combustion process, a severer fire behavior and a higher risk resulting from the unstable electroactive materials, where highly delithiated electroactive materials become more reactive for LIB with higher SOC [27].

The typical curves of surface temperature of packs with different SOCs under the heating of a 2 kW power are plotted in Fig. 4. Similar to what is mentioned above, the variations of surface temperature can also be divided into several typical stages. At stage (a), it can be seen that all of them arose synchronously under the effect of heater until the cracking of safety vent at around 130°. It resulted from the breakdown of SEI layer at 90–130 °C and the melting of polymer separator causing the metal oxide cathode materials decomposed and reacted with organic solvents [28], which generated large quantities of gases and destroyed the safety vent in the end. After safety vent cracking, the rise in surface temperature sped up with lots of exothermic reactions carrying on. At around 160°, the ejected gases were ignited resulting in a combustion and the temperature arose continually. Hereafter, the thermal runaway occurred and it could be observed that the temperature increased sharply to the peak.

It can be found that the differences between different packs appear obviously after the cracking of safety vent. The pack with higher SOC owns earlier fire behaviors such as earlier safety cracking, earlier ignition and earlier thermal runaway. Besides, the peak temperature has an uptrend with the growth of SOC which reveals that the pack with higher SOC possesses more violent combustion

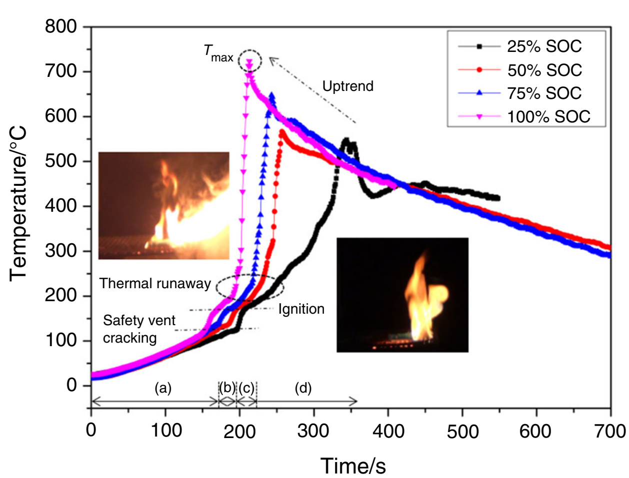

Fig. 4 The typical surface temperature curves of packs with different SOCs

corresponding to the results expressed in the combustion phenomena. Further, the key parameters including the time to safety vent cracking, the temperature to safety vent cracking, the time to ignition, the temperature to ignition, the time to thermal runaway and the temperature to thermal runaway are extracted from the curves and listed in Table 2.

It is presented that with the increase in SOC, time to safety vent cracking, ignition and thermal runaway has an advance trend that the pack with higher SOC, the earlier to safety vent cracking, ignition and thermal runaway. It is due to the quicker generations of combustible gases inside batteries for pack with higher SOC. With the increase in SOC, the electroactive materials of battery will become more reactive, and therefore it is easier to take reactions [6]. On the other hand, it is interesting to find that the temperature to safety vent cracking, ignition and thermal runaway exhibit similar values for all the packs as shown in Fig. 5. It indicates that these critical temperatures mainly rely on the battery properties and the incident heating but not SOC for the chemical reactions inside battery take place at critical temperature ranges under the same incident heating. And the finding is similar to what reported before [14].

HRR is the released heat in unit time during the combustion of materials under given conditions. It reveals the ability of fire source to release heat and is one of the most important parameters to define fire hazards. In this research, the HRR values were calculated by oxygen consumption principle proposed by Thornton [29]. Figure 6 presents the heat release rate versus time for the packs with different SOCs, and the THR (total heat released) can be calculated by integrating the HRR curve with time. From the figure, it is clearly seen that the HRR curves represent two obvious peaks except the pack with 25% SOC which corresponds to the ignitions and the later ejections of packs, respectively. The single peak of 25% SOC contributes to the enduring combustion after ignition, and it won't have the ejection process. This finding is consistent with the result of combustion phenomena described previously. The peak HRR values corresponding to 25%, 50%, 75% and 100% SOC are 6.2, 6.8, 9.2 and 4.1 kW, respectively. It illustrates that the pack with higher SOC will have higher peak HRR value except the 100% SOC. After integrating, it is calculated that the THR of them are 125.8, 195.0, 239.7 and 104.1 kJ separately. Obviously, the total heat released of packs increases with the growth of SOC apart from the 100% SOC whose THR has an obvious drop. It is attributed to the incomplete combustion during test for its much more violent fire behaviors, and there is no enough time for sufficient chemical reactions inside the battery to release energy for the fire behaviors of 100% SOC is much earlier than the

Table 2 Specifications of the surface temperature

Test no.	SOC/%	Time to cracks/s	Temperature to cracks/°C	Time to ignition/s	Temperature to ignition/°C	Time to thermal runaway/s	Temperature to thermal runaway/°C	The maximum temperature/°C
1	25	197	129	216	172	251	235	548
2	50	185	136	200	176	229	231	566
3	75	174	136	193	174	218	236	647
4	100	156	132	171	171	196	229	728

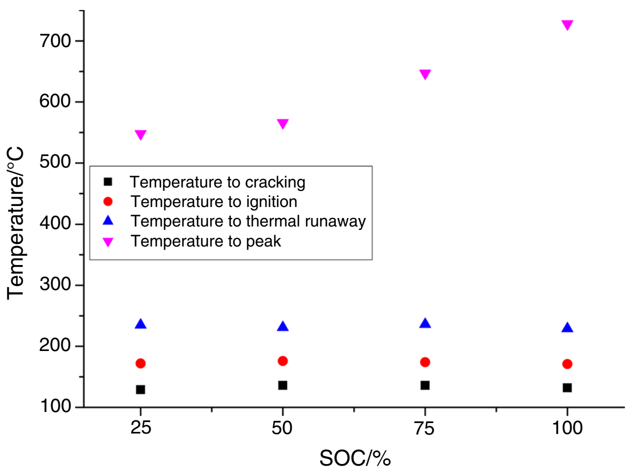

Fig. 5 The critic temperatures of packs in tests

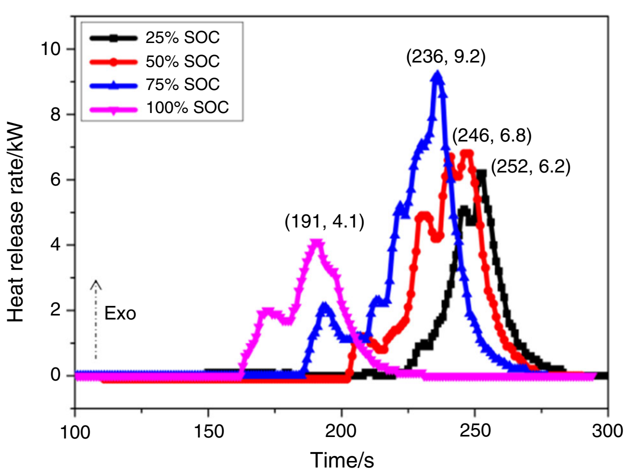

Fig. 6 The typical heat release curves of packs with different SOCs in tests

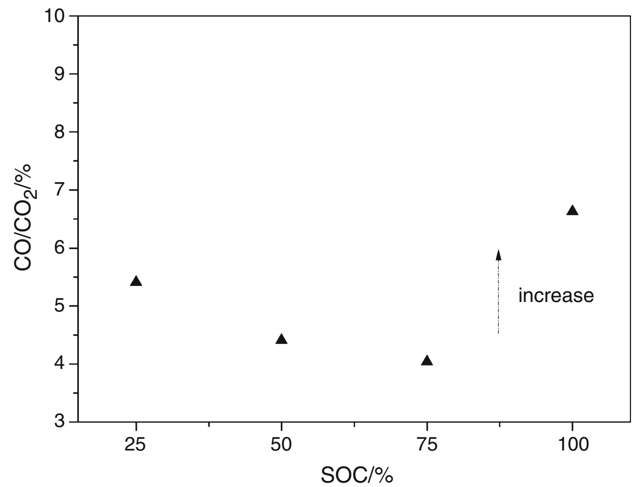

Fig. 7 Gas concentration increments with different SOC

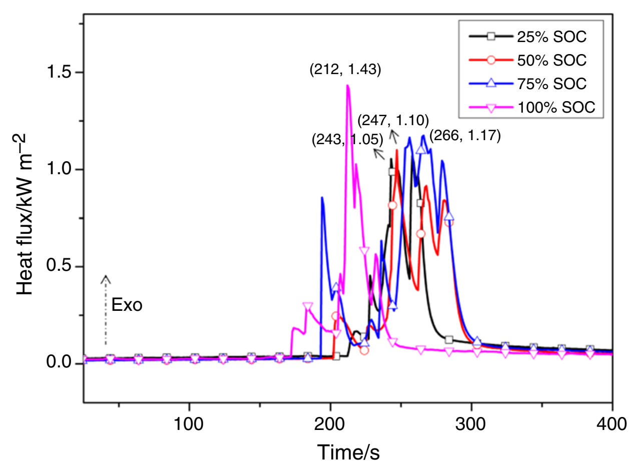

Fig. 8 Heat flux curves of packs in tests

others. And it can be confirmed by the variation of CO/CO_2 ratio measured in fire tests which is plotted in Fig. 7. It is shown that the CO/CO_2 ratio of 100% SOC has a sharp increase indicating an obvious decrease of combustion efficiency. Namely, the incomplete combustion increases.

In addition, radiative heat flux is another important parameter to research fire hazards. As a part of total heat release rate, it can be used to characterize the fire behaviors of materials, such as flame shape or flame temperature. Figure 8 plots the radiative heat flux curves of packs with different SOCs during tests. The peak heat flux corresponding to 25%, 50%, 75% and 100% SOC are 1.05, 1.10, 1.17 and 1.43 kW m^{-2} which reveals the pack with higher SOC possesses higher peak heat flux values and more violent fire behaviors. Besides, the total radiative heat flux was calculated by integrating the curves and has a result of

35.1, 42.8, 58.0 and 30.1 kJ m^{-2} for 25%, 50%, 75% and 100% SOC, respectively. It represents a similar phenomenon compared to the THR, and the details are listed in Table 3.

The effects of heating power

As what had been described in Sect. 3.1, the burning behaviors of packs under the effect of different heating powers had similar processes that consisted of the heating stage, the safety vent cracking, the ignition, the violent ejection and combustion, the flame abatement as shown in Fig. 9. Each pack possessed a 75% SOC. It can be seen that the fire behaviors including cracking, ignition and ejections of packs heated by 1.0 kW and 1.5 kW powers delayed obviously compared to that heated by a 2.0 kW power. Moreover, the ejection behaviors of them seemed to be moderate relatively than the latter one due to the lower heating power that would cause smaller quantities of flammable gases to release.

On the other hand, Fig. 10 shows the typical curves of surface temperature of the three packs heated by different powers. It can be obviously found that differences among them are evident. The pack heated by a higher power has a faster temperature rising rate and is earlier to the safety vent cracking, ignition and thermal runaway. Besides, it is revealed that the heating power has an influence on the peak temperature, which has an uptrend with the increase in heating power. According to the curves, the peak temperature increases from 589° to 648° as the heating power increases from 1.0 to 2.0 kW. Therefore, the pack under the effect of a higher heating power presents quicker fire behaviors and more violent combustion with a smaller cracking time, ignition time, thermal runaway time and a higher peak temperature. According to the researches of Ohlemiller et al. [30] and Ulas and Kuo [31], the relationship between ignition time of energetic materials and radiative flux can be expressed as follows, respectively:

$$\mathrm{Tig} = a/q^2 + b \quad (2)$$

$$\mathrm{Tig} = cq^{\mathrm{d}} \quad (3)$$

where *a, b, c* and *d* are constants related to the properties of materials, *q* is the radiative flux.

The fitting result of this paper is expressed in Fig. 11a according to the two kinds of models. Both of them reveal that the ignition time will be shortened with the increase in heating power. For a solid fuel, its ignition time is dependent on heating time, mixing time and chemical induction time. In which, the dominant factor is the heating time. With the increasing heating power, the heating time decreased resulting in a smaller ignition time [8]. Additionally, the specifications of the surface temperature curves are listed in Table 4 and further presented in Fig. 11b. Different to the results of packs with different SOCs, it can be seen that the critical temperature of packs heated by different powers has an uptrend with the increase in heating power in Fig. 11b. The pack heated by higher power possesses a higher cracking temperature, ignition temperature, thermal runaway temperature and peak temperature which are attributed to the variation of incident heating that these critical temperatures will rise with the increase in incident heating [32].

Figure 12 shows the HRR profiles of packs heated by different powers. It is found that the heating power has a great influence on the fire behaviors of packs. With the increase in heating power, the peak to HRR appears earlier and the peak value has an evident growth increasing from 4.0 to 9.2 kW as the heating power increases from 1.0 to 2.0 kW. Additionally, it can be calculated that the THR of 1.0 kW, 1.5 kW and 2.0 kW has a value of 120.0, 139.0 and 239.7 kJ, respectively. Namely, the pack heated by a higher heating power releases more heat during test. The increasing heating power has a strong effect on the intensities of thermal degradation and thermal runaway reaction which leads to earlier and severer fire behaviors of packs.

Besides, the radiative heat flux curves of packs under different heating powers are exhibited in Fig. 13. Similarly, the influence of heating power on the fire behaviors of pack can also be seen by the variations of radiative heat flux. The pack heated by a higher power represents earlier heat flux peak, and it increases from 0.74 to 1.17 kW m^{-2} when heating power increases from 1.0 to 2.0 kW, which verifies the increase in the strength of ejection behaviors with the increase in heating power described above. In addition, the total radiative heat flux grows from 32.4 to 59.9 kW m^{-2}, and the details are further summarized in Table 5.

Table 3 Heat release and radiative heat flux results of packs in tests

Test no.	SOC/%	Peak HRR/kW	THR/kJ	Peak heat flux/kW m^{-2}	Total heat flux/kJ m^{-2}
1	25	6.2	125.8	1.05	35.1
2	50	6.8	195.0	1.10	42.8
3	75	9.2	239.7	1.17	58.0
4	100	4.1	104.1	1.43	30.1

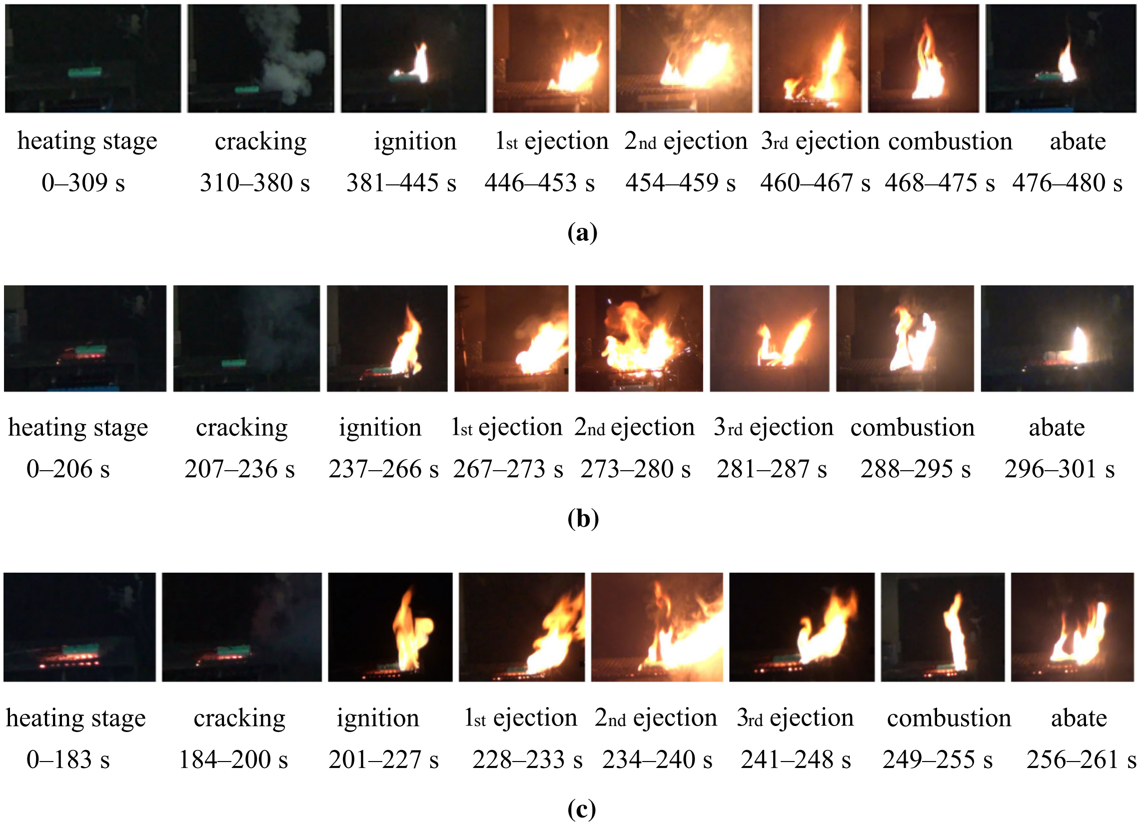

Fig. 9 Combustion phenomena of packs in tests: **a** 1.0 kW; **b** 1.5 kW; **c** 2.0 kW

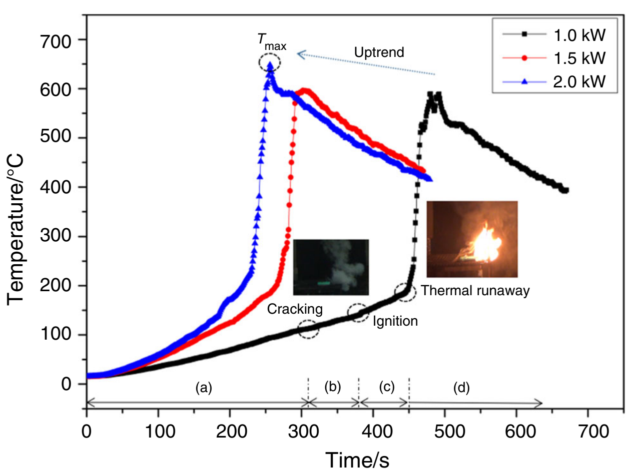

Fig. 10 The typical surface temperature curves of packs under different heating powers

The effects of charge/discharge treatment

Figure 14 shows the combustion phenomena of packs without treatment, with charge treatment, with discharge treatment, respectively. Due to the short time before battery cracking, a relatively large rate (3C) was applied to charge/discharge these packs to strengthen the effects of charge/discharge treatment, where the packs had an original capacity of 75% SOC. It is shown that the combustion phenomena resemble what was discussed in Sects. 3.1 and 3.2. After comparing, it can be found that the fire behaviors of pack with charge/discharge treatment has a quicker fire behavior such as ignition and ejection than the pack without any treatment. Besides, the severity of them also presents much more violent than that of the latter, which reveals that charge or discharge treatment will increase the risks of packs including the advance of fire behaviors and the severer consequences if heated.

In addition, the surface temperature curves of the three packs with 75% SOC under charging, discharging and without treatment are shown in Fig. 15. And the specifications of the surface temperature curves are extracted and listed in Table 6. Compared to that of the pack without treatment, the curve of pack under charging/discharging has a quicker temperature rise which leads to the earlier fire behaviors, especially for the pack with charging. This may be attributed to: (1) the heat generation during charge/discharge, including irreversible heat and reversible heat, (2) battery materials become more positive when battery is in charge/discharge so that it is easier to react with each other and leads to thermal runaway. Finally, it can be seen that charge/discharge treatment has little influence on the peak temperature and all of them float around 650°.

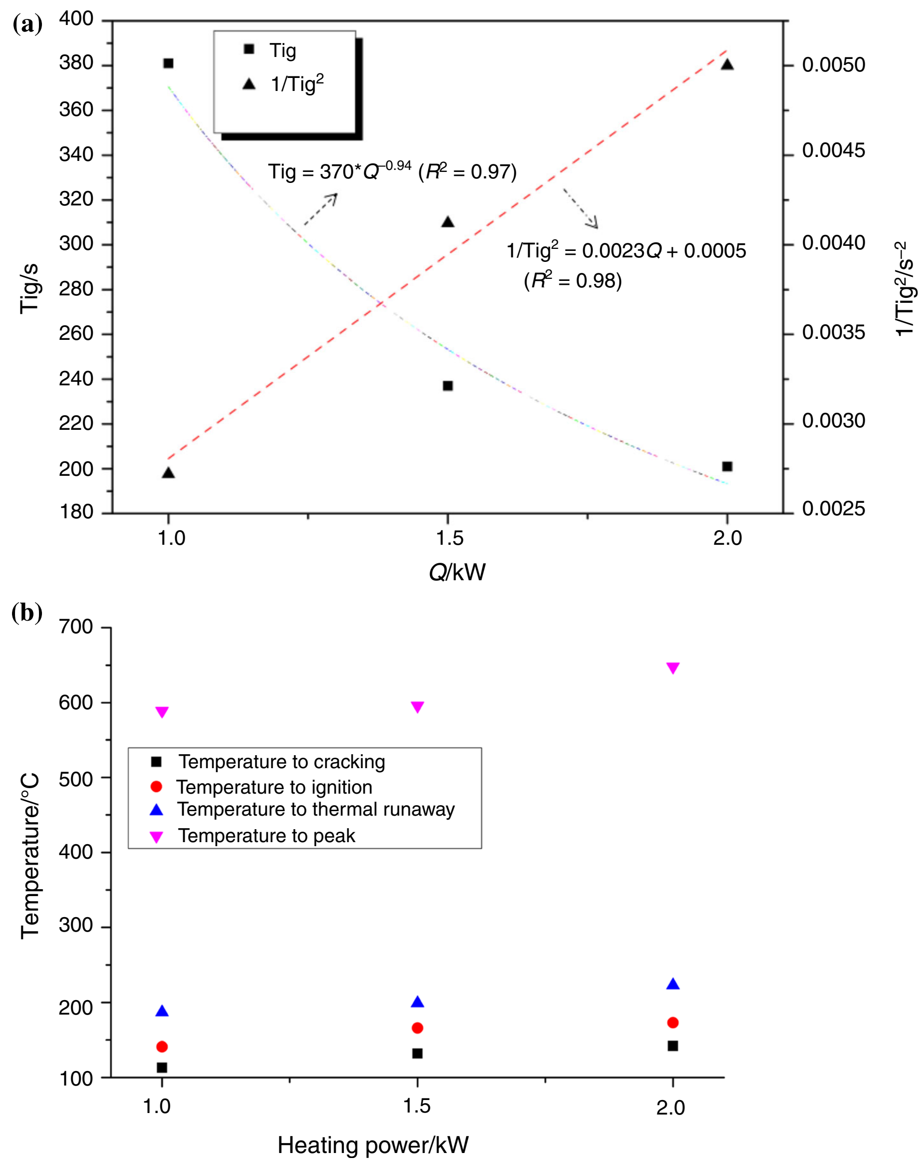

Fig. 11 **a** The relationship between ignition time and heating power; **b** the critical temperatures of packs in tests

Table 4 Specifications of the surface temperature

Test no.	Heating power/kW	Time to cracks/s	Temperature to cracks/°C	Time to ignition/s	Temperature to ignition/°C	Time to thermal runaway/s	Temperature to thermal runaway/°C	The maximum temperature/°C
1	1.0	310	113	381	141	446	187	589
2	1.5	207	132	237	166	267	199	596
3	2.0	184	142	201	173	228	223	648

Figure 16 shows the HRR profiles of packs with different treatments during heating including discharging treatment, charging treatment and without treatment, respectively. From what was described above, the pack with discharging/charging treatment has earlier fire behaviors and it can be verified by the HRR profiles. The pack with discharging/charging treatment appears earlier peak to heat release rate, and the peak values corresponding to discharging treatment, charging treatment and without treatment are 4.5, 5.6 and 9.2 kW, respectively. In addition, it is found that the THR of them are 125.9, 152.4 and 239.7 kW separately. It reveals that discharging/

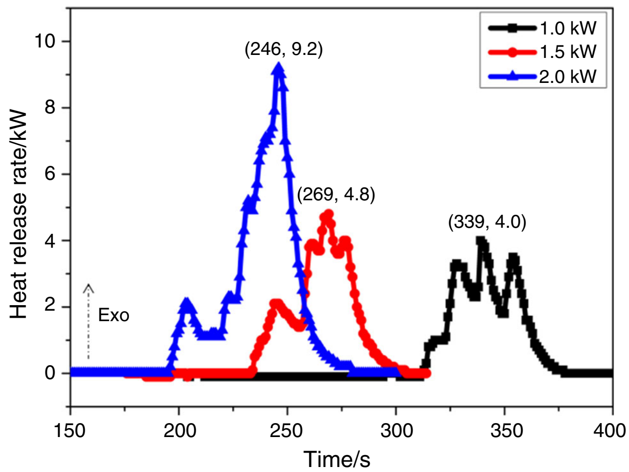

Fig. 12 The typical heat release curves of packs under different heating powers in tests

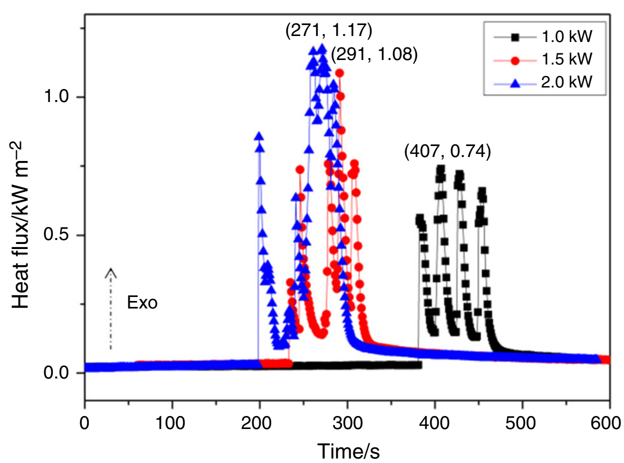

Fig. 13 Heat flux curves of packs under different heating powers in tests

charging treatment has huge effects on the heat release of packs in tests. The pack with discharging/charging treatment has much lower heat released. And the result can be explained by that the pack with discharging/charging treatment exhibits more violent fire behaviors which results in the incomplete burning and the incomplete release of energy. As for the difference between pack with discharging treatment and charging treatment, it mainly results from the energy releasing due to discharging treatment and the energy supplement caused by charging treatment.

The radiative heat flux curves of packs with different treatments are shown in Fig. 17. The peak values of heat flux corresponding to discharging treatment, charging treatment and without treatment are 1.26, 1.58 and 1.17 kW m^{-2}, respectively, which reveal the severer fire behaviors of pack with discharging/charging treatment during tests. Finally, the total heat flux of them are 31.3, 43.8 and 59.9 kW m^{-2} separately after integrating which is similar to the results of HRR. Table 7 shows the detailed information of the heat release and heat flux in tests.

Discussions

Firstly, the experimental results represent that SOC has a great influence on the fire behaviors of packs. In order to have a better understanding on how SOC affects the fire behaviors, the mechanism of LIB thermal runaway has to be explained. The electrochemical reactions of the NMC battery during charge and discharge can be presented as:

$$\mathrm{Li(Ni_xMn_yCo_{1-x-y})O_2} + 6\mathrm{C} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Li_{1-z}(Ni_xMn_yCo_{1-x-y})O_2} + \mathrm{Li_zC_6} \quad (4)$$

During charging, lithium ions will be extracted from the cathode crystal and exchanged to anode embedding with graphite leading to the decrease in lithium ions in cathode materials. And the discharging has an opposite process with lithium ions returning to cathode. In tests, the cathode materials will take place the decomposition reaction with the continuous growth of temperature and the reaction can be expressed as:

$$\begin{aligned}\mathrm{Li_{1-z}(Ni_xMn_yCo_{(1-x-y)})O_2} &\rightarrow (1-z)\mathrm{Li(Ni_xMn_yCo_{(1-x-y)})O_2} \\ &+ \frac{xz}{2}\mathrm{Ni_2O_3} + \frac{yz}{3}\mathrm{Mn_3O_4} + \frac{(1-x-y)z}{3}\mathrm{Co_3O_4} \\ &+ z\left\{1 - \left[\frac{3}{4}x + \frac{2}{3}y + \frac{2}{3}(1-x-y)\right]\right\}\mathrm{O_2}\end{aligned} \quad (5)$$

Hereafter, the reaction products Ni_2O_3, Mn_3O_4 and Co_3O_4 will decompose further and release O_2 at high

Table 5 Heat release and radiative heat flux results of packs in tests

Test no.	Heating power/kW	Peak HRR/kW	THR/kJ	Peak heat flux/kW m^{-2}	Total heat flux/kJ m^{-2}
1	1.0	4.0	120.0	0.74	32.4
2	1.5	4.8	139.0	1.09	37.3
3	2.0	9.2	239.7	1.17	59.9

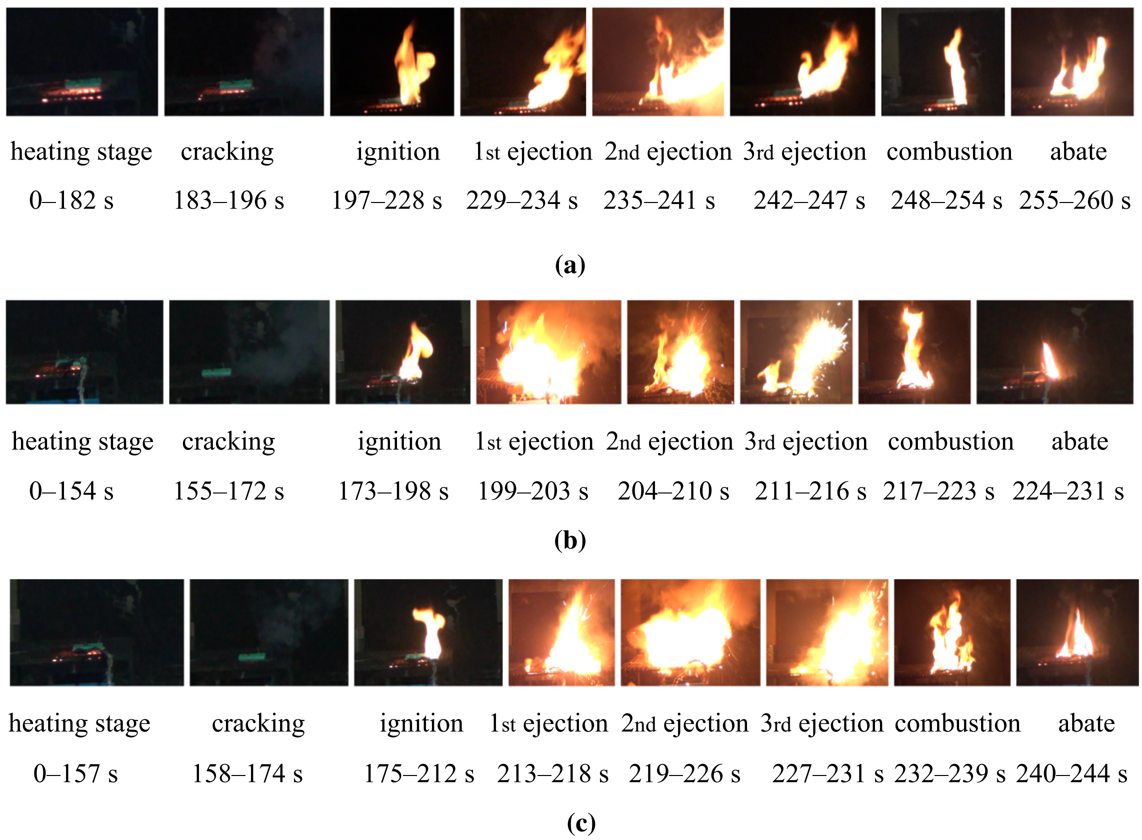

Fig. 14 Combustion phenomena of packs in tests: **a** without treatment; **b** charge treatment; **c** discharge treatment

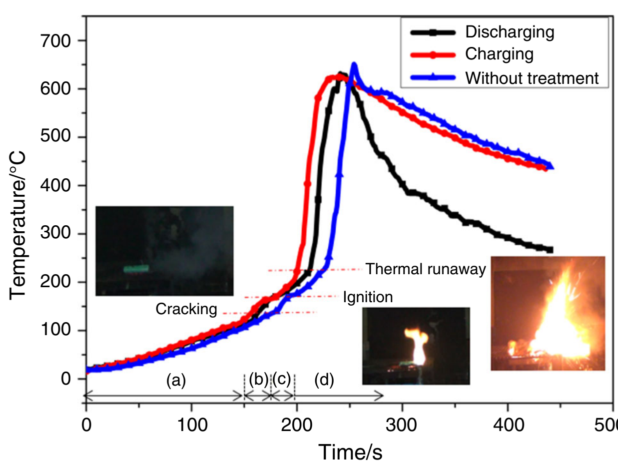

Fig. 15 The typical surface temperature curves of packs under different treatments

temperature. The generated O_2 reacts with the electrolyte and releases much heat [31], which is as follows:

$$Ni_2O_3 \rightarrow 2NiO + \frac{1}{2}O_2 \tag{6}$$

$$Mn_3O_4 \rightarrow 3MnO + \frac{1}{2}O_2 \tag{7}$$

$$Co_3O_4 \rightarrow 3CoO + \frac{1}{2}O_2 \tag{8}$$

$$O_2 + \text{electrolyte} \rightarrow CO_2 + CO + H_2O + \text{heat} \tag{9}$$

All these reactions are affected by the internal lithium ions distribution, and the distribution is related to the battery's SOC. The higher the SOC, the more oxygen will generate resulting in more violent reactions which explains how can SOC have such huge influence on the fire behaviors of packs.

Secondly, it can be assumed that thermal runaway takes place when a critical heat is accumulated, contributed by external heating and the exothermic reactions inside battery, namely [20, 33]:

$$Cm(T_{tr} - T_0) = Pt + Q_{chem} \tag{10}$$

where C is the average specific heat of battery; m is battery mass; T_{tr} is the critical temperature to thermal runaway; T_0 is the initial temperature; P is the heating power; Q_{chem} is the heat generated by the chemical reactions inside battery.

When pack is affected by a larger heating power, the temperature of pack is relatively higher and the heat generated by the chemical reactions is also higher resulting in the earlier and severer thermal runaway.

Table 6 Specifications of the surface temperature

Test no.	Treatment	Time to cracks/s	Temperature to cracks/°C	Time to ignition/s	Temperature to ignition/°C	Time to thermal runaway/s	Temperature to thermal runaway/°C	The maximum temperature/°C
1	Without treatment	183	145	197	173	229	239	651
2	Discharge	158	122	175	165	213	234	642
3	Charge	155	133	173	162	199	214	634

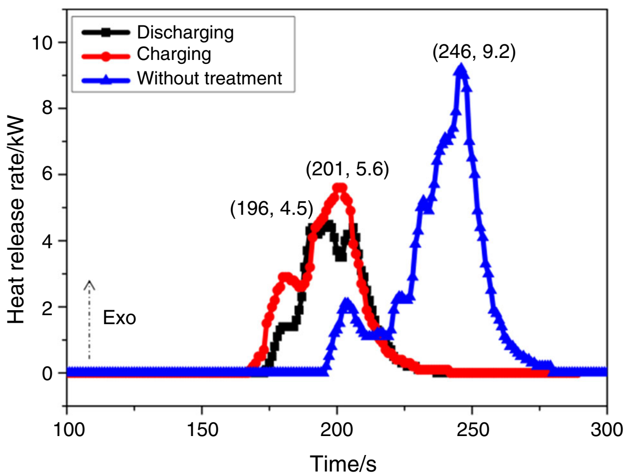

Fig. 16 The typical heat release curves of packs under different treatments in tests

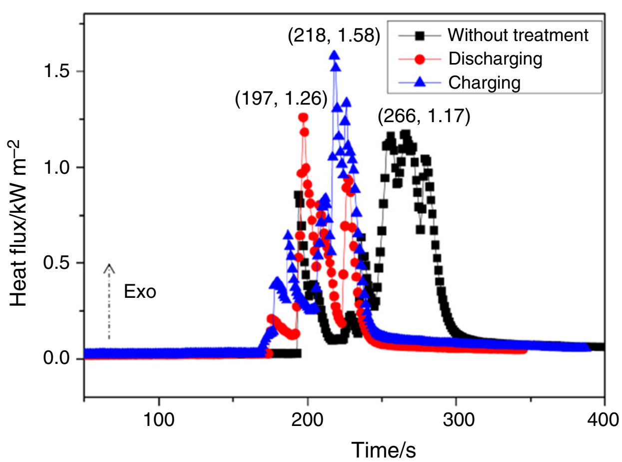

Fig. 17 Heat flux curves of packs under different treatments in tests

Finally, the thermal runaway of battery is the result of the SEI layer breaking and the polymer separator melting, leading to the intercalated lithium reacts with the organic solvents, the metal oxide cathode materials decompose and react with solvents. If a battery is in charge or discharge, the heat generation due to charge/discharge will exacerbate the temperature rise of battery. In addition, the battery materials including Li^+ and electrolytes become more positive so that it is easier to react with each other, the lower activation energy and the larger reaction rate can also be achieved [28]. Therefore, charge/discharge treatment affects the fire behaviors of pack greatly.

Conclusions

In this work, some researches of the fire behaviors of batteries pack with three cells were performed to explore the influence of different SOCs, external heating powers and the charging/discharging treatment. Detailed information on the combustion photographs, battery surface temperature, HRR and radiative heat flux was recorded and analyzed. According to the results, some main conclusions were drawn as follows:

1. With the increase in SOC, the fire behaviors of batteries pack will appear in advance and behave more violent including earlier safety vent cracking, earlier ignition, earlier ejection and severer ejection behaviors. The critical temperatures such as the temperature to safety vent cracking, ignition and thermal runaway of packs with different SOCs are similar for these parameters mainly rely on the battery properties and

Table 7 Heat release and radiative heat flux results of packs in tests

Test no.	Treatment	Peak HRR/kW	THR/kJ	Peak heat flux/kW m^{-2}	Total heat flux/kJ m^{-2}
1	Without treatment	9.2	239.7	1.17	59.9
2	Discharge	4.5	125.9	1.26	31.3
3	Charge	5.6	152.4	1.58	43.8

the incident heating but not SOC. The THR and the total heat flux of packs in tests have an uptrend with the increase in SOC apart from the 100% SOC. It is attributed to the incomplete combustion during test for its much more violent fire behaviors, and there is not enough time for sufficient chemical reaction inside the battery to release energy.

2. The pack heated by a larger power has a faster temperature rising rate and is earlier to the safety vent cracking, ignition and thermal runaway. Besides, the fire behaviors are also more violent. After fitting, it is revealed that the ignition time of pack will be shortened with the increase in heating power so that it is easier to take fire. Additionally, the pack heated by a higher heating power releases more heat during test according to the results of THR and the total heat flux.
3. It is found that the fire behaviors of pack with charge/discharge treatment have a quicker fire behavior such as ignition and ejection than the pack without any treatment. Besides, the severity of them also presents much more rigorous than that of the latter. Compared to the pack without any treatment, the pack with discharging/charging treatment has a much lower heat released including the THR and the total heat flux which is owing to the pack with discharging/charging treatment has more violent fire behaviors resulting in the incomplete burning and the incomplete release of energy.

In the end, it is expected that the results of this work could contribute to a better understanding on the fire behaviors of batteries packs with different SOCs, external heating powers and the charging/discharging treatment. Hoping it could be used as a guide for the batteries pack thermal runaway and safety prevention design.

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