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Research and analysis of electric vehicle fire accidents and review of lithium-ion battery thermal runaway mechanism

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Abstract: *The rapid development of electric vehicles is accompanied by numerous security issue, which has caused people great concern. This paper counts the electric vehicle fire accidents in the past six years, and from three different perspectives: the time of the accident, the type of vehicle involved and the type of vehicle power to discuss these accidents. Then analyzed the various causes of electric vehicle fire accidents, such as spontaneous combustion, crash fire, etc. Explaining the three major causes of thermal runaway and the mechanism of thermal runaway in batteries. Proposing some measures and suggestions to solve the thermal runaway of electric vehicles. Through the conclusion and analysis of these accidents, this paper hopes that the new energy electric vehicles can be developed more safely and better.*

Keywords: *New Energy Vehicle, Thermal runaway, Lithium ion Battery, Safety accidents*

1. Introduction

According to the data indicates that the proportion of China's imports of crude oil, natural gas and other energy sources is increasing year by year from 2011 to 2020.In 2020, the imports of crude oil has reached 542 million tons, rising 7.26%[1].In order to reduce the dependence on imports crude oil, alleviate the pressure of the oil resource shortage in China, ensure the energy security, and decrease the air pollution caused by conventional fuel vehicles. The new energy vehicles with the theme of environmental protection and low carbon have gradually become the development strategy of China[2]. In fact, as early as 2012,China has already released a document called the “Energy Conservation and New Energy Vehicle Industry Development Plan (2012-2020)”.This document set a goal for the new energy vehicle industry to produce 2 million new energy vehicles and the sales volume reached 5 million units by 2020.With the support of national policies, China's new energy vehicle industry has been developing sharply. In 2020, total sales of new energy vehicles in China has grown to 1.367 million units, up 10.9% year-on-year, continuing to show rapid double-digit growth[3].Since then, in 2021,China's new energy vehicle sales achieved the original goal, selling a total of 3,334,100 units over the task, and it is expected that the sales of new energy vehicles will be as high as 4,731,900 units in 2022[4].And in December 2021, China also published a document named "Notice on the Advance Issuance of the 2022 Energy Conservation and Emission Reduction Subsidy Budget", which provided newer and better policy for the new energy vehicles development in 2022.

However, with the large number of electric cars are put into use, many electric car fire safety accidents also coming. In December 2021, there was a "triple burn" of electric car fire accident [5]. On December 20, a new energy vehicle being charged and suddenly spontaneous combustion in Zhengzhou; On December 22, a stationary parked electric vehicle suddenly caught fire in Sanya; On December 23rd,in Haikou, an electric car parked street and suddenly caught fire, but also ignited the surrounding vehicles and buildings, causing considerable economic losses. In just a few days there were three electric car fires accidents in a row, and they were all burned badly, and the surrounding vehicles and buildings were affected seriously by these fires(Fig.1. shows[5]).Although there were no people injuries in these accidents, all three incidents have raised concerns and fears about the safety of electric vehicles. Over time, the safety issue of electric car fires has become the focus of society and the general public. Therefore, this paper summarizes the data of new energy vehicle safety accidents in China during the period of 2016 to 2021, deeply study the electric vehicle fire accidents and causes, analyzes the mechanism of thermal runaway of electric vehicles, and organizes relevant information to put forward some suggestions about the prevention of electric vehicle safety hazards.

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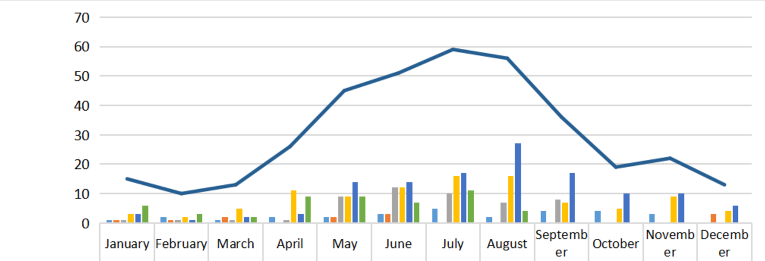
Figure 1: Pictures of electric car fire accident scene

2. Accident statistics and analysis

Through publicly available information on the Internet, not all statistics of electric vehicle fires total 365 incidents from 2016 to 2021[6][7][8].Since hundreds of accidents occurred in six years, in order to better analyze the electric vehicle fire accidents, three different perspectives will be explored respectively in terms of accident time, vehicle power type and vehicle type.

Figure 2 counts the number of car fires that occurred in each month between 2016 and 2021, from the perspective of accident time, according to the picture it can be seen that the accident rate is low from January to March, with 15, 10 and 13 safety accidents, respectively, and the accident rate increased rapidly from March onwards, from 13 accidents to 56 accidents in August. And it can be seen from the graph that June, July and August are all high accident months, with the total number of accidents over 50, accounting for half of the annual number of incidents. Especially in July, there are 59 accidents, which is the highest number of accidents in the year. However, accidents drop from August onwards. This shows that summer is the most common time for electric car fires, and the cause of electric car fires may be related to the weather temperature.



	January	February	March	April	May	June	July	August	September	October	November	December
2016	1	2	1	2	2	3	5	2	4	4	3	0
2017	1	1	2	0	2	3	0	0	0	0	0	3
2018	1	1	1	1	9	12	10	7	8	0	0	0
2019	3	2	5	11	9	12	16	16	7	5	9	4
2020	3	1	2	3	14	14	17	27	17	10	10	6
2021	6	3	2	9	9	7	11	4	0	0	0	0
Total	15	10	13	26	45	51	59	56	36	19	22	13

Figure 2: Monthly distribution of electric vehicle fire accidents

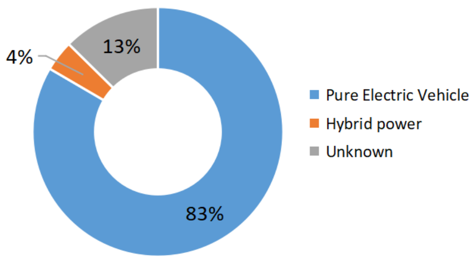


Figure 3: Safety accident vehicle power type

In terms of power type, Figure 3 shows that 83% of the vehicles involved in accidents within six years has a power type belonging to pure electric vehicles, 13% of vehicles with hybrid power type and 4% with unknown power type. At present, China's new energy vehicles are mainly pure electric vehicles, which have a larger sales base than hybrid vehicles, and thus the spontaneous combustion accidents of pure electric vehicles will be higher. The main power component of a pure electric car is the battery, and the long time use of the car will make the battery easy to work overload, which will lead to problems such as battery short circuit and causing the vehicle to catch fire. Hybrid car power

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source is the cooperation of generator and battery, thus the battery working time is shorter compared to pure electric car battery, battery discharge time is also shorter, and the accident probability of battery fire in hybrid is lower than pure electric car. But whether it is pure electric vehicles or hybrid electric vehicles, it is often difficult to put it out in time when the fire occurs, and there is a lot of safety risks.

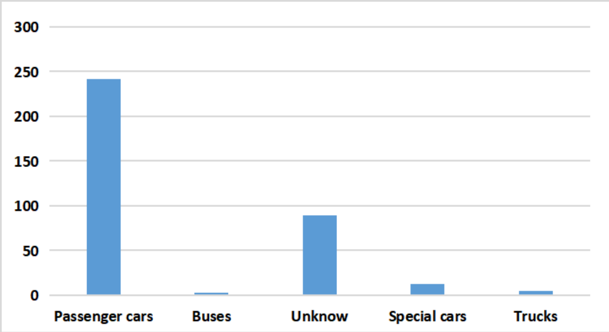

Figure 4: Accident vehicle type statistics

From the analysis of the accident vehicle types, Figure 4 does not fully summarize the vehicle types of the accident.As can be seen from the figure, the main type of vehicles involved in the accidents are passenger cars, with 242 safety accidents, accounting for the highest proportion of all vehicles, 69% of the total vehicles involved in accidents. And according to the accident scene in Figure 1, the types of vehicles in the picture are all passenger cars. Secondly, 13 cases of special vehicles occurred, accounting for 4%. There were 5 trucks, accounting for 1.4%. According to the available data, there was only 1 bus count, accounting for 0.3%. However, there are still a large number of 89 unknown vehicle types, accounting for 25%. In order to better study EV fire accidents, it is also necessary to further understand the causes of EV fire accidents.

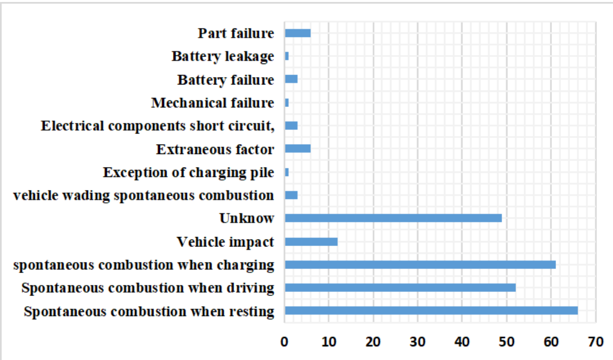

Figure 5: Statistics on the causes of electric vehicle fires in 2016-2021

3. Analysis of the causes of safety accidents

Figure 5 summarizes the causes of more than 100 electric vehicle fire accidents in China from 2016 to 2021.As seen in the figure, the highest frequency of vehicle fires caused by spontaneous combustion, a total of 179 accounted for 68% of the full accident causes. This includes spontaneous combustion when the vehicle is stationary, spontaneous combustion when driving, spontaneous combustion when charging, and spontaneous combustion when the vehicle is involved in water. The second leading cause of accidents is vehicle crashes, with a total of 12. There are also other causes of vehicle fires. And there are fires caused by other than the car itself, such as abnormal charging pile, human external factors, etc. There are also factors of the car itself, such as short circuit of electrical components, mechanical failure, battery failure, battery leakage, parts failure, etc. The proportion of these fire starting factors are low. But in addition there are still 19% of the accident causes unknown, which also reflects the accident scene investigation and the car company safety research after the accident still has some shortcomings.

As can be seen from Figure 5, the proportion of spontaneous combustion occurs in four different states of the vehicle is very different. The highest proportion of spontaneous

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combustion occurred when the vehicle is stationary, with a total of 66 accidents. The second vehicle is spontaneous combustion when charging, with 61 cases. A total of 52 spontaneous combustion cases occurred when the vehicle is driving. There are only 3 accidents that vehicle wading spontaneous combustion. One of the reasons for spontaneous combustion, the vehicle is sitting for a long time when the temperature is too high, the weather is too hot, the vehicle is bursting sun and the environment is relatively closed unfavorable to the car heat dissipation, it will electric car battery will be prone to short circuit phenomenon, thus causing the car fire spontaneous combustion. This is one of the reasons why, as shown in Figure 2, most electric vehicle fires occur in the summer months. That's why most electric car fires occur in the summer months, as shown in Figure 2.Secondly, when electric vehicles are driven under a long time, the power battery runs for a long time, the cooling system runs poorly and the current is too high, which leads to thermal runaway spontaneous combustion triggered by internal short circuit of the battery[9].Third, when the vehicle charging time is too long, the vehicle BMS does not detect the voltage of the battery in place, resulting in excessive battery energy, which eventually leads to a short circuit of the battery and triggering thermal runaway [10]. Fourth, when the vehicle is wet or soaked in water for a long time, the poor sealing of the vehicle battery leads to water entering the battery inner group triggering battery short circuit, which eventually leads to battery thermal runaway.

In addition, the vehicle is strongly impacted, the power battery is squeezed and deformed and short-circuited, or the battery is damaged by external impact, causing a short circuit, which eventually leads to thermal runaway of the battery[11]. Figure 5 the statistics of the electrical components short circuit, mechanical failure, battery failure, battery leakage, parts failure and other reasons are also because of the battery short circuit caused by thermal runaway, finally leading to spontaneous combustion of the vehicle. Therefore, according to the investigation and analysis can be known that the battery thermal runaway is the main cause of spontaneous combustion of the vehicle[11][12].

4. Thermal runaway triggers occur in lithium-ion batteries

Thermal runaway refers to the internal temperature of the battery is too high, the battery material thermal decomposition, and even the release of toxic gases, and in the end lead to battery fire and explosion. The causes of thermal runaway are mainly summarized in the following categories: mechanical abuse, electrical abuse and thermal abuse.

Mechanical abuse is mainly caused by crushing, collision and puncture inside the battery, resulting in damage to the battery diaphragm. When the vehicle crashes or receives a pinprick, the case of the electric box will be damaged and deformed, and the electrolyte will leak, which further leads to a short circuit of the battery. When the battery is squeezed, the diaphragm inside the battery will rupture, causing the air outside to enter the battery, which will oxidize and release a lot of heat inside the battery.

Electric abuse is because the battery is over-charging, over-discharging or external short-circuiting, resulting in thermal decomposition of materials inside the battery produces a lot of heat accumulation. Over-charging refers to the battery in the case of already fully charged, but still continue to charge, so that there is excess energy inside the battery appears, the battery voltage is higher than the cut-off voltage, and the continuous current makes the battery internal electrochemical reaction release a lot of heat finally lead to the battery short circuit triggered thermal runaway [13]. Over-discharge means that a large number of lithium ions enter from the negative terminal to the positive terminal, making the potential difference between the positive and negative terminals become large, which in turn induces an internal short circuit in the battery leading to thermal runaway. External short circuit is the increase of electric flow and the continuous rise of resistance heat, which induces thermal runaway of the battery.

Thermal abuse means that the battery continues to work or the surrounding temperature is too high, which makes the battery internal temperature rise, because the battery heat dissipation rate is lower than the heat production rate, the battery heat cannot be released in time, and the battery temperature keeps rising finally causing the battery thermal runaway [14][15].

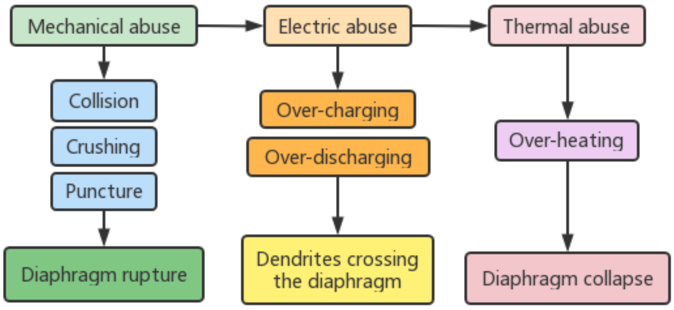

Figure 6: Three abuse relationships and consequences

Mechanical abuse, electrical abuse, and thermal abuse are related to each other, and the relationship can be shown in Figure 6 [16].When the battery because of mechanical abuse, namely the damage of external force battery diaphragm damage, positive and negative pole short circuit, battery active material molecular materials began thermal decomposition, the battery quickly releases heat accumulation cause electric abuse, because the temperature and decomposition gas pressure are too large, battery heat dissipation rate, thermal balance is damaged, the temperature increased further, battery internal side reaction form chain reaction, eventually formed the battery thermal runaway [17][18]. Therefore, we will further study the occurrence mechanism of thermal runaway.

5. Thermal runaway mechanism of lithium-ion batteries

When the battery produces a thermal runaway, a series of side reactions will occur. The main reactions experienced are: the decomposition of SEI membrane, the chemical reaction of negative electrode and electrolyte, the melting of diaphragm, the chemical reaction of positive electrode and electrolyte, the decomposition of electrolyte, the redox reaction of positive and negative electrode, and the adhesive reaction. The chain reaction process occurring during the thermal runaway process of the lithium-ion battery is shown in Figure 7[19].

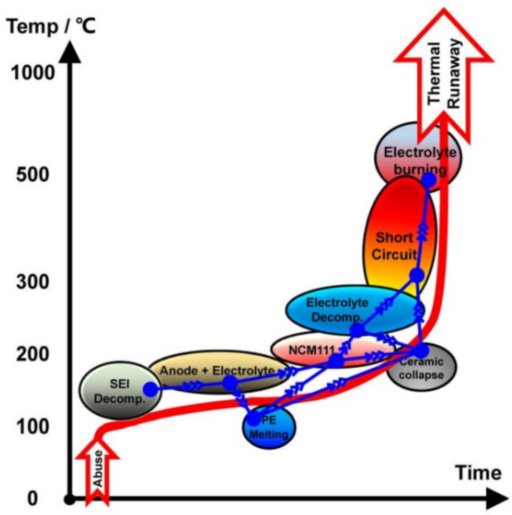

Figure 7: Chain reaction process formed by side reactions produced by thermal runaway of lithium ions

(1) The decomposition of SEI membrane. The SEI membrane, also known as solid electrolyte interface, is a surface passivation layer formed by the reaction between electrode material and electrolyte at the solid-liquid phase interface. According to the large heat energy generated by the decomposition of the SEI membrane triggers the next reaction, the decomposition of the SEI membrane is also considered to be the main cause of thermal

runaway[20]. The SEI membrane is mainly composed of a suitable layer ($CH_2OCO_2Li_2$) and a stable layer (Li_2CO_3). Taking vinyl carbonate ($C_3H_4O_3$,EC) as an example[21], the SEI membrane is generated by reacting with the negative electrode during the discharge as follows:

$$2C_3H_4O_3+2Li \rightarrow (CH_2OCO_3Li)_2+C_2H_4 \quad (1)$$

When the cell temperature reaches 80-120°C[22], the SEI membrane on the negative electrode surface undergoes thermal decomposition reactions to release heat, and toxic gases. Experimentally, it was demonstrated that a significant exothermic peak occurs around 90-100°C[20]. During the thermal decomposition reaction of the SEI membrane, it changes from a sub-stable layer to a stable layer. The process is as follows[23].

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + 0.5O_2 \quad (2)$$

$$2Li + (CH_2OCO_2Li)_2 \rightarrow 2Li_2CO_3 + C_2H_4 \quad (3)$$

The sub-stable layer ($CH_2OCO_2Li_2$) undergoes a decomposition reaction to produce a stable layer (Li_2CO_3), which also emits toxic ethylene gas (C_2H_4).And the release of oxygen indirectly accelerates the thermal runaway process, which is one of the factors that make it difficult to extinguish the fire when an electric car is on fire.

(2) Chemical reaction of the negative electrode and the electrolyte. After the SEI membrane thermal decomposition reaction occurs, the negative active material, without the protection of the SEI membrane, reacts directly with the electrolyte chemically and releases a large amount of heat at about 120°C[24].The SEI membrane is also formed when the negative electrode reactive material reacts with the electrolyte, which is called the SEI membrane’s regenerative reaction[25]. Studies have found that the reaction process can be the following [26]:

$$2Li+C_3H_4O_3(EC) \rightarrow Li_2CO_3+C_2H_4 \quad (4)$$

$$2Li+ C_5H_{10}O_3(DEC) \rightarrow Li_2CO_3+C_2H_4+C_2H_6 \quad (5)$$

$$2Li+ C_3H_6O_3(DMC) \rightarrow Li_2CO_3+C_2H_6 \quad (6)$$

$$2Li+C_4H_6O_3(PC) \rightarrow Li_2CO_3+C_3H_6 \quad (7)$$

Among them, EC is ethylene carbonate, DEC is diethyl carbonate, DMC is dimethyl carbonate, and PC is propylene carbonate. However, the structure of the newly generated SEI film is not stable, and the reaction between the negative electrode active substance and electrolyte cannot be effectively prevented, so the reaction continues. It was shown that the new SEI film generated by the reaction between the negative electrode active substance and electrolyte was not destroyed until about 250°C, which also led to a significant increase in the heat release from the reaction[27].

(3) Membrane melting. There are two main types of diaphragms commonly used in lithium-ion batteries on the market today: polyethylene diaphragms and polypropylene diaphragms. They all play an important role in Li-ion batteries. Under the thermal decomposition of the SEI membrane and the chemical reaction of the cathode material and the electrolyte, the whole reaction temperature is gradually increasing. When the temperature reaches the polyethylene melting point (135°C) or the polypropylene melting point (165℃), the diaphragm will start to melt. In the melting process, lithium ions can not pass freely because of the micro-pore closure on the diaphragm, resulting in the current blocked. Although the current is briefly blocked to a certain extent to protect the battery, but when the temperature continues to rise, the diaphragm will shrink, and with the temperature rise and continues to shrink, and finally will lead to the positive and negative electrodes because there is no diaphragm and direct contact makes the battery short circuit, but also generate a lot of heat further triggered the thermal runaway.

(4) Chemical reaction of the positive electrode with the electrolyte. When the diaphragm shrinks to disintegration due to the increase in temperature, the positive electrode thus reacts chemically with the electrolyte. However, the different materials of the positive electrode also make the positive electrode react with the electrolyte. At present, the commonly used lithium-ion battery cathode materials are: ternary materials, lithium cobalt oxide, lithium iron phosphate, and lithium manganese oxide. According to the study and comparison of the reactivity of these four cathode materials, lithium cobalt oxide > ternary materials > lithium manganese > lithium iron phosphate[28]. Taking lithium cobalt oxide LCO as an example, LCO is commonly used in mobile phones, computers and other devices. the shortage of resources of Co leads to high cost of LCO preparation, and its poor stability and high reactivity. The decomposition reaction of LCO is:

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$$3Li_xCoO_2 \rightarrow 3xLiCoO_2 + (1-x)\ Co_3O_4 + (1-x)\ O_2 \quad (8)$$

$$Co_3O_4 \rightarrow 3CoO + 0.5O_2 \quad (9)$$

When the reaction occurs, oxygen is released from the oxidation reaction of Co, and a lot of heat is released from the whole reaction. However, no matter which cathode material is used, it will eventually react with the electrolyte after the diaphragm disintegrates and continues to emit a lot of heat leading to increased thermal runaway of the battery.

6. Measures to prevent thermal runaway accidents

Through the analysis of electric vehicle fire accidents, we can know that the harm caused by thermal runaway of electric vehicle battery is very serious. In order to avoid and reduce the occurrence of electric vehicle fire accidents and casualties, we summary some solutions and countermeasures.

① Develop battery cooling technology. When the battery is working or discharging for a long time, it can detect the temperature change inside the battery in time. When the temperature exceeds the safety value, it can take cooling measures in time to enhance the heat dissipation inside the battery and reduce the heat generated by the battery. This technology can effectively hinder the occurrence of thermal runaway of the battery.

② Improve the diaphragm material. Most of the current lithium-ion battery diaphragm materials are mainly polyolefin materials, which have low wettability in the electrolyte and is easy to shrinkage at high temperatures. Therefore, in order to effectively prevent the occurrence of thermal runaway in electric vehicles, the diaphragm material can be improved to have better electrochemical properties as well as thermal stability to prevent the occurrence of thermal runaway caused by the contact between the positive and negative electrodes.

③ Improve the cathode material. Commonly used lithium-ion battery cathode materials include lithium cobalt oxide, lithium iron phosphate and lithium manganese, all of which have the advantages of high efficiency and high energy density, but the cathode materials are not thermally stable and will decompose and release large amounts of oxygen, generating a lot of heat. Therefore, the cathode material needs to be improved to make its structure more stable and less likely to decompose at high temperatures.

④ Strengthen the anti-collision performance of cars. Improve the ability of electric vehicles to prevent collision, pinprick and extrusion, prevent thermal runaway caused by mechanical abuse to a certain extent, reduce the probability of thermal runaway from the source, and reduce the fire accidents of electric vehicles due to collision.

⑤ Design of automobile safety detection system. Through this system, the safety of electric vehicle wiring is detected comprehensively, and problems such as short circuit of electrical components, mechanical failure and battery failure are found in time, and certain safety brakes can be applied in case of accidents. When the car is over-charged or over-discharged, it can detect and limit the current in time, reduce the battery voltage and ensure the battery is in a safe state.

7. Conclusions

At present, from the world's development trend, the new energy electric vehicles development is gradually becoming mainstream. However, there is no more direct and effective solution to solve the problem of electric vehicles thermal runaway. Only by continuously testing and researching the inside and outside of the battery, optimizing the structural performance from the inside out, reducing the impact of each link caused by the thermal runaway chain reaction, enhancing the prevention and monitoring capability of the vehicle itself, and reducing the harm when thermal runaway occurs. This paper analyzes electric vehicle fire accidents and the causes of fire accidents, and then suggests that the causative factors for the occurrence of thermal runaway include mechanical abuse, thermal abuse, and electrical abuse. Then it starts to describe the development mechanism of thermal runaway, such as the decomposition of SEI membrane, the melting of diaphragm, and the chemical reaction between negative electrode and electrolyte. Finally, relevant suggestions on measures to prevent thermal runaway are presented. It is hoped that this review will help improve the performance of electric vehicles and that future researchers and scientists will explore better measures to address thermal runaway so that people can use electric vehicles more safely, develop them better, and protect the environment better.

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