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Review

Intrinsic Safety Risk Control and Early Warning Methods for Lithium-Ion Power Batteries

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Abstract: Since 2014, the electric vehicle industry in China has flourished and has been accompanied by rapid growth in the power battery industry led by lithium-ion battery (LIB) development. Due to a variety of factors, LIBs have been widely used, but user abuse and battery quality issues have led to explosion accidents that have caused loss of life and property. Current strategies to address battery safety concerns mainly involve enhancing the intrinsic safety of batteries and strengthening safety controls with approaches such as early warning systems to alert users before thermal runaway and ensure user safety. In this paper, we discuss the current research status and trends in two areas, intrinsic battery safety risk control and early warning methods, with the goal of promoting the development of safe LIB solutions in new energy applications.

Keywords: electric vehicles; energy storage; lithium-ion batteries; intrinsic safety; early warning

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1. Introduction

With the intensifying global issues of resource shortages, environmental pollution, and climate change, green development has become a unified global strategy, and developed countries have announced plans to achieve carbon neutrality within this century. These global environmental strategies have profoundly impacted the electric vehicle industry, making it a key factor in reducing carbon emissions and environmental pollution, and the electric vehicle industry, bolstered by supportive policies and benefitting from environmental advantages and low use costs, has grown rapidly. The United States, Japan, and some European countries started researching electric vehicles relatively early and have more advanced technology as a result. China had a later start in electric vehicle development, but the country has seen rapid development in the industry since 2014.

Driven by the interest in electric vehicles, the power battery industry has experienced rapid growth in recent years, especially in lithium-ion battery development. Lithium-ion batteries (LIBs) have been widely used for electric vehicles due to their high energy density, low self-discharge rates, and broad operating temperature range, but LIBs still face challenges in terms of cost, lifespan, and safety. Explosion accidents caused by thermal, electrical, and mechanical abuse as well as battery quality issues have led to loss of life and property, and as a result, the safety of lithium-ion battery applications has garnered widespread attention from researchers and practitioners around the world [1–3]. Lithium-ion battery cells are coupled electrothermal multi-physical field reaction systems that inevitably experience aging phenomena, such as capacity decay, gas generation, and lithium plating, during use [4,5]. These aging phenomena can negatively impact battery performance and thermal stability, and statistics on safety issues indicate that battery thermal stability and battery management system (BMS) failures are two major aspects of battery safety [6]. These issues must receive more attention to ensure safety in lithium-ion battery designs and applications.

In LIBs, thermal runaway can be triggered under conditions of mechanical, electrical, or thermal abuse, leading to a series of chain reactions within the battery and the rapid release of a substantial amount of heat [7]. In a thermal runaway event, various processes and reactions, such as decomposition of the solid electrolyte interphase (SEI) membrane, anode–electrolyte reactions, cathode–electrolyte reactions, electrolyte decomposition, and anode binder decomposition, generate considerable heat, and if the heat is not effectively dissipated, it accumulates and triggers thermal runaway [8]. In the battery system, thermal runaway of a certain cell may result in the release of high-temperature gas, which may exacerbate the thermal runaway. Therefore, venting gas management is also beneficial in mitigating serious thermal runaway issues [9].

Addressing lithium-ion battery safety centers around two main topics, enhancing the intrinsic battery safety and improving battery safety control. Enhancing intrinsic battery safety requires improvements in various battery safety indices, including thermal stability and deformation resistance, from a materials perspective. This includes advancements in key battery materials and the introduction of safety protection measures. Improvements in battery safety control primarily include the implementation of early warning systems to detect imminent thermal runaway and ensure user safety.

In this paper, we review the current state of research and development trends in intrinsic safety risk control and early warning methods for LIBs in new energy applications to promote the development of safety aspects in these batteries, using Google Scholar to search the scientific databases. We first discuss the methods of improving the intrinsic safety of batteries through material development for specific battery components, such as positive and negative electrodes, electrolytes, and separators. We then analyze the current state of research in thermal runaway early warning models and sensors. Finally, we present four suggestions for solving future battery safety issues.

2. Intrinsic LIB Safety Risk Control from a Materials Perspective

Battery safety issues primarily manifest as thermal runaway events caused by internal defects or external misuse, as illustrated in Figure 1. Internal battery factors include lithium dendrites, material defects, aging decay caused by normal battery use, and manufacturing defects in the form of burrs on electrode sheets, misalignment of positive and negative electrodes, or uneven electrode sheet coating. External misuse encompasses thermal abuse, electrical abuse, and mechanical abuse. Specifically, thermal abuse refers to usage in extreme high temperatures (over 65 °C) or low temperatures (below 0 °C). Electrical abuse includes overcharging and overdischarging as well as repeated cycles of micro-overcharging and micro-overdischarging, i.e., frequent full charge and discharge cycles from 100% state of charge (SOC) to 0% SOC before recharging. Mechanical abuse mainly refers to compression, dropping, and other impacts, as well as long-term exposure to vibration and physical impacts in vehicles, all of which can lead to battery safety failure.

From the perspective of battery safety, focusing on the triggering mechanisms of thermal runaway and mitigating its progression is crucial, and designing safe individual cells at the battery material level is critically important. Enhancing the safety of LIBs involves the design and improvement of four key materials, namely, cathode materials, anode materials, electrolytes, and separators, and among these, electrolyte additives and novel separator materials have received increased levels development of attention. These design and improvement measures related to battery materials aim to decelerate the process of thermal runaway due to internal and external factors, thereby elevating the safety levels of batteries under various operating conditions.

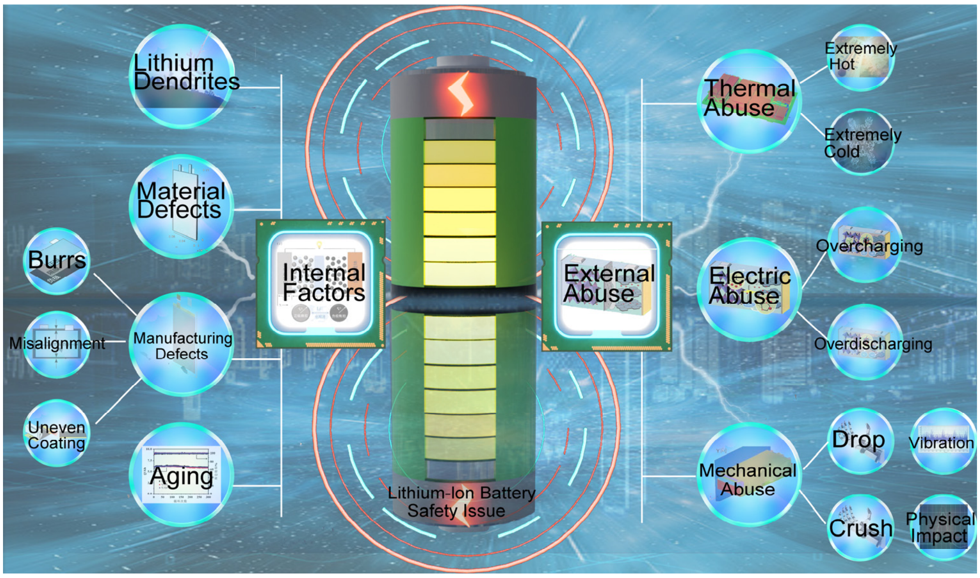

Figure 1. Classification of factors causing safety issues in lithium-ion power batteries.

2.1. Improvement of Cathode Materials in Lithium-Ion Power Batteries

Currently, the cathode materials commonly used in power batteries include lithium iron phosphate (LFP) and various compositions of ternary materials such as nickel–cobalt–manganese (NCM). Both LFP and NCM compositions are extensively used in passenger vehicle power batteries, and although NCM is sometimes favored for its high energy density, it has inferior thermal stability compared to LFP. The primary methods for enhancing the safety of cathode materials include optimizing material structure and surface coating and using core-shell structures, surface coatings, and doping techniques to treat cathode materials. These methods have been shown to be effective [10,11]. The performance of the cell could be impacted whether cathode material surfaces are modified or new materials are used, and material cost must be considered for practical application. Therefore, we consider either the structural modification of commercialized cathode materials or doping with other commercialized materials with better thermal stability as effective ways to improve the safety of cathode materials.

2.1.1. Surface Coating

Surface coating technology is vital in enhancing the thermal stability of cathode materials in LIBs. By applying a coating of thermally stable materials on the cathode surface, direct contact between the cathode material and the electrolyte can be effectively prevented. This improves battery thermal stability by not only helping to suppress phase transitions but also reducing the disorder of cations at lattice sites. In one example, Nitou et al. significantly increased thermal stability by coating cathode materials with phosphates and fluorides [12]. Cai et al. developed surface-functionalized $Ti_3C_2T_z$ MXene cathode materials and used annealing to modify the surface functional groups of $Ti_3C_2T_z$, eliminating irreversible lithium metal plating [13]. This strategy effectively mitigated exothermic reactions during thermal runaway, enhancing the anode's initial Coulombic efficiency and cycle stability. Furthermore, in situ thermal analysis showed that the thermal runaway onset temperature of the modified $Ti_3C_2T_z$ lithium cobalt oxide (LCO) full cell (195 °C) was significantly higher than that of the graphite LCO full cell (169 °C), indicating the effectiveness of the modification in improving battery thermal stability.

2.1.2. Material Structural Optimization

Chiba et al. achieved a breakthrough in material structure optimization by comparing single-crystal and polycrystalline particle $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) as cathode materials combined with natural graphite (NG) as the anode material to fabricate full cells [14].

The differences in safety aspects were verified using an accelerating rate calorimeter (ARC), and the results demonstrated that batteries with single crystal NCM811 exhibited significantly better thermal safety compared to those with polycrystalline NCM811. Their finding provided an important reference for optimizing the crystal structure of cathode materials and opened a new pathway to enhancing battery thermal stability.

2.2. Improvement of Anode Materials

Common anode materials in power batteries include graphite, hard carbon, and silicon-based compounds. Currently, lithium titanate oxide (LTO) stands out among anode materials due to its superior safety characteristics, but the relatively low energy density of LTO batteries limits their peak voltage and suitability for passenger vehicle power batteries. In contrast, silicon-based materials offer high specific capacity and charge–discharge rates that can enhance overall battery performance, and these materials provide a solution to some of the disadvantages of graphite anodes. Unfortunately, pure silicon suffers from volume effect issues, significantly shortening its cycle life compared to graphite materials and limiting commercial application. As a solution, silicon can be combined with graphite, graphene, or other carbon materials to overcome the volume effect issue of pure silicon.

While graphite anodes are relatively stable, lithiated graphite can continuously react with the electrolyte at high temperatures, and this reaction exacerbates the initial heat accumulation in thermal runaway and promotes the progression of thermal runaway chain reactions. To enhance the stability of the anode, a common solution is to form an SEI layer on its surface. This layer effectively isolates the anode from direct contact with the electrolyte to reduce side reactions and is key in improving battery safety. From the perspective of surface modification, artificial SEI layers, such as metal deposition layers, metal oxide deposition layers, polymers, or carbon coatings, can be constructed to improve the thermal stability of anode materials. The improvement of anode material safety requires an improvement in the structural stability of the materials themselves to avoid the generation of lithium dendrites due to the collapse of the material structure during the lithium deintercalation process.

2.2.1. Material Structural Optimization

Effectively reducing the lithiation amount or the specific surface area of the anode can decrease the reaction between lithium embedded in the anode and the electrolyte and enhance battery safety. However, it is important to note that excessively reducing the lithiation amount or the specific surface area of the anode may lead to a decline in a battery's rate performance and low-temperature performance. Therefore, battery designers must find an appropriate balance between safety and electrochemical performance, and determining this balance point will promote the development of safe, high-performance battery technology [15].

2.2.2. New Anode Materials

In addition to material structure optimization, exploring new anode materials, such as Li_xSn_y, is another effective approach to enhance battery safety. These materials demonstrate better safety due to their higher thermal decomposition temperature, showing potential to simultaneously improve battery performance and safety. Battery materials research is an exciting field expected to provide new opportunities to enhance battery performance and safety in the coming years [16].

2.3. Improvement of Electrolytes

The $LiPF_6$ electrolyte is widely used, but it has several undesirable characteristics, including poor thermal stability, flammability, and the release of large amounts of gas upon decomposition at high temperatures, that significantly impact battery safety. To overcome these issues, modern batteries increasingly adopt liquid electrolyte additives. These additives include borates, phosphates, nitrates, hypophosphites, and polymers, which can effectively inhibit the formation of the solid electrolyte interface and dendrite layer. This chemical approach to electrolyte improvement provides benefits in battery safety and performance by enhancing battery thermal stability, improving cycling characteristics, and prolonging battery lifespans [17]. The extensive use of flame-retardant electrolyte additives will impact the electrical performance of cells, and a small amount of any additive will not play a substantial role in improving safety. Therefore, the application of fully solid-state electrolytes is an important direction for solving intrinsic battery safety issues in the future.

2.3.1. Use of Additives

Electrolyte additives can improve the flame-retardant properties of the electrolyte, enhancing the safety of the battery under abuse conditions [18,19]. Liu et al. reported a multifunctional additive, diethyl (2-(triethoxysilyl)ethyl) phosphate, that could inhibit the flammability of the electrolyte and enhance the cycling stability of NCM811 [20]. After 400 cycles at 1 C, the battery capacity retention was 89.9%, compared to only 61.3% for the battery with the blank electrolyte. Additionally, DESP showed good compatibility with the graphite anode, causing no impacts to electrochemical performance. Lei et al. developed a nonflammable electrolyte with dual-phase fire-extinguishing capabilities by introducing two flame retardants into carbonate electrolytes using a cosolvent bridge approach [21]. This electrolyte not only exhibited excellent electrochemical performance but also suppressed the combustion of flammable gases and liquid electrolytes. A 2.9-Ah capacity $Li[Ni_{0.78}Co_{0.10}Mn_{0.12}]O_2$/graphite pouch cell with this enhanced electrolyte maintained 87.5% capacity after 1000 cycles at 0.5 C, and during nail penetration tests, the battery only smoked, achieving a 300 °C reduction in the maximum temperature of thermal runaway. Additionally, the onset of thermal runaway was delayed by 86 s in thermal abuse tests, demonstrating that carefully designed electrolyte additives can significantly improve battery safety and performance.

2.3.2. Development of New Electrolytes

In addition to using additives to improve electrolyte properties, research groups are investigating the development of new electrolytes. Long et al. designed a smart self-adaptive gel polymer electrolyte (GPE) based on a novel functionalized copolymer that, through the synergistic action of its side chains, assisted lithium ion migration, provided redox stability, facilitated ring-closing reactions, and inhibited combustion [22]. This copolymer-based GPE not only provided excellent long-term cycling performance for various batteries at room temperature; it achieved thermal shutdown at high temperatures and provided flame retardancy during fires. Their results indicate that adding flame retardants to the electrolyte or introducing flame-retardant structures into the polymer matrix can improve fire safety while avoiding negative impacts on battery electrochemical performance due to chemical and/or physical incompatibility with the electrolyte and electrodes.

2.4. Improvement of Separators

The separator is another lithium-ion battery component crucial in ensuring safe operation and optimizing electrochemical performance. The physical and chemical properties of separators directly affect overall battery performance, and the key performance parameters of separators include porosity, shrinkage, melting temperature, and pore-closing temperature [23,24]. The porosity determines the electrolyte retention capacity, shrinkage affects thermal stability, and melting and pore-closing temperatures are directly related to separator safety performance under high-temperature conditions. Unfortunately, the widely used polyolefin separators, such as polyethylene (PE) and polypropylene (PP), exhibit significant limitations at high temperatures, and when the temperature rises to a certain level, these separators are prone to rupture, perforation, or melting, leading to potential internal short circuits and safety risks. Therefore, the development of high-performance, high-temperature-resistant separators, designed with coating modifications or new materials, is crucial in enhancing the safety of LIBs. Separator coating modifications involve applying a layer of modified material, such as inorganic nanoparticles or organic polymers, to the surface of the separator, and new material approaches involve separators designed with alternative materials or modifications to current separator materials. The goal in either approach is to enhance the high-temperature performance and electrochemical stability of the separator beyond current state-of-the-art [25].

2.4.1. Coating Modification

Roh et al. developed a functional flame-retardant ceramic-coated separator (F-CCS) that enhanced the safety features of LIBs while maintaining optimal performance [26]. This innovative separator integrated encapsulated flame retardants and hydroxide ceramics to effectively suppress ignition and form a protective layer. Liu et al. fabricated a thermally responsive composite separator by coating a commercial polyolefin separator with ceramic silica microcapsules that encapsulated phase change materials and flame retardants [27]. Their design stored heat within the battery, reducing temperature rise and controlling the thermal release of flame retardants to prevent short circuits. Xiao produced a high-density polyethylene (HDPE) and (γ-AlOOH, AO)/PE composite coating that halted lithium-ion transmission at approximately 130 °C, markedly enhancing battery safety and inhibiting self-discharge to improve long-term cycling performance [28]. Chen et al. focused on improving large lithium-ion battery safety by incorporating low-melting-point PE microspheres into a commercial ceramic-coated PE separator [29]. Their approach resulted in a functionalized PE separator (FPES) that significantly lowered the shut-down temperature and improved tolerance to overcharging and internal short circuits. Gou applied a Co/N-C modification derived from zeolitic imidazolate framework 67 (ZIF-67) to a commercial separator to enhance the wettability and electrolyte absorption rate as well as to reduce thermal shrinkage at high temperatures [30].

The current trend in improving polyolefin separator thermal stability and electrolyte wettability involves introducing coatings conducive to large-scale production. However, challenges remain in developing high-temperature-stable separators with functionalities like thermal shut-off, optimal porosity, and mechanical strength to resist lithium dendrite penetration. Therefore, further development in new separator material systems or separator structure is required.

2.4.2. Development of New Materials

In one approach to new separator materials, Lv et al. developed a thermoplastic polyurethane/polyurethane acrylate semi-interpenetrating polymer network ceramic separator [31]. This separator exhibited an electrolyte retention of 200% and an interface adhesion strength of 6.6 N without compromising energy density, and an NCM811 battery using this separator showed outstanding electrochemical performance with a discharge capacity of 3677 mAh after 300 cycles and a capacity retention rate of 93%. This new composite separator also demonstrated excellent thermal stability and flame-retardant properties. Liao et al. reported a bacterial cellulose composite separator (BA@ATP), designed using a paper-making method, to create a cost-effective, high-ionic-conductivity, and excellent flame-retardant separator [32]. This separator exhibited self-extinguishing properties upon ignition with significantly low heat and smoke production during combustion for improved battery safety. Based on the work by Liao et al., this flame-retardant material could provide an effective approach to improveing battery fire resistance while maintaining other performance metrics. In another approach, Yu et al. designed and fabricated a flexible heat-resistant porous separator based on polyphenylene sulfide (PPS) ultra-thin fibers and a network of glass nanofibers (GNFs) [33].

By thermally pressing and modifying the separator with a silane coupling agent (γ-3-glycidoxypropyltrimethoxy silane), a hierarchical network structure was formed, creating a highly flexible separator with excellent mechanical properties, and this novel composite separator demonstrated no thermal shrinkage after 30 min at 250 °C, showcasing outstanding thermal stability and flame-retardant properties. The inherent polarity and porous structure of the PPS-GNFs separator also achieved a contact angle of 18.2° and an electrolyte absorption rate of 253% for the liquid electrolyte ($LiPF_6$), indicating superior wettability compared to commercial polyolefin separators. Tang et al. fabricated a porous composite membrane based on para-aramid nanofibers (para-ANFs) using electrospinning and applied this membrane as a separator in LIBs [34]. The obtained para-ANF/PEO (poly(ethylene oxide)) separator exhibited excellent morphology and high porosity, promoting high electrolyte absorption. Therefore, batteries with the para-ANF/PEO separator not only showed superior electrochemical performance but also maintained a tensile strength of 41.52 MPa after heat treatment and a porosity of 75.85%. The thermal stability of the para-ANF/PEO separator was also nearly unchanged after 1 h at 200 °C, showing no thermal shrinkage. Compared to the Celgard 2400 separator, the para-ANF/PEO separator exhibited better electrochemical performance and thermal stability while maintaining good mechanical strength and flexibility for a harmonious balance between electrochemical performance and safety. These studies indicate that separators with comprehensive properties like para-ANF/PEO are promising candidates for high-performance LIBs.

Lin et al. proposed a hydrophilic crosslinking strategy to modify and strengthen porous flame-retardant polyarylene ether nitrile (PEN) polymer membranes to enhance the safety and thermal resistance of lithium batteries [35]. They successfully fabricated PEN@PDA-PEI composite separators with a three-dimensional porous structure and excellent thermal stability, exhibiting no shrinkage at temperatures up to 200 °C. Moreover, the abundant polar groups, such as cyano, amino, and hydroxyl groups, in the composite membrane gave it outstanding electrolyte affinity, with a contact angle of 0° and a very high electrolyte absorption rate that ranged from 400% to 618%. This design approach provided highly reliable separators for lithium batteries with exceptional performance under various conditions. Long et al. developed a high-temperature and fire-resistant nano-$CaCO_3$-based composite membrane (Poly(vinylidene fluoride-hexafluoropropylene), CPVH) that showed almost no shrinkage at 300 °C, exhibiting excellent nonflammability and a low heat release at approximately 11% of that of PP. Additionally, the alkaline nano-$CaCO_3$ could neutralize the inevitable hydrofluoric acid in $LiPF_6$-based electrolytes, ensuring long-term stability of the battery interface layer. The $LiFePO_4$/Li battery with that membrane demonstrated an excellent discharge capacity of 133.6 mAh/g at 0.5 C and maintained a capacity retention rate of 93% after 650 cycles with a Coulombic efficiency of 99.9%. Stringent safety tests also showed that the circuit remained safe and stable at temperatures of 150 °C, and the heat release during thermal runaway was significantly reduced [36].

Zhang et al. used a traditional paper-making method to fabricate a novel paper-based composite separator that consisted of electrochemically friendly cellulose fibers (CF) and thermally stable ANFs, and the ANFs, acting as functional nano-fillers, played a key role in improving the large pores, low mechanical strength, and high flammability of pure CF separators. Specifically, the CF/ANF-20 composite separator with 20 wt% ANFs provided enhanced battery safety performance with narrow micropores, satisfactory tensile strength (33 MPa), excellent thermal resistance (no dimensional shrinkage at up to 200 °C), and flame retardancy [37]. Chen et al. enhanced glass fiber/polyacrylate (GFP) separators by impregnating polyacrylate into glass fibers, followed by a rolling and drying process [38]. Compared to polyolefin (PE) separators, GFP separators demonstrated superior thermal stability, electrolyte wettability, ionic conductivity, and liquid absorption capacity. After annealing at 350 °C for 30 min, the GFP separators exhibited almost no shrinkage. In stringent tests on $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ pouch cells, GFP separators effectively suppressed heat generation within the batteries. Liu et al. used electrospinning to fabricate poly(phenyl benzimidazole) (OPBI) nonwoven fabric separators. The thermal stability, flame retardancy, electrochemical stability, and dendrite growth resistance of the OPBI membrane were studied extensively, and the OPBI membrane exhibited exceptional stability with no shrinkage at 200 °C and weight retention of over 54% at 800 °C without ignition.

Additionally, the electrochemical stability window of the OPBI membrane relative to Li+/Li exceeded 5.75 V, demonstrating superior performance at high temperatures [39].

Wu et al. reported a novel high-performance core-shell PI/SiO_2 inorganic–organic composite separator featuring good flame retardancy, strong mechanical properties, high thermal stability, and excellent ion transfer efficiency. Unlike traditional ceramic-modified separators, the PI/SiO_2 nanofiber separator, formed by a silica nanoshell, exhibited an ultra-high tensile strength of 73.69 MPa, a contact angle of only 6.8°, and exceptional thermal stability at 378 °C [40]. Li et al. prepared a high-safety poly(ethylene-vinyl acetate)/polyetheretherketone/poly(ethylene-co-vinyl acetate) (EVA/PEEK/EVA) composite separator through dip-coating and thermally induced phase separation. Once the temperature exceeded the onset temperature of thermal runaway (80 °C), the EVA layer of the EVA/PEEK/EVA separator transformed into a barrier membrane, cutting off ion transport and preventing battery reactions. Meanwhile, the PEEK substrate maintained dimensional stability even at temperatures as high as 240 °C [41].

Separator modification with new material development is one of the most effective ways to enhance battery safety, but the technical feasibility must be considered in coordination with the cost and reliability of materials. For commercial application, further development of safe, low-cost electrolytes and separators that can be produced in large volumes is required, and it is essential to ensure their reliability under various automotive operating conditions to comprehensively improve battery safety.

3. Early Warning Systems for Safety Risk

In addition to modifying intrinsic battery properties, early warning systems to detect battery failures are also vital in battery safety risk management. It is necessary to first analyze typical battery safety failure scenarios and then to select reasonable warning methods based on these scenarios. The overall development of early warning systems involves several aspects, including the creation of warning models and the use of sensors to monitor specific signals during the failure process.

3.1. Analysis of Battery Failure Scenarios

Common faults in LIBs include sensor failure, connection failure, insulation failure, external short-circuit faults, internal short-circuit faults, overcharging, overdischarging, and thermal faults [42,43]. Of the various possible lithium-ion battery faults, internal short circuits are relatively common, pose a serious threat to battery safety and reliability, and are a leading cause of safety incidents. As a result, the detection of internal short circuits has become a topic of interest worldwide and is a primary focus for early warning methods.

Typical scenarios leading to battery internal short circuits include the following:

(1) Nonstandard operating environments during manufacturing that may lead to foreign objects entering the battery;
(2) External mechanical damage;
(3) Anomalies caused by overcharging and overdischarging;
(4) The impact of environmental conditions, such as extreme temperatures, on battery performance.

Through the development of advanced materials, innovative designs, and integrated monitoring systems, significant progress can be made in risk management to prevent safety incidents, as shown in Figure 2.

Early warning systems are crucial in avoiding catastrophic failure scenarios, and the development of these systems generally includes establishing early warning models and using sensors to monitor battery parameters in real time. Real-time model-based performance modeling enables rapid response and intervention in battery failure scenarios.

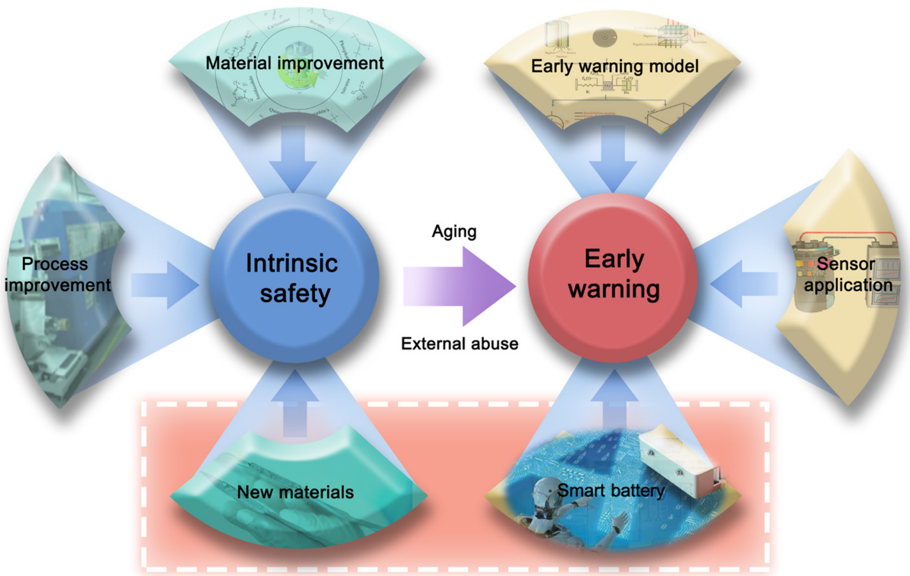

Figure 2. Path to improving battery safety.

3.2. Early Warning Systems for Safety

Ensuring safe and stable operation in energy storage stations and electric vehicles is key to improving battery resistance to thermal runaway risks and avoiding internal short circuits. This requires improvements in battery design and material selection to enhance the battery's intrinsic safety characteristics as well as comprehensive development of battery management and monitoring systems. To guarantee the safe application and use of battery products, research and development in early warning systems to detect thermal runaway in LIBs is particularly important [44]. Early warning systems are vital in the detection of thermal runaway in LIBs to prevent internal faults and identify potential anomalies in advance of catastrophic failures as the early warning system plays a decisive role in taking timely measures to ensure the safe operation of battery systems. Consequently, advancements in lithium-ion battery early warning systems to detect thermal runaway are significantly important in the development of applications such as electric vehicles and energy storage stations. This research not only contributes to enhancing the safety and reliability of these applications but also supports the broader adoption and technological evolution in the field of sustainable energy.

Presently, there are two main approaches to providing early warnings of thermal runaway. One approach is to use a warning model, and the other approach is to use sensors for process monitoring to detect warning signals. Regarding the use of warning models, the development of a model requires a large amount of data analysis, and model generalizability for different types of batteries needs to be strengthened. Regarding the use of sensors, the addition of various external sensors for signal acquisition will increase the overall system cost, and the sensors will have a certain hysteresis. Therefore, adopting built-in sensors to monitor the voltage, temperature, and gas signals of the battery in real time is an important direction for future development.

3.2.1. Early Warning Models

Currently, research on battery risk control primarily focuses on two aspects: the fault early warning capability of the vehicle battery management system (BMS) and model-based analysis for status monitoring and risk prevention. Vehicle BMS fault early warning mainly involves real-time monitoring of basic battery parameters, i.e., voltage, current, and temperature, using on-board sensor information. The BMS compares the real-time values against thresholds for early warning to prevent sudden vehicle failures. Unfortunately, such warnings are only applicable for immediate situations with relatively short warning times. Alternatively, model-based early warning uses historical big data to develop long-term trends and performance models, and this approach employs data processing, data-driven algorithms, and warning models to screen for abnormal batteries and provide fault warnings. This method mainly relies on the deviation of temperature, voltage, and other data, using classification methods to identify abnormal batteries. In some cases, this type of early warning has certain accuracy deviations and specific fault causes are not easily explained, and as a result, researchers are dedicated to optimizing early warning models to improve their accuracy and timeliness. The data-driven, model-based early warning method has become the predominant research focus, aiming to continuously improve warning systems for the more precise and timely detection of battery anomalies and enhance the overall safety of battery systems [45].

In one model-based early warning approach, Jia et al. developed a battery safety risk classification modeling framework based on machine learning algorithms that was capable of accurately and quickly categorizing potential safety risk levels [46]. Using a small portion of cycling data, the framework could identify batteries with defects and internal shorts as well as batteries potentially undergoing thermal runaway. Approximately 3×105 samples, generated based on an electrochemical–mechanical model and covering a wide range of charging states, short-circuit resistances, and charging/discharging rates, served as training and prediction datasets for the machine learning algorithms. The developed classifier exhibited satisfactory performance and robustness, and the study showed that when the internal short-circuit resistance was less than 102 Ω, the model could correctly classify batteries with better than 95% accuracy in just 5 min with a voltage error of less than 0.1 mV. This study presented an effective tool for assessing battery safety via machine learning with rapid and accurate classification of battery safety risks.

In addition to purely data-driven methods, early warning approaches for progressive battery failures based on battery characteristic parameters have become a research focus in recent years [47]. These methods require identifying parameters that adequately represent battery safety characteristics, such as the rate of change in voltage, temperature, capacity decay, expansion force, pressure, and gas composition. Voltage, temperature, capacity decay, and expansion force rates are suitable for early warnings, while pressure and gas composition analysis are applicable for pre-accident alerts. Typically, external sensors monitor these characteristic parameters, but real-time monitoring of internal pressure changes and gas emissions can detect the state of LIBs more accurately and enabling effective accident warnings. This not only provides more evacuation time for people in the near vicinity of the pending accident but also prevents significant economic loss. Wang et al. proposed a safety model for cylindrical LIBs using discrete Fourier transform analysis of experimental data [48]. The model incorporated a battery rupture angle model completely dependent on the load characteristic with minimal impact from charging states under identical load conditions. Additionally, they developed a fault prediction model and validation system for internal short circuits that could, in a timely manner, warn of internal shorts under certain safety thresholds. With further research, safety performance models based on puncture displacement and failure prediction can be combined with other failure signals to provide more reliable battery safety information.

3.2.2. External Sensors Application

During the thermal runaway process in batteries, characteristic gases such as CO, H_2, O_2, and gaseous alkenes are produced, leading to a rapid increase in the concentration of these gases in the surrounding environment. Therefore, gas signals can also serve as early warning signals for battery thermal runaway. Compared to traditional surface temperature sensors, gas sensors have a faster response time and are more suitable as early warning signals for battery thermal runaway, and by monitoring the real-time generation and accumulation of gases inside the battery, the battery's safety health status can be effectively assessed. In the case of LIBs undergoing thermal runaway, monitoring the real-time gas generated during this process is crucial for early warning. By analyzing the composition and timing of the gases produced, the differences in safety among different batteries can be evaluated based on the explosive limits of the gas components, adding a theoretical foundation for using gas sensor technology to detect early signs of thermal runaway. The earliest types of volatile gases released from the electrolyte during thermal runaway can be determined, and this information can be used as the primary basis for selecting sensor types. These studies provide new methods and means to enhance the safety of battery systems based on the real-time physical properties of the battery [49].

In one approach, Jin et al. developed a method based on H_2 detection for the early identification of minute lithium dendrites and verified their approach through overcharge experiments on LFP cells [50]. Subsequent experiments involved placing H_2, CO, CO_2, HCl, HF, and SO_2 gas sensors in a battery compartment, and the results showed that H_2 was detected first, where H_2 capture occurred 639 s earlier than smoke detection and 769 s earlier than fire detection. By taking timely measures, even in the absence of smoke and fire, the growth of lithium dendrites could be completely halted to effectively inhibit the progression of thermal runaway. Song et al. proposed a safety early warning method based on module space air pressure changes for battery thermal runaway [48]. During the battery venting process, the air pressure in the module space changes. Under thermal runaway conditions induced by 13 A (1 C) overcharging, the air pressure in both sealed and ventilated module spaces was 19.3 kPa and 3.05 kPa higher than under normal conditions, respectively, and under thermal runaway conditions caused by 6.5 A (0.5 C) overcharging, the air pressure in the sealed module space increased by 14.43 kPa. Alternatively, the sealed module space air pressure increased by 6.52 kPa under overheating-induced thermal runaway. When an air pressure change signal was detected, immediate measures were taken to effectively prevent the occurrence of thermal runaway, and the average interval between the warning signal and battery thermal runaway was 473 s [51].

While gas sensors hold great potential for early warning in lithium-ion battery thermal runaway, single-gas sensors are prone to environmental interference, posing potential failure risks. A more effective approach involves utilizing a sensor array for tiered monitoring of various gases emitted by LIBs, significantly enhancing system reliability. To effectively detect gases released during thermal runaway and provide early warning of such events, it is essential to select sensors with high target gas selectivity and utilize artificial intelligence (AI) algorithms for feature extraction from sensor array responses to improve target gas recognition. Additionally, the sensor array must meet automotive-grade reliability standards to ensure robust performance in real-world applications. In an alternative to gas sensors, Su et al. proposed a method for safety early warning in MW-level lithium-ion battery stations using venting sound signals, characterized by fast implementation, high sensitivity, and low cost [52]. The method was used in actual energy storage cabins with commercial battery cells and modules during thermal runaway experiments induced by overcharging. The results showed that venting sound signals could accurately and rapidly detect thermal runaway, and timely measures could effectively suppress the development of heat accumulation. Considering the diversity of noise interference, the research team built a noise subtraction method based on spectral subtraction, and to eliminate similar interfering signals after noise reduction, the team utilized an extreme gradient boosting model to build an acoustic signal recognition classifier, achieving an identification accuracy rate of 92.31%.

3.2.3. Application of Embedded Sensors

External sensors, like those outlined above, are physically placed in the external space of the battery module or system, which may induce a certain lag in monitoring danger signals. In contrast, battery operating conditions can be determined in real-time if the internal physical field parameters of the battery can be obtained directly. Currently, internal embedded sensors used to monitor internal lithium-ion battery conditions include stress sensors, temperature sensors, and gas sensors.

Pressure Sensors

Internal pressure sensors in batteries are mainly used to sense changes in internal stress. Battery degradation produces gases, and since the inside of the battery is a closed space, the extent of side reactions can be judged by measuring changes in internal gas pressure. Additionally, thermal runaway in LIBs is almost always accompanied by pressure changes. Gases are released inside the battery due to internal structural changes and side reactions in the early stages of thermal runaway, leading to an increase in internal pressure. Some studies have integrated miniature pressure sensors into batteries to monitor internal gas pressure in real-time, but existing pressure detection devices are generally relatively large, limiting their scope of application. Therefore, there is an urgent need to develop miniaturized and implantable gas pressure detection devices for batteries.

Gas Sensors

The design of gas sensors involves both hardware and software aspects. Minimizing the number of sensors and adopting intelligent measurement and control strategies allows for optimization of the sensor topology array to achieve accurate detection and timely early warning of gases released during lithium-ion battery thermal runaway. The design must consider the sealing of the lithium-ion battery packaging to ensure that electrolyte leakage does not interfere with the warning results. Additionally, attention should be paid to the temperature, humidity, and adaptability of the gas sensors to complex atmospheres to ensure their long-term stable operation in various climatic environments for reliable early warning systems.

Lyu et al. addressed the challenge of measuring internal gases in batteries by placing CH_4, C_2H_4, and CO_2 gas sensors in a sealed can with the batteries. They established a method of monitoring the concentration of gases inside the battery without affecting its operation. By comparing the gas evolution in ternary-graphite and LFP-graphite batteries during cycling, they analyzed the effects of temperature and voltage on internal gas generation and studied the reaction pathways of O_3 during the battery cycle. This study showed that gas sensors could be used to monitor the degradation process of batteries, and embedding gas sensors effectively could detect internal gas evolution behavior and predict thermal runaway [53].

Temperature Sensors

Sensing the internal temperature of batteries is crucial for understanding battery mechanisms, optimizing thermal management, and improving battery performance, lifespan, and safety [54]. Common sensors in the field of temperature sensing include thermocouples, thermal resistors, and fiber optic sensors, and by monitoring temperature, these sensors can also provide information on internal pressure and gas composition.

Micro thermocouples, fiber Bragg gratings (FBG), thin-film thermistors, and resistance temperature detectors (RTDs) are widely utilized for internal battery temperature sensing due to their compact size, and several studies have shown that implanting temperature sensors within the internal cavity of 18,650-type batteries can effectively monitor internal temperatures [55,56]. Unfortunately, sensor integration still faces compatibility challenges with battery manufacturing processes. For cylindrical cells, embedding sensors within internal cavities effectively avoids direct contact with electrode materials and electrolytes and minimizes damage to the battery; however, in the case of prismatic and pouch cells, the main challenge lies in protecting the sensors from electrolyte corrosion while minimizing their impact on electrode materials and battery performance.

Temperature sensors are critical for accurately detecting the internal conditions of LIBs, particularly during thermal runaway events. These sensors provide valuable data for battery management systems to take timely action to prevent battery failure or mitigate the effects of thermal events. Advanced temperature sensors can be embedded within battery cells to provide real-time data on the internal temperature gradients, which are crucial for detecting hotspots that could indicate the onset of thermal runaway, but additional research is needed to overcome challenges associated with embedding temperature sensors in certain types of battery cells.

Integrated Sensor Systems

Individual sensors can provide specific, compartmentalized battery information, but the integration of various sensors into a comprehensive monitoring system provides a more robust approach to battery safety. By combining data from temperature, pressure, and gas sensors, an integrated sensor system can offer a more accurate and timely warning of potential battery failures [57]. This system can analyze the battery's condition in real-time and predict potential safety issues before they become critical. The development of such integrated systems is a key area of research in battery technology, aimed at enhancing the overall safety and reliability of LIBs.

4. Conclusions

In this paper, we presented an in-depth investigation of safety risk control and early warning methods for lithium-ion power batteries. The increasing demand for electric vehicles and the widespread application of LIBs highlight the importance of addressing safety concerns associated with these batteries. Through the development of advanced materials, innovative designs, and integrated monitoring systems, significant progress can be made in enhancing the intrinsic safety of LIBs and providing effective early warning systems to prevent safety incidents. Ongoing research and development in this field are critical to ensure safe and sustainable growth of the lithium-ion battery industry, especially considering the global shift toward green energy and electric vehicles.

In terms of future work, we propose the following subject areas to continue enhancing lithium-ion battery safety:

(1) Development of thermal runaway inhibition materials: Investigate the internal mechanisms of thermal runaway in battery systems and develop materials capable of suppressing such events. This includes the integration of safety mechanisms to prevent overcharging and short-circuiting, culminating in the creation of novel battery systems that address inherent issues of thermal instability and combustible components in existing battery materials.
(2) Electrical–thermal–pressure–gas coupled safety warning model: Construct a comprehensive warning model that integrates electrical, thermal, pressure, and gas dynamics. Develop an array-type multicore chip warning module to enhance the precision, timeliness, and reliability of safety alerts, addressing the limitations of delay, false alarms, and sensitivity in single-signal warning systems.
(3) Big data and AI integration in battery management: Utilize big data and artificial intelligence to refine commercial battery management systems and supplement these systems with sensor arrays. Focus on building a comprehensive database delineating normal and thermal runaway battery states. Develop neural-network-based analytical models for more accurate recognition of battery states and predictive analysis of potential future battery conditions.
(4) Smart batteries with embedded sensors: Fabricate intelligent battery systems equipped with embedded sensors for real-time monitoring of internal resistance, temperature, and gas emission. Incorporate these insights into the warning model to facilitate direct and early detection of potential safety hazards.

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