

# Thermal Runaway Mechanism and Prevention Methods of Lithium-ion Batteries

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## Abstract

With the development of lithium-ion batteries, it has been found that lithium-ion batteries exhibit advantages such as high energy density and long cycle life. Thus, people began to apply lithium-ion batteries to the invention of electric vehicles. However, in recent years, there have been numerous cases where lithium-ion batteries experience thermal runaway and lead to explosions. Aiming at the thermal runaway problem of lithium-ion batteries, this paper explains the mechanism of thermal runaway in lithium-ion batteries. Subsequently, it proposes corresponding prevention and control strategies: the method involves coating the separator with a ceramic layer to protect it, or using a highly heat-resistant polymer substrate to prepare a composite separator as a replacement for the original separator; optimizing the electrolyte by substituting solid electrolytes, flame-retardant electrolytes, etc. for the original liquid electrolyte, or adopting high-concentration electrolytes or local high-concentration designs to inhibit side reactions; and improving the positive and negative electrodes by using alternative electrode materials, or coating the surface of the positive electrode, or optimizing the electrolyte formula for the negative electrode. Finally, the challenges and prospects for the development of high-safety lithium-ion batteries are presented.

## Keywords

Lithium-ion battery, thermal runaway, electrolyte, electrode, separator

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## 1. Introduction

With the rapid development of electric vehicles and large-scale energy storage systems, the advantages of lithium-ion batteries in high energy density and long cycle life have become increasingly prominent. Nevertheless, lithium-ion batteries are prone to thermal runaway under abusive conditions such as overcharge, over-discharge, high temperature and mechanical damage, causing a chain reaction of thermal runaway, which seriously threatens the safety of the system. Thermal runaway usually involve multiple factors such as the flammability of the electrolyte, thermal shrinkage of the separator, and side reactions at the electrode material interface separator thermal shrinkage, and interfacial side reactions of electrode materials, and its essence is closely related to the thermal and electrochemical stability of the material system. In recent years, in-depth analysis of the thermal runaway evolution mechanism and the development of efficient prevention and control methods have become research focuses in the field of battery safety. For example, Huang Qian studied the

thermal effects and safety performance of lithium-ion batteries [1], Xia Lan et al. researched the safety technologies of lithium-ion batteries [2], and Wang Li et al. investigated the ARC method for the safety assessment of lithium-ion batteries [3]. Starting from the chain reaction mechanism of thermal runaway, this paper systematically analyzes the key reaction processes at each stage. Since the core components of lithium-ion batteries are separators, electrolytes and electrodes [4], this paper focuses on these three core components to summarize the current main safety improvement strategies, providing a theoretical reference for the design and development of lithium-ion batteries with high safety and high energy density.

## 2. Thermal Runaway Mechanism of Lithium-ion Batteries

Thermal runaway refers to the phenomenon where a battery, under the influence of internal or external factors (such as overcharging), resulting in ineffective heat dissipation of the battery [5], a sharp rise in temperature, and ultimately possible combustion or explosion. This process usually exhibits obvious chain reaction characteristics and can be divided into the following stages with the increase of temperature:

### 2.1 SEI Film Decomposition

When the temperature of a lithium-ion battery rises continuously to 80°C~120°C, the solid electrolyte interphase (SEI) film covering the surface of the graphite negative electrode of the battery decomposes first. The decomposition reaction of the SEI film is generally regarded as the starting point of this exothermic chain reaction. After the SEI film decomposes, the active materials are directly exposed to the electrolyte, and under the action of electrode potential,  $Li^+$  reacts with the electrolyte and regenerates the SEI film on the surface of the active materials. Therefore, the decomposition and regeneration of the SEI film continuously generate heat and heat up the battery [6]. In addition, the SEI film is insulating, and its decomposition also continuously consumes the electrolyte inside the battery and releases a large amount of heat. After the decomposition of the SEI film, the highly reactive graphite electrode exposed to the electrolyte will undergo a violent chemical reaction with the electrolyte. Under the influence of these factors, the temperature of the lithium-ion battery will keep rising.

### 2.2 Reaction between Negative Electrode and Electrolyte

After the complete destruction of the SEI film, it loses its protective effect on the negative electrode. At this time, the highly reactive graphite negative electrode will have a violent redox reaction with organic electrolytes (such as EC, DEC, etc.), and the reaction will be more intense when lithium deposition exists. Flammable gases such as hydrogen ( $H_2$ ) and methane ( $CH_4$ ) are generated during the reaction, accompanied by the release of a large amount of heat, which is one of the main heat generation links in the thermal runaway process.

### 2.3 Melting and Collapse of Separator

When the temperature of the lithium-ion battery rises to 130°C~180°C, the separator, an important internal component of the lithium-ion battery, is made of polyolefins (such as PP/PE). This material will melt and shrink at high temperatures, leading to large-area contact between the positive and negative electrodes, triggering more serious internal short circuits and accelerating the heat generation rate.

### 2.4 Decomposition of Positive Electrode Materials

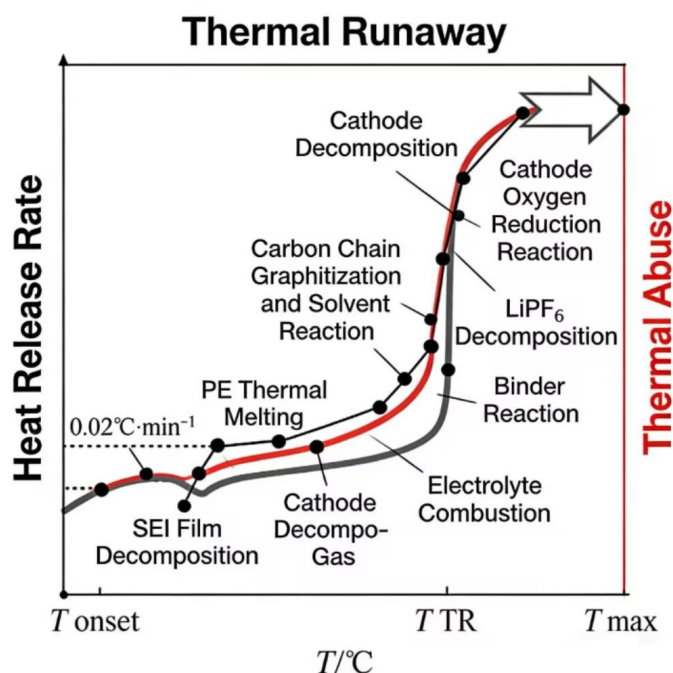
When the temperature of the lithium-ion battery rises to 180°C~250°C, some positive electrode materials of lithium-ion batteries (such as Ni-rich ternary materials) decompose at high temperatures and release oxygen ( $O_2$ ). The reaction of lithium-ion battery cathode decomposition is a strong exothermic reaction

### 2.5 Decomposition and Combustion of Electrolyte

When the temperature of lithium-ion batteries reaches a sufficiently high level, the electrolyte itself undergoes decomposition and gasification. When the decomposed and gasified electrolyte mixes with the oxygen released by the decomposition of the positive electrode, combustion or even explosion will occur under ignition conditions.

The general process of the above stages is shown in Figure 1.

Figure 1: Chain reaction in thermal runaway of lithium-ion batteries [7]



### 3. Solutions to Thermal Runaway of Lithium-ion Batteries

Aiming at different incentives and evolution stages of thermal runaway, current research on safety improvement is mainly carried out systematically from three aspects: separators, electrolytes and electrode materials.

#### 3.1 Separator Modification

To solve the problem of internal short circuit caused by high-temperature melting of the separator, its thermal stability and mechanical strength can be improved by surface coating with ceramic layers (such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ) or preparing composite separators with high heat-resistant polymer substrates (such as polyimide, aramid fiber), so as to delay or prevent the shrinkage of the separator at high temperatures. Bai Li et al. developed a functional coating with thermal shutdown performance [8], which is a polymer microsphere functional coating. At room temperature, the polymer microspheres are closely packed to form a porous structure, which allows the normal passage of lithium ions and has no adverse effect on the internal resistance and electrochemical performance of the battery. When the battery internal temperature rises to the critical point due to abuse, the polymer microsphere melt rapidly and cover the interface between the electrode and the separator, forming a dense insulating layer, thus blocking the lithium ion transport channel and stopping the internal reaction of the battery. This method can effectively solve the short circuit problem of the separator caused by high temperature. The coating used in this method has a temperature-triggered switch and will not affect the normal operation of the lithium-ion battery at normal temperatures.

#### 3.2 Electrolyte System Optimization

The flammability and high reactivity of traditional liquid electrolytes are also important incentives for thermal runaway. In solving such problems, the current development trends include replacing liquid electrolytes with solid electrolytes (polymer, oxide, sulfide systems), developing flame-retardant electrolytes, and using high-concentration electrolytes or local high-concentration designs. Replacing liquid electrolytes with solid electrolytes can fundamentally eliminate the risk of combustion; developing flame-retardant electrolytes can reduce electrolyte flammability by adding phosphate esters, fluorinated solvents, etc.; and adopting high-concentration electrolytes or local high-concentration designs can expand the electrochemical

window and inhibit side reactions. Yan Mingbao et al. mentioned solid polymer electrolytes in the Polymer Bulletin [9], adding inorganic substances as fillers to the polymer matrix, and conducting a lot of work and improvements on the preparation and modification of polymer/inorganic composite solid electrolytes. Polymer/inorganic composite solid electrolytes are expected to combine the advantages of inorganic fillers and polymer materials, becoming a reliable means to solve electrolyte flammability. Centered on the functionalization and compounding of inorganic fillers, this method optimizes the electrolyte system through systematic improvements in preparation processes and interface modification. It not only breaks the bottleneck that the ionic conductivity, mechanical strength and interface stability of traditional solid polymer electrolytes are difficult to be balanced simultaneously, but also constructs a high-performance and high-safety polymer/inorganic composite solid electrolyte system, providing a better solution for electrolyte optimization.

### 3.3 Electrode Material and Interface Design

When the temperature of lithium-ion batteries keeps rising, one of the causes leading to thermal runaway is that chemical reactions will occur at sufficient temperatures in both the positive and negative electrodes. To avoid this situation, more stable materials (such as lithium iron phosphate) can be used for the positive electrode, or surface coating and bulk doping with certain materials (such as aluminum oxide) can be adopted to improve its structural stability and inhibit oxygen release; for the negative electrode, the formation of lithium dendrites can be inhibited by optimizing the electrolyte formula, using three-dimensional structured negative electrodes, composite lithium metal negative electrodes, etc., or other electrode materials (such as lithium titanate) can be used to improve the heat resistance of the negative electrode. Yang Xiaoyan et al. prepared lithium-titanium composite oxides by three methods [10], and verified through a series of experiments (such as X-ray diffraction) that lithium-titanium composite oxides have a clear and stable charge-discharge platform, as well as high initial capacity, excellent cycle reversibility and strong structural stability. They show good compatibility in special cases (such as composing key parts of lithium-ion batteries with specific electrolytes), indicating that lithium-titanium composite oxides are likely to coexist with some electrolytes in contact.

## 4. Challenges and Prospects

At present, There are many challenges in reducing thermal runaway in lithium-ion batteries. From the perspective of the preventive measures proposed in this paper to inhibit thermal runaway by optimizing various components of lithium-ion batteries, optimizing the components to ensure safety will inevitably have an impact on the advantages of high energy density, performance and cost of lithium-ion batteries. In the optimization of separators, the proposed strategy of ceramic coating will increase the thickness and areal density of the separator and reduce the ionic conductivity, ultimately leading to a decrease in the energy density of the entire lithium-ion battery; in the optimization of electrolytes, the ultimate method of using solid electrolytes to replace traditional electrolytes will increase the production cost of lithium-ion batteries due to the higher price of solid electrolytes; in the optimization of electrode materials, for the positive electrode, the use of lithium iron phosphate and doping will reduce the energy density, and surface coating will reduce battery performance and increase costs; for the negative electrode, adding additives to the electrolyte to inhibit lithium dendrites and using composite lithium metal negative electrodes will reduce the service life of lithium-ion batteries, and the use of three-dimensional structured negative electrodes will thicken the SEI film, leading to a sharp rise in resistance. Therefore, how to improve the safety of lithium-ion batteries while minimizing these side effects is a tricky challenge at present. It is hoped that in the future, the most suitable materials for manufacturing lithium-ion batteries that meet our needs can be found.

## 5. Conclusion

Although lithium-ion batteries have the advantages of high energy density and long cycle life, they face the risk of thermal runaway during use. This potential hazard not only seriously hinders the commercialization of lithium-ion batteries, but also reduces their application value. Therefore, how to reduce or even avoid the occurrence of thermal runaway in lithium-ion batteries has become an urgent problem to be solved. Aiming at this problem, this paper first explains the mechanism of thermal runaway in lithium-ion batteries and analyzes each stage experienced by lithium-ion batteries during thermal runaway, then proposes solutions to thermal runaway from the aspects of separators, electrolytes and electrodes. In general, the development trend of

lithium-ion batteries will inevitably focus on improving their energy density and safety. However, the increase in energy density will inevitably reduce the safety performance of lithium-ion batteries, so the safety of lithium-ion batteries is relative—that is, it is difficult to ensure the safety performance while maintaining the high energy density of lithium-ion batteries.

It is believed that with the joint efforts of researchers, the thermal safety of high-energy density metal lithium batteries will be further improved in the future, and their commercialization and practical application will ultimately be realized.

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