Spontaneous combustion of lithium batteries and its preventive measures

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Abstract. The new round of global scientific and technological revolution and industrial transformation are developing vigorously. The integration of automobiles with the energy, communications and other industries has been accelerated, and profound changes have taken place in automobile product forms, transportation modes, energy consumption structure and social operation modes, and the new-energy automobile industry is facing unprecedented opportunities for development. However, lithium battery, the main component of new energy vehicles, has become a power source and an energy storage power source for peak-frequency modulation due to its advantages of high voltage, good cycling performance, high specific energy and small environmental pollution. With the development of new battery material technology, the energy density and electrochemical performance of batteries have been greatly improved, but this often leads to the decrease of safety performance, resulting in frequent fire accidents of lithium batteries. In this paper, the fire causes of lithium batteries are analyzed and the frontier research on fire causes of lithium batteries is described. Secondly, the combustion mechanism of lithium battery is analyzed, including the process of thermal runaway and diffusion. Thirdly, the improvement measures in material, technology, design and control system of lithium battery are put forward. It is hoped that these Suggestions can promote the prevention of spontaneous combustion of lithium batteries.

1. Introduction
Affected by the epidemic, governments around the world have increased subsidies for new energy vehicles as a means to boost their economies. Such as the European market can meet requirements of environmental protection of the traditional automobile enterprises, could face a huge amount of fines. In addition, China, the United States, Germany, France and other auto countries have introduced a new round of electric vehicle subsidy policies, further boosting the demand for new energy vehicles. Traditional car manufacturers such as Volkswagen, Toyota and BMW are taking advantage of the trend to accelerate the electrification, while Tesla and BYD are constantly introducing new models [1]. Worldwide shipments of electric vehicles maintained a high growth rate (CAGR 3 approximately 56.8%) during the 2015-2018 period. In 2019, the growth rate of shipments slowed down significantly, only increasing by 9% [2] compared with the same year last year, but the penetration rate of electric cars increased to 2.5% compared with 2.2% in 2018. Electric-vehicles use battery to lithium battery. Lithium-ion batteries with high energy density, high working voltage, low natural discharge rate and long cycle life, charge and discharge with high efficiency, wide working temperature range, low environmental pollution, etc. Which is the development direction of modern high-performance batteries. With the significant improvement of power battery performance, the application range can be gradually...
widened. At present, the consumption field has gradually moved to new energy vehicles, energy storage, digital, electric bicycles, power tools and other fields. However, due to the thermal instability of lithium-ion batteries, in extreme conditions of fire explosion risk is very big. Lithium battery fire and explosion is a series of chain reaction of thermal runaway will generate a domino effect, produce more and more heat, eventually cause fire or explosion.

2. The cause of the fire of lithium-ion batteries
Lithium battery is a kind of chemical power supply. If it is heated, pricked, squeezed, impinged or not used in a standard way, lithium battery will often cause the fuse of diaphragm, which will lead to the direct contact between positive and negative electrodes of the battery and internal short circuit will occur. Under the effect of high temperature, a variety of exothermic reactions will occur in the electrode material, and the continuous accumulation of heat may cause the battery to catch fire. Battery fires occur in various places of use, including mobile phones, electric cars, electric motorcycles, electric buses, battery factories and so on. The main causes of battery fire are collision [3], charge and discharge [4], high temperature spontaneous combustion [5] and so on. At present, some scholars have studied the battery safety and fire risk. The combustion of alkanes, olefin gases and electrolyte vapors generated by the reaction inside the battery is the main reason for the battery fire. These alkanes and olefin gases are mainly produced by the reaction of the electrolyte with lithium embedded in it at high temperature, and formed by the decomposition of the electrolyte itself. 26 gases were detected in the gas products of the 100% SOC battery [6]. Some of the organic solvents in the electrolyte evaporate at temperatures above 130 °C and form electrolyte vapors, which account for a high proportion of the combustible gas. Moreover, the content of gas components generated under these high temperature conditions is related to the charge state of the battery [7-11]. Harris et al [12]. believe that the thermochemical and combustion characteristics of these combustible gases determine whether the battery will burn and the energy generated by combustion. Therefore, considering the selection of electrolytes with low thermochemical and combustion characteristics in the material selection process, the fire risk of batteries can be reduced.

The merits of the quality of battery performance, the increase of battery quantity, the expansion of battery capacity and the increase of energy density will greatly increase the probability of accidents and the danger degree of accidents. Particularly in large-scale applications such as energy storage power grids, the international space station, the battery will likely lead to fire flame spread throughout the region, bring immeasurable loss. Therefore, it is very important to study the fire risk and preventive measures of large lithium-ion batteries and battery packs such as power batteries and energy storage batteries, and it conforms to the development requirements.

3. Combustion mechanism of lithium batteries
Thermal runaway and subsequent propagation are the main factors to cause catastrophic consequences in lithium-ion battery packs. Exploring the thermal runaway propagation is thus of great fundamental and practical interest in understanding the mechanism of battery safety [13].

3.1. Thermal runaway
Thermal runaway refers to as lithium batteries in various under the action of external and internal causes, such as external heat, or internal short circuit, or flow into the battery pack, or the battery under the condition of high current charge and discharge, these will lead to positive and negative electrode inside the battery itself fever, or directly short circuit, which can lead to heat diffusion, the temperature is gradually increased, Further lead to battery cathode surface in the SEI (Solid Electrolyte Interface) membrane, Electrolyte, is negative and so on a series of thermal runaway reaction at high temperatures (pyrolysis). Until a certain temperature point, temperature and internal pressure increase sharply, the energy of the battery is converted into heat energy in an instant, forming a single battery to burn or explode. There are many complex factors that cause a single battery to lose control of heat, but most of them are caused by too much current or too high temperature. The mechanism of such loss control is
highlighted below. Take lithium ion battery as an example. When the temperature reaches 90 °C, the SEI membrane on the negative electrode surface begins to decompose. This tends to happen around 69 °C [14], with some reports at temperatures as low as 57 °C [15]. After the temperature rises again, the diaphragm (PP or PE) between the positive and negative poles will contract and decompose at high temperature. The positive and negative poles will contact directly, and the short circuit will cause a lot of heat and sparks, which will further increase the temperature. For 100% state of charge (SOC) cells, the fire is blown out at the TR process. Jet fire is only observed for 50% and 100% SOC batteries, respectively. In some failure events, lithium-ion cells can undergo thermal runaway, which can result in the release of flammable gases that pose fire and explosion hazards for the compartment housing the cells [16]. In a normal charging and discharging process, a small amount of free oxygen from the positive electrode reacts with the carbon negative electrode to form a small amount of flammable gas CO, which will not contribute to combustion at normal temperature. However, due to the short circuit, decomposition reaction of positive electrode oxide will occur and free oxygen will be produced. These free oxygen and CO will further burn together with electrolyte steam at high temperature, forming a vicious cycle.

3.2. Thermal runaway diffusion
Uncontrolled thermal diffusion is a phenomenon in which the heat generated by a single battery inside the battery pack is rapidly diffused to the surrounding batteries by means of heat conduction, convection and radiation. At this moment, the heat dissipation device cannot exclude the heat, and the thermal control extends to the surrounding batteries, causing a chain reaction. When the surface temperature of the battery reaches 650 ~ 1000 °C, the battery pack burns. The package with more batteries has higher average MLR and fire propagation has a great effect on the combustion efficiency of LIB [18]. TR propagates faster in parallel module than in series and unconnected modules, and TR spreads faster in series modules than in unconnected module [19]. At the same time, the pressure relief valve of the battery pack is opened, and the flame and smoke extend to the outside of the battery pack. The smoke may be seen outside the car, and then it will ignite the combustible materials around the battery in the car, finally causing the whole car to catch fire. The combustion occurs often can use sprinkler, also can use dry powder fire extinguishers, carbon dioxide fire extinguisher, sandy soil is also a safe fire extinguishing tools, the most practical fire extinguishing agent or a lot of water, it can quickly cool the battery pack [20].

4. Measures to eliminate the risk of battery burning

4.1. Improve the material performance in the battery and the process of producing the battery.
The modification of anode and cathode materials mainly consists of two aspects: surface coating of electrode and material formulation. The lamination process is an important technical measure to improve the shape of electrode, which has a certain effect on reducing thermal runaway. Improvements to the high safety electrolyte, including the development of new lithium salts, solvent modification and the addition of electrolyte additives. High strength inorganic diaphragm or intelligent diaphragm is developed to replace the organic diaphragm materials currently used. Intelligent diaphragm technology is more flexible for controlling the internal temperature of lithium batteries. At the beginning of thermal runaway, the gas pressure in the battery increases, and when the gas reaches a certain limit, it can be discharged to effectively prevent combustion. The battery cover is a key security technology to prevent burning. Add a notch to the surface of the battery cover. When the internal thermal runaway gas pressure reaches a certain level, the gas will burst through the notch and be discharged out of the battery cover.

4.2. Improve battery pack structure and safety design
When thermal runaway and diffusion occur, the severity of the accident should be minimized. In addition to BMS safety management, battery pack safety structure technology and active safety
technology need to be optimized. The internal layout of the battery pack must be optimized in electrical layout design to reduce the number of connectors and unreasonable wiring direction, so as to make the overall layout more compact.

In addition, the explosion-proof design of active safety technology is adopted. In case of mechanical collision and charge oversaturation of the battery, thermal control inside the battery will occur. Therefore, in the process of battery layout, we try to make the battery emit gas to the designated safe direction, so as to ensure that a large amount of high-pressure gas is enclosed in the battery, so as to prevent further expansion of the danger. Or an active fire extinguishing device adopting active safety technology. Fire extinguishing equipment can be timely started, timely extinguishing, active injection of inert gas or refrigerant to cool the battery.

4.3. BMS thermal management and control
Thermal management and control technology can prevent and prevent the occurrence of uncontrolled heat, and play a mitigation role in the initial stage of uncontrolled heat to inhibit the spread of uncontrolled heat. Thermal management and control technology is a part of BMS function [21], which can make all battery packs work within the optimal temperature range, prevent the occurrence and expansion of thermal control, and timely send voltage and temperature monitoring and alarm. During the charging process, BMS will automatically provide the best charging scheme according to the change of battery state, the information is fed back to the charging pile to implement the best charging method.

5. Conclusion
With the rapid development of lithium battery industry, the application of new materials and new technologies are constantly emerging. The ultimate goal of the study on the fire risk of lithium battery is to fully understand and control the occurrence of battery fire. Based on this research, the battery risk can be graded in the future, and different control methods can be adopted according to different grades. It can also design safety prevention systems for large-scale battery use sites such as electric vehicles and energy storage power grids to protect the safety of life and property.

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