Research papers

Novelty method based on thermal trigger mechanism for high energy density lithium-ion battery safety

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ABSTRACT

Thermal runaway is the most serious issue for high energy density lithium-ion batteries. Adding flame retardants to electrolytes is a general way to improve safety of lithium-ion batteries. However, the addition of flame retardants will give rise to adverse effects on the electrochemical performance of batteries, especially phosphate ester flame retardants decompose on the surface of the negative electrode. This research innovatively outlines a heat-triggered addition method of flame retardants using the polypropylene film (PP film) package. Only under abusive circumstances can the flame retardants be released and have a profound effect. The feasibility of this addition method is verified by the battery thermal safety testing. This ingenious addition method not only avoids the negative effects of flame retardants on battery performance, but also provides a new way to prevent thermal runaway of batteries.

1. Introduction

Lithium-ion batteries have the advantages of low cost, high energy density, weak self-discharge effect, and long service life, which makes them the mainstream of power batteries for electric vehicles (EVs) [1–3]. Meanwhile, it is a promising representative of energy storage devices in portable electronic devices and energy storage system. However, the lithium-ion batteries are facing great challenges in various applications because of the safety anxiety [4].

The safety of lithium-ion batteries effectively limits the application range of lithium-ion batteries. Under the storage or operation condition advised by the manufacturer, the chance of lithium-ion battery thermal runaway is only one in 40 million. However, with the development of high energy density batteries, it dramatically arises the possibility of battery thermal runaway. Moreover, some unforeseen abuse circumstances (thermal abuse, electrical abuse, mechanical abuse) during battery transportation and use further increases the likelihood of battery thermal runaway [5,6]. The battery temperature will increase and result in the degradation of battery materials under high temperature when the thermal runaway occurred. Thermal runaway occurred in the lithium ion battery, including solid electrolyte interphase (SEI) decomposition, active material decomposition and electrolyte deposition, result in the

temperature increasing and even injury to personnel [5–10].

To avoid the thermal runaway of the lithium-ion battery, the safety design of the cell mainly starts with the material. For positive active materials, coating and doping is an effective method to improve the thermal stability of the material [11–13]. For negative active material, functional protective interface and high specific capacity electrode materials enhance the stability of SEI and negative electrode [14–18]. For the electrolyte, the use of a solid electrolyte can enhance the safety of the cell [19–21]. For separator, ceramic coating is verified a promised method to by our group [22–27]. In addition, there are many ways to improve battery safety, such as the innovative and optimized electrolyte systems (e.g.,ionic-liquids (ILs), polymer electrolytes, and solid electrolytes) [8,28–40].

In general, the method above can't perfectly resolve the anxiety of high energy density battery from the technology view. Because the chemical modification of most materials will directly affect the electrochemical performance of the battery, the balance between the thermal safety performance and the electrochemical performance of the material needs to be considered [41–43]. Meanwhile, this technology is too expensive and complicated to implement for manufactory. Moreover, the new materials which have higher stability and performance simultaneously do not emerge overnight. With the degeneration of

battery capacity during cycle life, the occurrence of side reactions cannot be avoided, which means that thermal runaway is inevitable to some extent. Therefore, effective and inexpensive technique is urgently needed to ensure the safety of the battery.

In this study, a novel method based on thermal trigger mechanism for high energy density lithium-ion battery safety is reported, which can significantly reduce damage of thermal runaway. Unlike traditional methods, the flame retardant is wrapped on both sides of the battery using PP film and only play important role under the abuse condition. Trimethyl phosphate (TMP) is selected as an additive from the differential scanning calorimetry (DSC) test. The proportion of TMP in the electrolyte is determined by the combustion self-extinguishing time (SET) experiment. Based on the above results, spike test and accelerating rate calorimetry (ARC) experiments are performed on the battery and module to verify the validity of the design. The result shows that our method can ensure the safety of the battery within low cost and simple operation. Furthermore, this method is expected to be widely deploy.

2. Result & discussion

2.1. Optimization of packaging

PP film is a thermoplastic resin that has been polymerized from propylene. It is appropriate for the inner layer material of aluminium-plastic film used in lithium-ion battery outer packaging because of its high toughness, tensile strength, and resistance to electrolyte and flame retardant corrosion.

The traditional structure of the pouch battery is: the middle layer is the pole pieces and the separator, which are packaged with aluminium-plastic film, and it is filled with a certain amount of electrolyte at the same time. The PP film is bonded to the innermost PP film of the aluminium-plastic film, and the flame retardant is placed in the finished bag, as shown in Fig. 1(a). The battery is then encapsulated with the modified aluminium-plastic film, and the PP film separates the flame retardant from the electrolyte. The schematic cross-section of the battery is shown in Fig. 1(b). During the regular use of the battery, the PP film separates the flame retardant from the battery reaction system without direct contact with each other, and the flame retardant will not affect the battery. When a battery has a safety problem, such as the internal short circuit, the temperature of the battery rises dramatically. When the temperature reaches the melting point of the PP film, the film is ruptured, the flame retardant is released, and the flame is extinguished.

The reason why we choose PP film is that on the one hand, it has a good bonding effect with the innermost PP film of the original aluminium-plastic film. And on the other hand, it has high tensile strength and corrosion resistance. In addition, its melting point is close to the boiling point of the chosen flame retardant, which will be mentioned in the following discussion.

There are many types of commonly used flame retardants, including phosphorus flame retardants, nitrogen-containing flame retardants, halogen flame retardants, composite flame retardants, etc. Among many flame retardants, phosphate ester flame retardants have the advantages of good flame retardancy, low cost, and wide application. Therefore, liquid trimethyl phosphate (TMP) and solid triphenyl phosphate (TPP) are initially selected.

The DSC test results of TMP and TPP are shown in Fig. 1(c). The boiling point of TMP is about 150 °C, and the melting point and boiling point of TPP are 50 °C and 320 °C. The DSC test results of PP film are shown in Fig. 1(d). At about 160 °C, there is an endothermic peak, which is presumed to be the melting point of PP, and there is an exothermic peak at 230 °C, which is exothermic from the decomposition of PP.

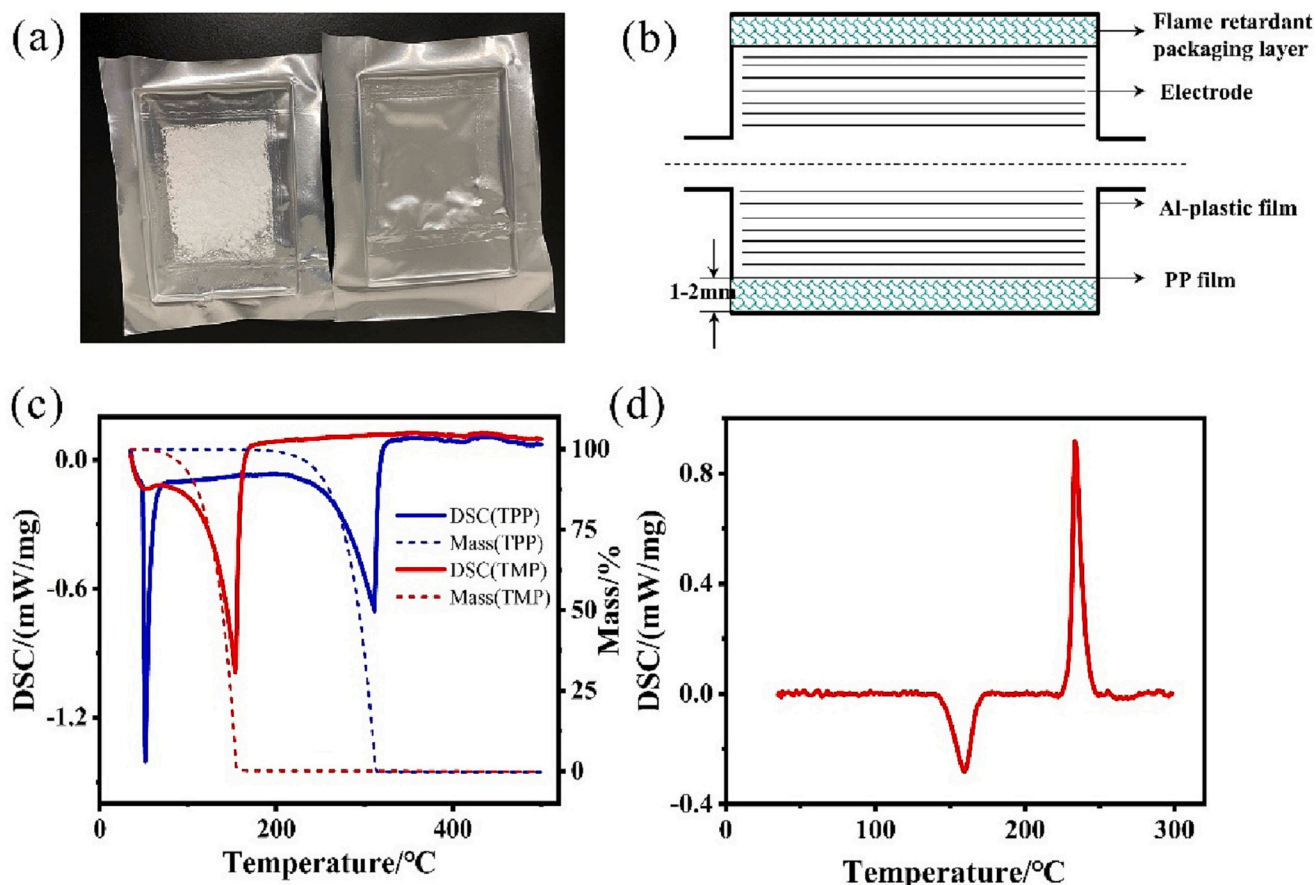For the combustion of lithium-ion batteries, carbonate-based

Fig. 1. (a) Physical picture of flame retardant added (b) Schematic diagram of battery assembly cross-section (c) DSC of flame retardant (d) DSC of PP film.

electrolytes are usually burned.

Among them the combustion equation [42,44]:

1. The gaseous carbonate solvent decomposes in the flame to produce hydrogen radicals.

$$RH \rightarrow R\cdot + H\cdot$$
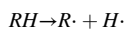
2. Hydrogen radicals react with oxygen to generate oxygen radicals and hydroxyl radicals. Oxygen may be produced by the thermal decomposition of cathode materials or electrolyte components.

$$H\cdot + O_2 \rightarrow HO\cdot + O\cdot$$
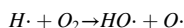
3. Oxygen radicals and hydroxide radicals react with hydrogen to produce more hydrogen radicals. Hydrogen may be produced by the reduction and decomposition of electrolyte and water impurities.

$$HO\cdot + H_2 \rightarrow H\cdot + H_2O$$

$$O\cdot + H_2 \rightarrow HO\cdot + H\cdot$$
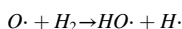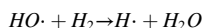
At present, the flame-retardant mechanism of phosphate ester flame retardants in lithium-ion batteries is mainly the gas-phase flame-retardant mechanism.

Taking TMP flame retardant as an example, the flame retardant usually plays the following roles:

1. The flame retardant is heated to produce free radicals that can capture the growth of the combustion reaction chain;
2. The flame retardant is heated to generate fine particles that can promote the combination of free radicals;
3. When the flame retardant is heated and decomposed, it can release a large amount of inert gas that dilutes the combustible gas and reduces the temperature of the combustible gas;
4. The flame retardant is heated to release high-density steam that can cover the combustible gas.

Take TMP flame retardant as an example. The mechanism of action is [42]:

An external heat source heats the TMP solvent to evaporate and reach the flame in a gaseous form

$$TMP_{liquid} \rightarrow TMP_{gas}$$
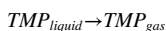
Gaseous TMP decomposes into phosphorous radicals in the flame [45]

$$TMP_{gas} \rightarrow [P]\cdot$$
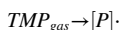
Phosphorus-containing radicals scavenge hydrogen radicals, which is the main active agent in the branching reaction of the combustion chain [46]

$$[P]\cdot + H\cdot \rightarrow [P]H$$
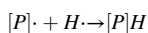
Thus, the subsequent combustion split-bond reaction is effectively suppressed due to the lack of hydrogen radicals [47].

Comprehensive consideration, because the melting point of PP film at 160 °C is close to the boiling point of TMP at 150 °C, and the boiling point of TMP is slightly lower. When the temperature reaches 150 °C, the vaporization of TMP increases the air pressure in the PP package, which can promote the rupture of the PP film. At the same time, the temperature continues to rise to melt the TMP, which can ensure that the TMP is discharged in the gas phase form, and can better play its role. Therefore, TMP is chosen as the main research object.

2.2. Flame retardant non-combustibility test

In order to verify the flame retardant effect of TMP and determine the amount of TMP added, SET experiments are performed on the flame retardant and the electrolyte. The main component of glass fiber is SiO_2, which cannot be ignited. Therefore, in the SET, it is mainly the combustion of electrolyte rather than the combustion of glass fibers. Moreover, before and after the SET, there was almost no change or obvious burning trace in the glass fiber after the SET. Therefore, the glass fiber will not burn to generate CO_2 to interfere with the experimental results.

The electrolyte tested here is 1.0 M $LiPF_6$ in EC/DMC (1:1, w/w), termed LB#301, extensively used in lithium-ion batteries. Add a quantitative amount of electrolyte to the glass fiber (Fig. 2(a)), as shown in Fig. 2(c) and Video S1, the #301 electrolyte is highly flammable. It ignites easily and then burns ferociously. However, as demonstrated in Fig. 2(d) and Video S2, with a TMP concentration of 40 % (weight percent) in EC/DMC, the flame self-extinguished swiftly. The results are displayed in Fig. 2(b), the SET of #301 electrolyte can reach about 80 s/g. When a particular amount of TMP is added, the SET reduces with the increase of TMP content. The decline is most noticeable when the content is 30 %. When the TMP content exceeds 50 %, the electrolyte can hardly be ignited. Considering that the PP package will increase the weight of the battery, 30 % of the TMP additive amount is determined to balance the weight of the battery and flame retardancy of electrolyte.

Verify the performance of the tiny package of aluminium-plastic film, flame retardant, and PP film combination at different temperatures. Fig. 3(a) (b) (c) are PP film at different temperature, and others are PP packages. Fig. 3(a) (d) (g) are at room temperature (25 °C). At 130 °C, as shown in Fig. 3(b), the edge of the PP film shortened, while as shown in (e) (h), the TMP and air in the flame retardant packet are thermally expanded, so the package swells. At 160 °C, the edges of the PP film shrink significantly in Fig. 3(c). And in Fig. 3(f) (i), due to the effect of temperature increase and internal air pressure, holes appear in the PP film and TMP is vaporized and released.

This simulates what happens to the PP package as the temperature rises owing to thermal runaway, illustrating that at 160 °C, the PP film ruptures and the TMP vaporizes and releases to extinguish the flame and prevent combustion.

2.3. Electrochemical test

Although TMP is helpful in lowering the flammability of the electrolyte, the direct addition of TMP to the electrolyte can have a significant detrimental influence on ionic conductivity and battery performance.

The ionic conductivity of the electrolyte reduces dramatically with increasing TMP content, possibly due to the increased viscosity. The TMP content in the #301 electrolyte needs to be at least 30 % to make the electrolyte non-flammable [42], which is also proved by our test results in SET. However, excessive addition of TMP will damage the electrochemical performance of the battery. The effect of TMP on the performance of the graphite anode (often used in commercial lithium-ion batteries) is evaluated in a pouch cell. A pouch cell with only one positive plate and one negative plate is built. The electrolyte was tested with pure #301 electrolyte and #301 electrolyte with TMP added (30 %) to assess its electrochemical performance. The #301 electrolyte and #301 electrolyte with TMP added (30 %) are used as electrolytes for the two batteries, respectively. In Fig. 4(a), the design capacity is 150 mAh, the capacity of the #301 battery is roughly 140 mAh, and the capacity of the battery with TMP (30 %) is only 50 mAh. For the layered battery (7 pieces of positive plate, 8 pieces of negative plate) containing 30 % TMP electrolyte, the battery creates gas and swells significantly during the charge/discharge processes, as illustrated in Fig. 4(b) (c). Since the bulging of the battery has affected the safety of the battery, making it impossible to use normally, there is no need to conduct safety experiments. The reason is that during the charging process, TMP is reduced
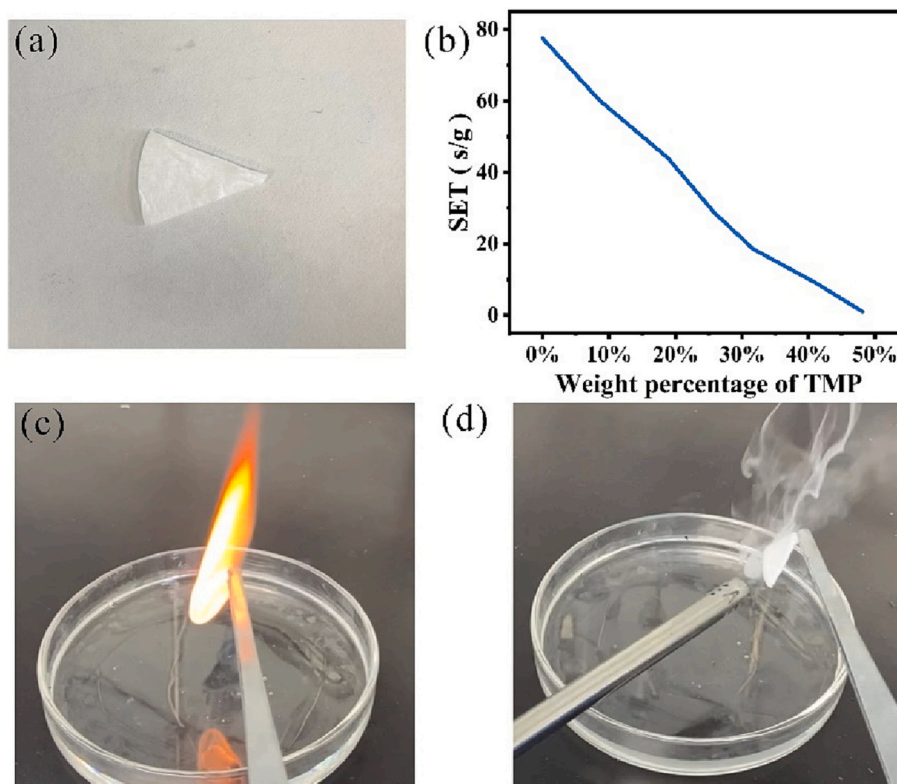
Fig. 2. Test SET for different electrolytes (a) glass fiber (b) SET curve with different TMP content (c) combustion diagram of #301 electrolyte (d) combustion diagram of 301 electrolyte containing 50 % TMP.
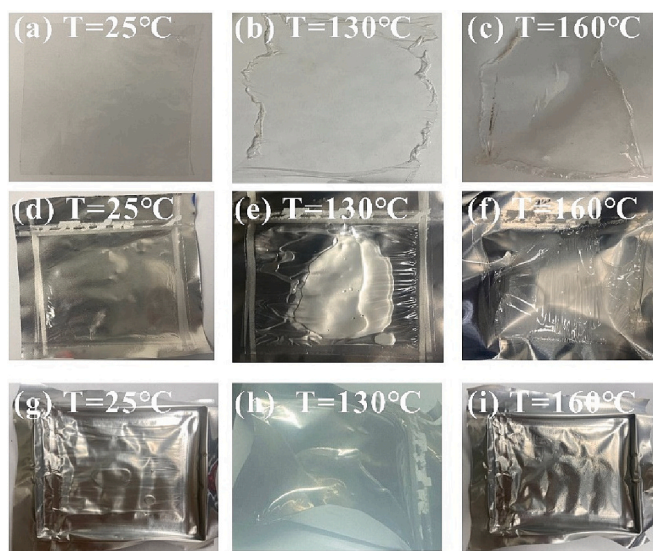
Fig. 3. The performance of PP film and the PP package in the oven at different temperatures (a) (d) (g) 25 °C (b) (e) (h) 130 °C (c) (f) (i) 160 °C, (a–c) PP film (d–i) PP package.

and decomposed at the graphite negative electrode to produce gas, causing the battery to swell [42].

Therefore, the use of PP package method can avoid the harm caused by the direct addition of TMP.

Then, in Fig. 4(d) (e), typical electrochemical tests (using pure #301 electrolyte) are performed on the assembled batteries, and the electrochemical performance of the three batteries tested shows consistency, ensuring the uniformity of the batteries used in the following thermal safety experiments. We only used batteries with little difference in electrochemical performance.

2.4. Overcharge test

Overcharge test is an important test for battery safety testing. As shown in Fig. 5, according to the results of the 10A (5C) overcharge test, the temperature will continue to rise when the battery is overcharged. When the temperature reaches 150 °C, the PP film will start to melt and TMP will be released into the electrochemical system. By disassembling the battery, it is found that the pp. film has been ruptured, and TMP has also been released. But thermal runaway does not occur.

The reason is that on the one hand, the release of TMP makes the electrochemical system of the battery non-flammable. On the other hand, thermal runaway cannot be observed during the overcharge due to the equipment's limits (the maximum overcharge current is only 10A). The reason is that the heat generation of the small-capacity battery during the overcharge process is less than the heat dissipation of the environment, so that the battery will be deactivated without thermal runaway.

2.5. Thermal safety experiment

Spike test is one of the easiest methods to trigger thermal runaway, and it is also one of the most challenging tests in the current safety test standards. That is , the battery is short-circuited by the puncture of the steel needle, resulting in thermal runaway. As demonstrated in the Video S3 and Fig. 6(a), the #301 battery burnt severely after being punctured by the steel needle, and the temperature also increases quickly to a high of 600 °C. However, the TMP battery is perforated by the steel needle, only the smoke is expelled but no fire. It can just smoke and no flames, and the highest temperature only reaches around 450 °C. It is obvious that the repeatability of the spike test is poor. On the one hand, due to
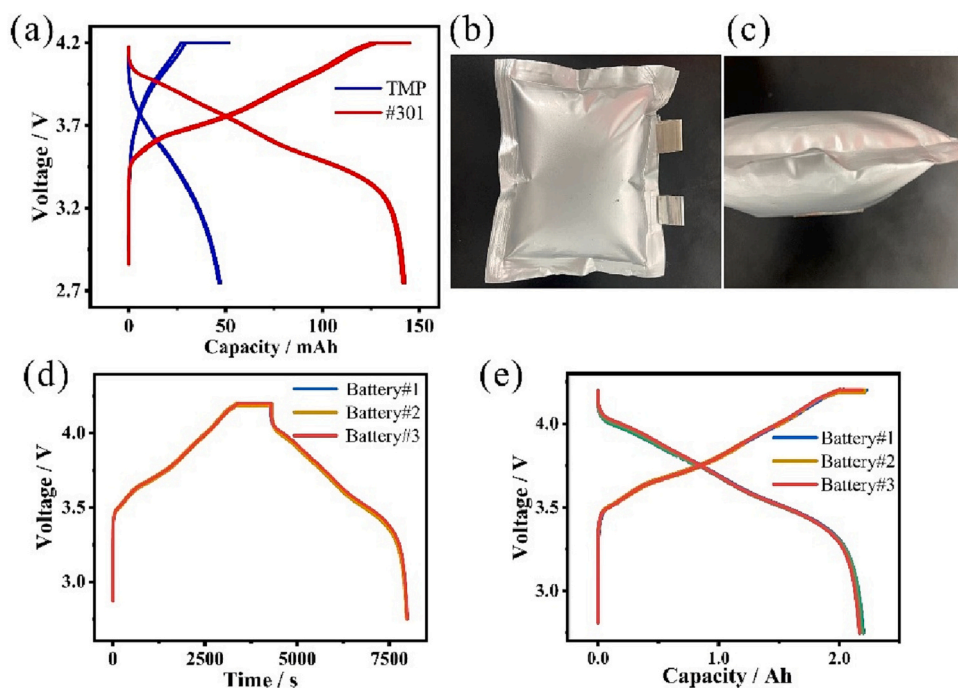
Fig. 4. (a) The electrochemical performance of #301 electrolyte and electrolyte containing 30 % TMP (b) (c) The swelling of the battery containing 30 % TMP after charging (d) (e) The electrochemical performance of batteries used in the experiment.
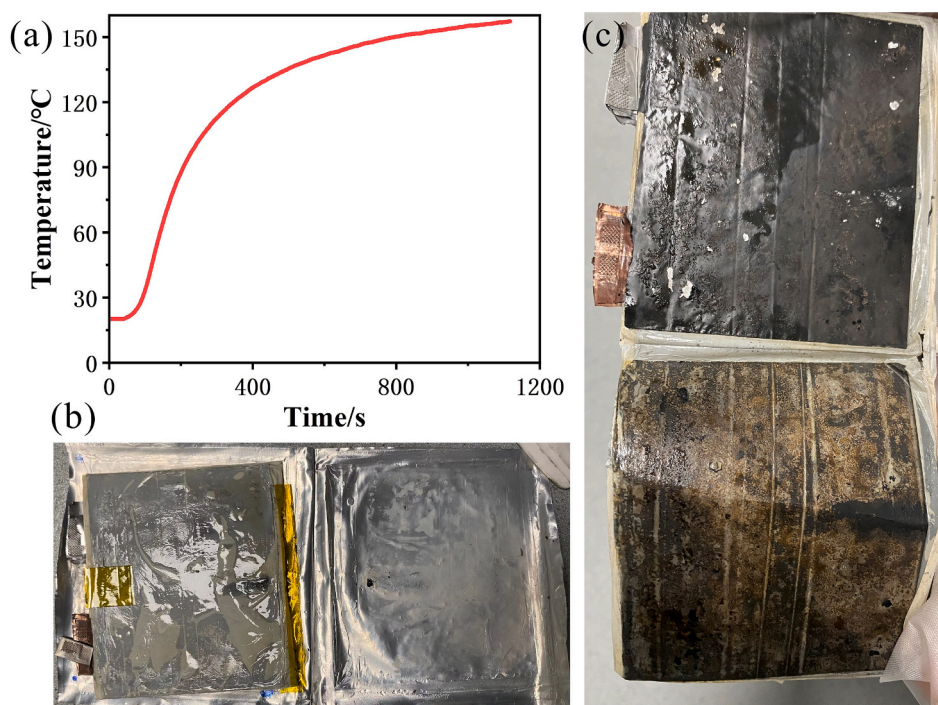

Fig. 5. (a) Temperature of overcharge test (b) (c) Picture of overcharged battery.

the fact that thermal runaway of batteries is a relatively complex process, the types, strength, and sequences of reactions cannot be completely the same. On the other hand, phenomena such as explosion and combustion may occur during thermal runaway, resulting in the displacement of the thermocouple. But the trend of experimental results is relatively similar, as shown in the Fig. 6(a). Although the temperature changes in spike test for the same group of batteries are different, it is evident that the temperature of the TMP battery is relatively lower that

of LB#301 battery. This demonstrates that the thermal safety performance of the battery including the PP package is actually enhanced in the spike test, which can avoid combustion and lower the temperature increase of the battery.

The ARC experiment is to heat the battery outside to make the battery self-heat, therefore inducing thermal runaway. The main working principle of the adiabatic calorimeter is to keep the sample temperature consistent with the temperature of the calorimetric chamber through the
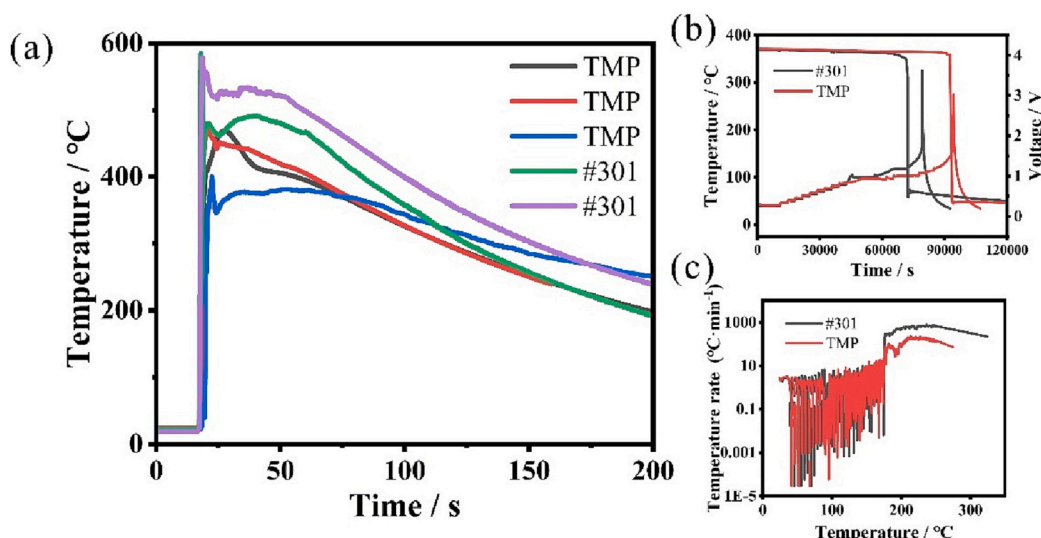
Fig. 6. Thermal safety test of battery (a) Spike experiments (b) ARC experiment temperature (c) ARC experiment heating rate.

control of the instrument, thereby providing an adiabatic environment. The ARC experiment is carried out on two sets of batteries, and the results are presented in Fig. 6(c) (d): The #301 battery opens circuit when the temperature is about 130 °C and the time is around 70,000 S, and the voltage decreased significantly. Then at around 80,000 s, thermal runaway occurs, the temperature increases fast to roughly 330 °C. The battery with TMP added does not open circuit at 130 °C, but at around 93,000 s and 150 °C, the voltage decreases significantly. After a short time, when it is around 94,000 s, the battery opens circuit and thermal runaway occurs, and the maximum temperature is also lower than that of #301 battery.

At 130 °C, the gas in the #301 battery expands due to the decomposition of the electrolyte, causing the battery to swell. This will lead to the separation of the positive/negative electrodes and the separator inside the battery, resulting in an open circuit of the battery. Then, the temperature continued to rise, and when the separator melted, the positive/negative electrode contact cause a short circuit and release a lot of heat, and eventually thermal runaway occur. While the TMP battery fill most of the battery area due to the growth of PP package, which has been demonstrated in previous oven experiments. The PP package on both sides squeezed the positive/negative electrodes within the battery, so that the positive/negative electrodes and separators are not separated, therefore circuit break does not happen and the voltage does not decrease significantly. As the temperature rises, the melting of the PP film resulted in the release of TMP, the battery voltage decrease significantly, the internal separator shrunk, and the battery is short-circuited, followed by thermal runaway. The highest temperature of thermal runaway is 260 °C, which is lower than that of the #301 battery.

As illustrated in Fig. 6(c), the heating rate diagram during the ARC experiment shows that the heating rate of the #301 battery during thermal runaway is significantly higher than that of the TMP battery. At the same time, the TMP battery has a peak of decreasing heating rate during thermal runaway, demonstrating that TMP has a great flame retardant effect.

In the safety test of the cell, the battery containing the PP package has shown an significant effect, which proves that the PP package does increase the safety of the cell.

2.6. Battery module experiment

Power batteries commonly form battery modules in series and parallel, therefore the battery module is created to further verify the feasibility of the method.

The results of spike test on the battery module are displayed in Fig. 7. (the whole process shows in the Videos S5, S6) As Fig. 7(a) (b) shows, the highest temperature of the three batteries containing TMP is less than 400 °C, whereas the #301 battery even approaches 600 °C. At the same time, in terms of the heating rate, it can be seen that the heating slope of the #301 battery is much greater than that of the TMP battery. And, via the Videos S5, S6, the contrast between the two groups of batteries when they are spiked is more obvious. Moreover, the antithesis between cell and module is clear. The #301 battery burned violently after spike and continued to burn. But the battery containing TMP only burns for about 3 s, the flame is extinguished, and then thick smoke is emitted. Compared with burning and catching fire, batteries that emit only smoke are less diffuse and dangerous.

Considering the safety performance of the battery pack, comparing the combustion performance and temperature performance, the safety of the battery pack containing TMP has been improved to a certain extent during spike test.

3. Experimental procedures

3.1. Battery parameters

The positive material used the $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, the negative material used the natural graphite. The design capacity of the pouch lithium-ion battery is 2.1 Ah, which the specific capacity of the positive and negative is 220 mAh·g^{-1} and 330 mAh·g^{-1} respectively. The capacity of a single chip battery is 150 mAh.

3.2. Electrochemical test

The constant current (CC) stage current of the formation process is set to 0.1C (0.210A), and the cut-off current in the constant voltage (CV) stage is 0.01C (0.021A). In addition, the discharge current is set to a constant current of 0.1C (0.210A). After 3 cycles at the rate of 1C, the battery is used for spike experiments or ARC tests. The working voltage windows of all batteries is set to 2.75–4.2 V.

3.3. Assembly method

The PP film is sealed in the inner layer of the aluminium-plastic film to assemble the flame retardant package, and the flame retardant is added to the package. PP film acts as a barrier layer to prevent the flame retardant from directly contacting the electrochemical reaction of the
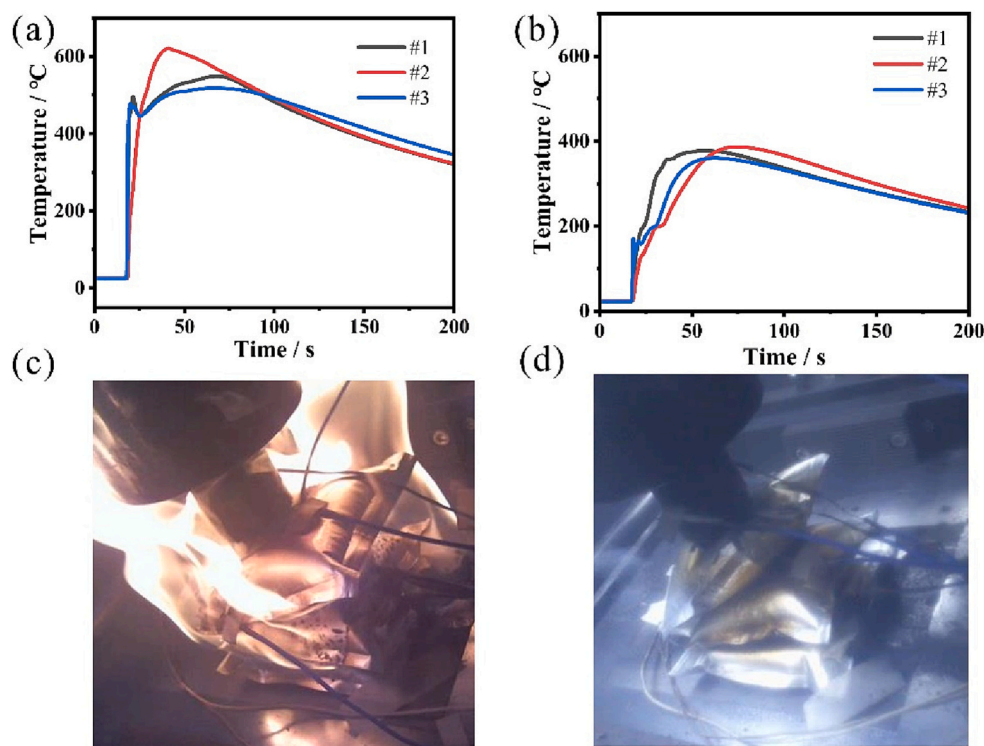
Fig. 7. (a) Temperature of #301 battery module (b) Temperature of TMP battery module (c) #301 battery module spike (d) TMP battery module spike. #1– 3 refers to three different batteries in the same battery module.

battery. The added amount of flame retardant is 3 g in each packet, 6 g in total. And the added amount of LB#301 electrolyte is 14 g.

The battery design parameters were list in Table 1 and Tables S1, S2.

3.4. Overcharge test

The overcharge current is set to a constant current of 5C (10A). Temperature changes are recorded during battery charging.

3.5. Thermal safety test

First, the assembled flame retardant package is put into an oven to heat up to verify the effect of the flame retardant package when the temperature increased.

To compare the flammability of electrolytes after adding TMP, the self-extinguishing time (SET) of electrolytes containing different concentrations of TMP was measured. SET is measured by using glass fibers to absorb a quantitative amount of electrolyte and recording the time from burning the glass fiber until it is extinguished. Five experiments are performed for each experimental sample, and the SET value is obtained according to the time required for continuous combustion of the electrolyte per unit mass.

In order to test the exothermic and endothermic heat generated during the heating process, the commonly used method is constant temperature scanning calorimetry, and the commonly used instrument is differential scanning calorimetry (DSC) [48–51]. TG and DSC

Table 1
Structural parameters of the battery.

	Positive	Negative	Electrolyte	PP package
TMP battery (test battery)	NCM811	Graphite	LB#301	Yes
LB#301 battery (control battery)	NCM811	Graphite	LB#301	No

experiments are carried out using a synchronous thermal analyser (STA 449 F3 Jupiter). The test temperature of DSC is 35–500 °C, and the heating rate is 5 °C/min. The PP films used are also tested at temperatures of 35–300 °C.

The spike test is performed using a battery penetration machine (Beier Experimental Apparatus Co., Ltd.), which looks like a fire room with battery holding tools and stainless steel nails [52–56]. In addition, the diameter of the nails is chosen to be 3 mm. The same thermocouple was placed at a distance of 5 mm from the nail point. Two batteries are connected with one battery in parallel and series respectively to form a battery module. A spike experiment is performed on the battery module. The battery is fully charged (4.2 V) prior to the spike test.

Heat production and self-generated heat production rate during thermal runaway are the most concerning issues in the study of thermal runaway mechanisms. Accelerated calorimetry (ARC) is one of the main experimental instruments for battery thermal runaway testing [51,57–60]. The battery is fully charged (4.2 V) prior to the ARC test. The same thermocouple was placed in the centre of the battery. The starting temperature is set to 40 °C, and the heating step is 5 °C. The detected self-heating rate is 0.02 °C/min, and the waiting time is 30 min.

4. Conclusion

An innovative method of flame retardants in power lithium-ion batteries is reported with abuse-triggered advantages. In order to prevent the flame retardant from affecting the fundamental electrochemical performance of the battery, the flame retardant is packed in the PP film inside the aluminium-plastic to prevent it from directly contacting the electrochemical system. Furthermore, the flame retardant makes the difference only in the case of the abuse.

The boiling point of the TMP is verified to be similar to the melting point of PP film, which contributes to the occurred of the vaporization of the TMP and the rupture of the PP film simultaneously. This design concept can ensure the flame retardant act in the abuse condition. The feasibility of the flame retardant releasing is further confirmed by the

heating oven experiment of the PP package The flame retardancy of TMP is verified by the SET test, which also determines the amount of TMP added to the lithium-ion batteries. In addition, the results of spike and ARC proved that the new assembly method used in battery suppressed the battery fire, reduced the maximum thermal runaway temperature of the battery, and improved the safety. Especially in the spike test of battery modules, the battery safety is significantly improved.

In conclusion, without affecting the electrochemical performance of the battery, this novel addition method can effectively enhance battery safety at a lower cost. This approach could provide a creative idea for improving battery safety in the future.

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CRediT authorship contribution statement

Weijie Ji: Conceptualization, Methodology, Investigation, Writing – original draft. **Hang Li:** Investigation, Validation, Writing – review & editing. **Wei Li:** Validation, Data curation. **Zheng He:** Formal analysis, Data curation. **Jinbao Zhao:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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