Mechanism and Protective Measures of Thermal Runaway in Lithium-ion Batteries

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Abstract. Due to its benefits of having a high energy density, safety, and being environmentally friendly, lithium-ion batteries (LIBs) have developed into the most widely used energy storage equipment. However, LIBs are prone to frequent safety mishaps because of thermal runaways in large-scale commercial applications in industries including electric passenger vehicles, portable electronic gadgets, and distributed energy storage. The primary cause is because mechanical, electrical, and thermal abuse of LIBs can result in thermal runaway and potentially hazardous conditions including combustion and explosion. As a result, this essay begins by examining the causes of thermal run away from the standpoint of LIB misuse. The investigation of LIBs' safety features became the primary concern after that. primarily separated into interior and exterior protection. The electrolyte, diaphragm, and electrode are the three primary areas that are optimized and improved when it comes to internal protection. Through battery management systems, cooling technology, and blocking technology, external protection primarily lowers dangers. Finally, to serve as a reference for future security research on LIBs, the pertinent security challenges of LIBs were prospected.

Keywords: LIBs, thermal runaway, prevention.

1. Introduction

LIBs play a very important role in the development of energy storage devices due to their excellent storage efficiency. Lithium-ion batteries are therefore extensively used. From the automotive battery business to the aerospace industry and even in hospitals, supermarkets, and other emergency power applications, lithium-ion batteries are employed in practically every industry. Safety is always put first when it comes to LIBs. The most prevalent of these reasons is thermal runaway. It is simple to set off the internal control and explosion of LIBs using lithium dendrites, diaphragm faults, lithium metal in the anode, and electrolyte solution reaction. These days, LIBs explode rather frequently due to their low safety. Lithium-ion battery safety must thus come first.

To prevent overcharge, over-discharge, overtemperature, and other abnormalities, there are numerous approaches to assure the safety of LIBs, such as the introduction of new materials or new sensors for management. Alternately, rigorously regulate the manual and mechanical replication processes to improve the battery's crash and stab resistance. Consequently, the likelihood of LIBs exploding is decreased. Additionally, how to limit the loss caused by thermal runaway in LIBs; and how to avoid it effectively. It seems appropriate to talk about lithium-ion batteries' greater safety in relation to these problems.

2. Reasons for thermal runaway of LIBs

2.1. Mechanical abuse

Mechanical abuse is mostly brought on by outside mechanical forces including piercing, squeezing, and impact, which cause the battery to overheat. Mechanical external pressures might harm the battery separator, resulting in internal short circuits and a quick battery drain that would immediately release a lot of heat. Additionally, mechanical external pressures and ruptures to the battery shell allow air to immediately enter the battery's interior where it undergoes oxidation-reduction processes with the electrolyte and active components, generating a lot of heat in the process. The two conditions mentioned above will further lead to battery thermal abuse. Under conditions of thermal abuse, a series of exothermic reactions start to occur, eventually causing the battery to reach thermal runaway. Due to the battery's compact internal structure, even if the shell flexes slightly under mechanical external forces without breaking, this could still cause a partial rupture of the diaphragm, localized electrode strain, or even direct contact with the electrode, which could cause internal short circuits [1]. The battery shell serves as the main layer of defense, therefore its capacity to withstand outside pressure and maintain temperature stability is essential. varied types of batteries.

2.2. Electricity abuse

The majority of electrical abuse involves external battery short connections. excessive charging, excessive discharge, etc. An increase in battery current density brought on by external short circuits can produce a lot of heat and gas, mostly Ohmic heat [2]. The battery may bulge, burst, and spill electrolyte if the temperature rises to a particular point (77-121 °C). If the battery energy while overcharging exceeds the nominal value, the risk is greater. In the first stage, the negative electrode achieves a state of saturation for lithium insertion, the efficiency of Li^+ insertion declines, and deposits on the negative electrode's surface receive electrons, generating metallic lithium. The electrolyte's ability to hold Li^+ is diminished, which improves the battery's polarization. Lithium dendrites, or dendritic metallic lithium, may form from the lithium evolution layer. Lithium dendrites might pierce the separator, resulting in internal short circuits and the battery overheating. In phase 2, an intensive and ongoing heat-generating process occurs inside the battery as a result of the lithium layer's reaction with the electrolyte. Due to excessive lithium removal and high-temperature effects, the positive electrode material decomposes, producing a significant quantity of heat and oxygen [3]. Oxygen can lead to electrolyte breakdown and other adverse effects, which release more gas and trigger the battery safety valve to open and discharge gas. External oxygen enters the battery, speeding up the electrolyte's breakdown, and interacting with combustible gases to raise the battery's temperature. Over-discharge may result in copper precipitation during charging, copper dendrite formation on the separator, piercing of the separator, and internal short circuits in the battery. Li^+ 's conduction and transportation behavior in a battery system is influenced by things like the electrode's conductivity and the electrolyte's ion diffusion coefficient.

2.3. Thermal abuse

A number of chemical processes take place inside LIBs under situations of thermal abuse, such as high ambient temperature or localized overheating of the battery, raising the internal temperature and eventually causing thermal runaway. In flexible packaging ternary positive electrode batteries, thermal runaway develops over the course of four stages at three distinct temperatures. Stage I: The negative electrode expands and decomposes when the battery reaches its heating temperature (70–120 °C), and the negative electrode interacts with the electrolyte to produce a new SEI film and release heat. The produced SEI film is in a metastable condition and continues to degrade and generate a cycle as the battery temperature rises. The electrolyte's available Li^+ concentration falls while electrode polarization rises. Stage II: When the battery temperature reaches the SEI's melting point, it will break and crack severely, leading to internal short circuits. Stage III: The positive electrode produces the oxygen species O_2^-, O^-, and O_2^{2-}, which react with the electrolyte and generate a lot of heat. The battery temperature increases to the starting point of thermal runaway as a result of a significant proportion of electrolyte decomposing and producing flammable gases. Stage IV: After passing through the electrolyte and separator, the oxygen generated by the positive electrode reacts with the negative electrode. The reaction heat between the positive electrode and electrolyte reaches its maximum at this moment, which causes the battery heating rate to increase by an order of magnitude. As a result of the interaction between combustible gases and the oxygen created by the breakdown of the positive electrode, the battery then undergoes combustion and achieves its maximum temperature. During this process, interactions between the positive electrode and electrolyte, oxygen and the negative electrode, and oxygen and combustible gases are the main sources of heat that drive the battery to continue heating up. The start and peak temperatures of the thermal runaway are determined by the stability of the positive active material, whereas the self-heating temperature of a battery is determined by the stability of the negative SEI layer.

3. Thermal runaway protection technology

3.1. Internal protection

3.1.1. Electrolyte

Currently, carbonate serves as the solvent, and lithium hexafluorophosphate ($LiPF_6$) is the solute in the electrolyte of LIBs. The flammability of the carbonate solvent raises the danger of monomer thermal runaway. The electrolyte can be upgraded in the following ways to address the issue of thermal runaway. (1) Additives for flame retardance: The flammability of organic electrolytes can be successfully decreased by adding flame retardant chemicals. The idea is to make the electrolyte more effective in removing free radicals from combustion [4]. In addition to phosphorus-containing compounds, common flame retardants include perfluoroalkanes, silane-type flame retardants, and ionic liquid flame retardants. Nonflammable electrolytes: Noncombustible electrolytes are the primary remedy for monomer thermal runaway, and flame-retardant additives can only lower the flammability of the electrolyte to the greatest extent feasible. (3) Solid electrolytes: The benefits of nonflammability, non-leakage, and extended service life are shared by all solid electrolytes, considerably enhancing lithium-ion battery safety. Sulfide electrolytes, of the many different solid electrolytes, have a high conductivity and have historically attracted the most interest. S has a low electronegativity and is less attracted to the easily migratory lithium ions.

3.1.2. Electrolyte

Lithium dendrites precipitating from the negative electrode will result in a short circuit between the positive and negative electrodes, which will pierce a diaphragm with poor mechanical strength. As an illustration, a separator with low thermal stability may distort or fuse during the thermal runaway process. The diaphragm plays a key role in the body's internal protection against thermal runaway. The majority of separators used in commercial LIBs nowadays are polyolefin-based because they are more effective in controlling heat shrinkage, have higher mechanical strength, and have self-closing properties [5]. Positive and negative pole contact as well as short circuits may result from the diaphragm's macroscopic size shrinking that occurs when the monomer temperature reaches the diaphragm's softening temperature. Tensile strength and puncture strength are both parts of the separator's mechanical strength. The ability of the separator to bend when the battery is subjected to external pressures can be improved by increasing the mechanical strength, which can stop burrs or lithium dendrites from penetrating the separator in the battery [6]. Before the monomer achieves thermal runaway, the diaphragm temperature reaches the closed pore temperature, forcing the hole to shut, closing the ion channel to stop the current, and preventing short circuits. This is referred to as the diaphragm's self-closing function. The ion transfer thermal cutoff technique is another name for it.

3.1.3. Electrodes

Electrodes, a crucial part of lithium-ion batteries, have seen a number of advancements and can provide batteries with significant safety assurances. When the monomer temperature climbs to the PTC material's Curie temperature, the resistance of the modified electrodes—known as positive temperature coefficient (PTC) materials—increases quickly, reducing current and preventing thermal runaway. Following research and a summary, there are three approaches: coating the electrode collector with PTC materials, coating the active substance with PTC materials, and employing PTC materials as conductive agents for the active substance [7].

3.2. External protection

3.2.1. Battery management system

Battery parameter monitoring (voltage, current, temperature, internal resistance), fault diagnosis, alarm, fault handling, charge and discharge control, battery pack balancing, and other tasks are all carried out by the battery management system to keep track of how LIBs are performing. The most important of them are battery parameter monitoring and battery pack balance. Battery parameter monitoring involves keeping track of each battery's voltage, current, internal temperature, and surface temperature to identify whether one of them poses a safety risk. When a safety concern arises, it needs to be managed and notified right away. Monitoring systems are getting smarter all the time now. Vary battery health states are caused by variations in individual cells, including voltage, internal resistance, capacity, and varying charging and discharging depths. In actual applications, many lithium-ion batteries must be linked in series to form groups to support the demands of high-power electrical equipment. Since each battery has small variations, the variations between battery groups will grow once they are connected in series, which makes equalization technology extremely crucial. Energy-dissipative and nonenergy-dissipative forms of balancing technologies exist. Nonenergy dissipative varieties are more energy-efficient when compared to the other two. They balance the energy of each battery pack by transferring electricity via capacitors or inductors.

3.2.2. Cooling technology

In actual use, LIBs packs have complicated electrochemical processes going on in addition to their intricate structural makeup. The internal temperature of the battery rises as the heat release does, speeding up some electrochemical reactions and creating a vicious cycle. The operating longevity of lithium-ion batteries is directly impacted by temperature changes [8]. The battery pack's rising temperature and inequitable temperature distribution would drastically shorten battery life and decrease battery performance. In the world of electric vehicles, air conditioning is frequently employed since it is inexpensive, has a straightforward design, and is simple to apply. To cool, air is drawn over the surface of the battery packs and used to remove heat. Uniform temperature distribution and improved thermal management are two current issues with air cooling. Aluminum foam was used by Mohammadian et al. to fill the air channel, which considerably increased the temperature distribution's uniformity [9]. Compared to air cooling, liquid cooling has a superior cooling effect because liquids transfer heat by liquid convection and have a higher specific heat capacity. Thermal management optimization, such as battery form and pipeline layout, devoted to optimizing cooling efficacy, is where liquid cooling technology faces its greatest challenges. Increasing the contact area between the battery and the liquid cooling pipeline and increasing the number of liquid cooling pipelines can effectively improve the cooling effect, and the temperature distribution is also more uniform, according to research by Rao Z et al. on the liquid cooling structures of cylindrical and square batteries [10].

Phase change cooling is the use of phase change materials to absorb or release heat during phase change to maintain a stable temperature state of the battery pack. This technique features a straightforward design, strong insulating properties, and a consistent temperature distribution.

3.2.3. Blocking technology

LIBs packs' safety may be ensured and prevented by monitoring and balancing the battery parameters. The development of cooling technologies can more efficiently disperse heat and boost safety capabilities. However, internal damage may result from unexpected mishaps including falls, short circuits, and external impacts. The preventive measures mentioned above cannot ensure your safety. Blocking technology can stop thermal runaway from spreading to additional single batteries or battery packs when it occurs in a single battery, minimizing the damage that thermal runaway causes. To successfully stop the propagation of monomer thermal runaway, blocking technology can be used in conjunction with cooling technology. In addition, the use of fuses installed at both ends of the positive and negative poles of a single body can provide safety assurance by timely cutting off the circuit when the internal current of the single body suddenly increases.

4. Summary

The process of thermal runaway is tightly tied to internal elements like battery SOC, material, and form as well as exterior ones like abuse circumstances and environmental temperature, which is a crucial issue faced by LIBs in their development. In a specific abuse scenario, the three abuse scenarios mentioned earlier are likely to set off a domino effect chain that eventually results in battery overheating. The internal factors that affect mechanical and electrical abuse include membranes, electrolytes, and shells; The determining factor for the characteristic temperature of thermal runaway is mainly the thermal stability of the internal materials of the battery, such as electrodes, electrolytes, and separators.

Despite significant progress in the understanding of LIBs thermal runaway, there are still open questions in a number of research areas. Due to the superposition of cycles, the investigation of how aging impacts LIBs safety has just recently begun, and there have been relatively few studies examining how aging routes and processes affect thermal stability. However, there are currently few experimental studies on the prediction and modeling of flame propagation following thermal runaway, as well as a few numerical simulation analyses of flame propagation. There is little doubt that further research is required to completely comprehend the thermal runaway safety management of lithium-ion power batteries, particularly in the areas of warning and blocking.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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