Li-ion Battery Failure Warning Methods for Energy-storage Systems

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Abstract: Energy-storage technologies based on lithium-ion batteries are advancing rapidly. However, the occurrence of thermal runaway in batteries under extreme operating conditions poses serious safety concerns and potentially leads to severe accidents. To address the detection and early warning of battery thermal runaway faults, this study conducted a comprehensive review of recent advances in lithium battery fault monitoring and early warning in energy-storage systems from various physical perspectives. The focus was electrical, thermal, acoustic, and mechanical aspects, which provide effective insights for energy-storage system safety enhancement.

Keywords: Lithium-ion batteries, energy-storage systems, thermal runaway, characteristic signals, fault warning

1 Introduction

Electrochemical energy storage possesses the advantages of large capacity and fast response, making it flexible for applications in the generation, transmission, distribution, and consumption of power systems. As a crucial technology in electrochemical energy storage, lithium-ion batteries (LIBs) play a decisive role in determining the energy-storage quality. However, current limitations in energy-storage development mainly stem from the insufficient resolution of safety issues associated with LIBs. Globally, battery-safety accidents have occurred repeatedly, and countries with large-scale energy-storage stations, such as the United States, the United Kingdom, Japan, and Republic of Korea, have experienced incidents of fires at energy-storage stations. In recent years, Republic of Korea has witnessed more than 30 incidents of lithium-ion battery grid energy-storage accidents. The overcharging-induced thermal runaway characteristic of lithium batteries is the main cause of accidents, such as fires and explosions, in energy-storage systems [1].

Whether in an energy-storage power station or a battery module, batteries are placed in a closed space that stores a large amount of energy. During charging and discharging, electrochemical reactions release heat, which poses inherent safety risks and potential thermal runaway hazards. In particular, in energy-storage power stations, the number of individual cells in a storage compartment can reach tens of thousands. If a single cell undergoes thermal runaway, it can trigger a chain reaction with the surrounding cells, leading to a fire or explosion. Therefore, the early detection of thermal runaway in LIBs is of significant research importance.

The primary component responsible for minimizing operational risks in lithium-ion battery packs is the battery management system (BMS) [2]. A typical BMS includes battery current, voltage, and temperature measurement [3]. However, as demonstrated by historical catastrophic incidents, the currently used BMSs are not sufficiently reliable for detecting battery faults. In their review of lithium-ion battery failure mechanisms, Wang et al. [4] identified a BMS fault that occurred in 2010. The main reason of thermal runaway is battery overcharging owing to BMS failures, which are applicable to electric scooters, electric vehicles, and aircrafts. Overheating and short circuits can also cause battery thermal runaway, as well.

During the thermal runaway process, a series of chemical reactions occur inside the battery. The

Manuscript received July 28, 2023; revised September 6, 2023; accepted October 1, 2023. Date of publication March 31, 2024; date of current version October 28, 2023.
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Digital Object Identifier: 10.23919/CJEE.2023.000037

detection of characteristic signals during the reaction process has been extensively studied and effectively utilized as a basis for the early warning of thermal runaway. As the internal temperature of the battery increases, various microscale phenomena occur in the early stages of thermal runaway, such as decomposition of the solid-electrolyte interphase (SEI) passivation layer, melting of the separator, contact between the positive and negative electrodes and the electrolyte, and contact between the electrodes and separator. Changes in the electrochemical parameters, such as the production of gases, internal gas pressure, and internal impedance, are accompanied by chemical reactions. Monitoring gases, gas pressure, and electrical parameters can enable early detection of thermal runaway.

Owing to the closed nature of internal changes during thermal runaway, the direct observation of internal battery materials is not feasible. Therefore, special equipment can be used to monitor the characteristics of internal battery materials. Based on the external structure of a lithium-ion battery, the opening and closing of safety valves are important indicators of internal faults. During process of thermal runaway (TR), the battery-safety valve opens when the internal pressure becomes too high. Sound, as an important signal of safety valve opening, can be captured and used for the monitoring and early warning of thermal runaway.

This article introduces the capture and detection of characteristic signals at different stages of thermal runaway and summarizes various physical dimensions, including electrical, thermal, acoustic, and mechanical dimensions. By comparing and combining various methods, this study provides insights into early warning measures for lithium-ion battery thermal runaway.

2 Characteristic signals of thermal runaway

During thermal runaway in LIBs, various characteristic signals can be observed, indicating the occurrence and progression of the thermal runaway events. These signals are crucial for the early detection and warning of thermal runaway.

2.1 Types of characteristic signals

During the thermal runaway process of a battery, the temperature increase and gas generation within the battery are prominent characteristic signals that occur in various types of faults. In the case of thermal runaway caused by overcharging, the generation of heat primarily stems from Ohmic reactions and side reactions. Belov et al. [5] conducted differential scanning calorimetry and scanning electron microscopy tests on different components recovered from overcharged batteries, and found that thermal runaway occurs when the generated heat does not equal the dissipated heat. Moreover, they observed that the reaction time for thermal runaway was shorter and substantial heat was produced at higher overcharge rates. Wang et al. [6] further discovered that in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-based Li-ion batteries, there is a significant increase in the temperature and heat generation of the cathode during normal charging because of reactions involving the electrolyte and evolved oxygen. This experimental phenomenon plays a crucial role in understanding the thermal behavior of lithium batteries during overcharge tests. The generation of gases, such as CO_2, H_2, and CO, is also a noticeable phenomenon. Ohsaki et al. [7] conducted experiments and found that multiple gases were released during overcharge reactions, with the quantity of released gases directly proportional to the increase in battery temperature. The release of gases increases rapidly at the end of the overcharging process, which is particularly evident from the increase in CO_2 at the cathode.

In the case of thermal runaway during overdischarge, Ouyang et al. [8] performed tests using a cone calorimeter and observed a noticeable temperature increase during battery discharge. The discharge current can accelerate the temperature rise, leading to early stage thermal runaway. However, the ability of overdischarge to reach thermal runaway is weaker than that of overcharging. Wang et al. [9] observed the discharge behavior of Li batteries in an adiabatic environment and found that higher overdischarge rates resulted in a faster temperature increase within the battery.

Changes in the internal physical parameters of the battery occur during thermal runaway. The BMS is responsible for determining the battery-safety status by monitoring data such as surface temperature, voltage, current, and other parameters during battery operation [10]. The BMS primarily relies on the real-time monitoring of current, voltage, temperature, and other surface parameters to determine whether the battery module is operating under normal conditions. Changes in impedance, as a physical parameter, are particularly evident in thermal abuse-induced local overheating and subsequent thermal runaway. Loose battery connectors can increase battery resistance. When a large current flows through the increased resistance, it generates a significant amount of heat, leading to local overheating and subsequent thermal runaway. Increasing the ambient temperature of the battery affects the internal temperature, eventually resulting in thermal runaway. This test is commonly employed in thermal abuse tests conducted before shipment of power batteries. Maleki et al. [11] investigated the effects of discharging commercial LIBs initially below 1.5 V, at different voltage levels. They found that discharging the batteries to 0.5 V has a minimal impact on thermal stability, overcharging performance, and AC impedance, but leads to significant expansion of the battery. Discharging the batteries to 0.0 V increases the thickness and AC impedance by 70% and 250% of their initial values, respectively, which demonstrates the impedance changes during the thermal runaway process.

2.2 Characteristic signal in different stage

The appearances of the characteristic signals differed. Physical parameters, such as battery voltage, current, and impedance, serve as continuous signals that can be continuously monitored and changed during the thermal runaway process. However, the occurrence of noncontinuous signals, such as gas, sound, and pressure, requires certain conditions to be fulfilled, and the signals must be captured promptly after they occur. The specific signature signals are shown in Fig. 1. The following describes the timing of the appearance of noncontinuous characteristic signals in the thermal runaway process is shown in Fig. 2.

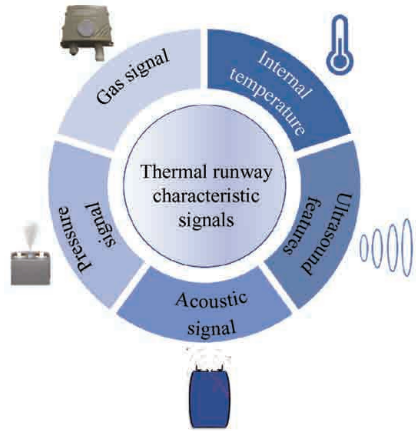

Fig. 1 Thermal runaway signature signal classification

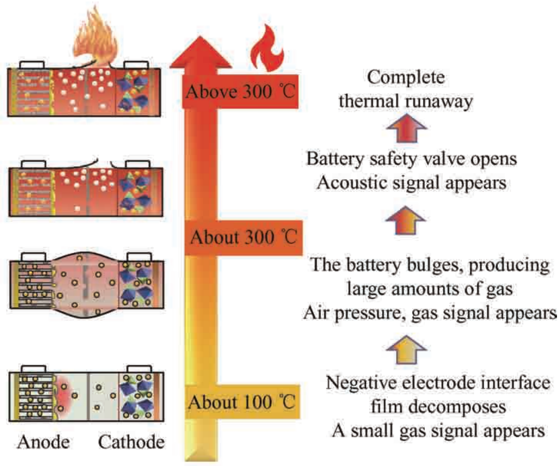

Fig. 2 Characteristic signal phase diagram

2.2.1 Stage 1: Early stage of thermal runaway

A small gas signal was observed during the early stages of thermal runaway, as the internal temperature of the battery rapidly increased to approximately 100 ℃. The SEI layer on the negative electrode surface of a battery undergoes decomposition reactions owing to an increase in temperature. This leads to a further increase in the temperature, and the decomposition of the SEI layer causes a loss in its protective properties. When the internal temperature exceeded 100 ℃, chemical reactions occurred gradually, resulting in the generation of gases such as CO_2. When the internal temperature of the battery rises to approximately 150 ℃, the polyethylene (PE) and polypropylene (PP) separators of the battery melt because of the high temperature, and the battery electrolyte continuously reacts with the positive electrode. As the temperature increases, the battery separators continue to melt and come into contact with the positive and negative electrodes, causing short circuits in the battery. This releases a large amount of energy, leading to a rapid increase in the temperature. The battery electrolyte and other organic solvents inside the battery undergo decomposition and exothermic chemical reactions, releasing gases, such as CO_2, HF, and H_2.

2.2.2 Stage 2: Battery swelling

Numerous gas- and pressure-change signals were observed. When the temperature rises to approximately 300 ℃, the lithium inside the lithium-ion battery undergoes chemical reactions with the electrolyte and organic solvents, resulting in the generation of a large number of flammable gases, such as methane and ethane. Because the battery itself forms a sealed space, gases cannot diffuse rapidly. At this stage, the battery swells, and at the same time gases accumulate significantly inside the battery, along with changes in pressure.

2.2.3 Stage 3: Burning and explosion

Sound signals appear. At this stage, if the battery is still in a charging state, the positive electrode of the battery continues to undergo intense oxidation-reduction reactions with the battery electrolyte. This process rapidly increases battery temperature and releases large amounts of toxic gases. Before this, the battery-safety valve opens because of the inability of the battery to withstand the internal pressure. Currently, most energy-storage facilities use storage compartments with densely arranged battery modules. Battery modules are prone to affect other battery modules because they can easily run away thermally owing to their high-temperature state. This results in a chain reaction that eventually leads to open flames and combustion, resulting in an explosion.

3 Thermal runaway warning technology based on characteristic signals

3.1 Internal temperature-based warning method

The internal temperature of a battery is the most direct and effective indicator of its safety. However, there is a significant temperature difference of up to 20 ℃ between the inside and outside of the battery module. Therefore, the surface temperature of the battery is insufficient to fully indicate its internal state. Measuring the internal temperature of a battery allows an accurate assessment of its state.

There are two primary methods for thermal runaway warning based on internal temperature: embedded sensor temperature measurements and impedance-temperature correlation measurements. Ganguli et al. [12] demonstrated the possibility of real-time monitoring of internal operating states of LIBs using embedded sensors. Raghavan et al. [13] embedded a Bragg fiber-optic sensor inside a lithium-ion battery to sense its internal operating state, as shown in Fig. 3. When the operating state of the battery changes, data such as the refractive index and wavelength of the light received by the fiber-optic sensor also change. By establishing a correlation between internal parameters, such as stress, temperature, and the wavelength of the refracted light received by the fiber-optic sensor, combined with the BMS, it is possible to more accurately monitor the real-time internal temperature and other performance indicators of the battery, enabling timely and effective thermal runaway warning.

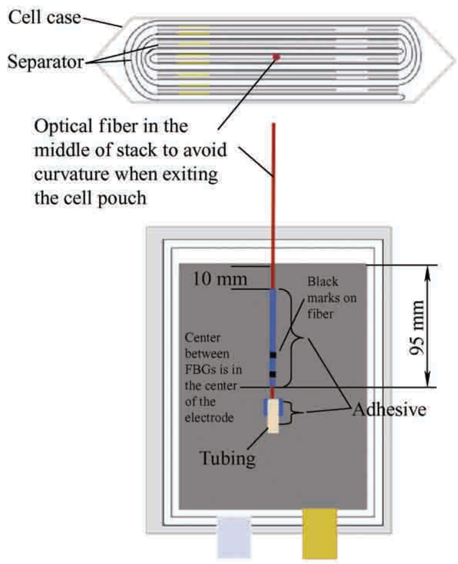

Fig. 3 Embedded fiber-optic sensor [13]

However, the embedded sensor method requires changes in the battery structure, making it difficult to match the existing battery production processes and challenging to promote practical applications.

Another early thermal runaway warning method based on impedance phase shift is used to monitor the internal temperature of the battery. This method effectively overcomes the limitations of embedded sensors. Srinivasan et al. [14] found a strong correlation between the internal impedance phase shift and internal temperature of the battery during its operation. They used a Solartron SI1287 electrochemical impedance analyzer and a Solartron-SI1250 frequency response analyzer to detect the internal impedance of the battery in real-time and measured the impedance of the lithium-ion battery under different charge-discharge rates and states of charge. The impedance phase shift and surface temperature variation curves of the lithium-ion battery are shown in Fig. 4. By correlating the internal impedance phase shift with the internal temperature of the battery, they found that in the early stages of thermal runaway, there was no significant change in the surface temperature, but the internal impedance phase shift exhibited a noticeable anomaly. This demonstrates the effectiveness of monitoring the internal impedance phase shift for early warning of thermal runaway in LIBs. They proposed integrating an internal impedance phase-shift monitoring device into an existing BMS to obtain a thermal runaway warning for LIBs. However, using the impedance phase shift to determine the thermal runaway state of a battery requires precise measuring instruments, which results in higher equipment costs.

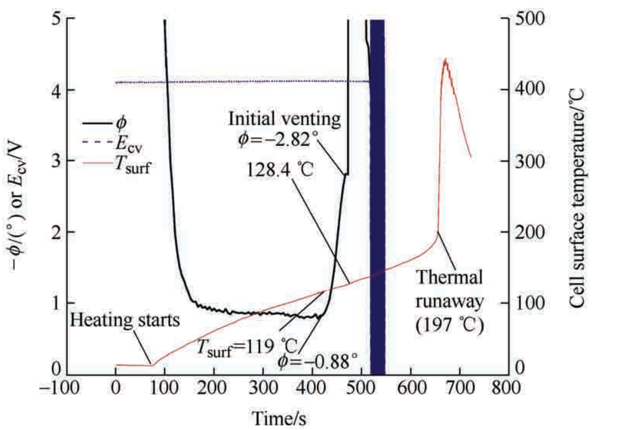

Fig. 4 Internal impedance phase shift and surface of lithium-ion batteries during thermal runaway temperature change curve [14]

Lyu et al. [15] discovered that when a battery is initially overcharged, the slope of the dynamic impedance in the frequency range of 30-90 Hz changes from negative to positive. The temperature-impedance early warning implementation scheme is shown in Fig. 5, which provides a theoretical explanation for this phenomenon. By observing the change in the slope, it is possible to successfully prevent thermal runaway accidents by interrupting the charging process, with an early warning time of 580 s ahead of the occurrence of thermal runaway. Furthermore, the identification of battery thermal runaway based on this characteristic does not require complex mathematical models or parameters, which makes it suitable for large-scale deployment. The team established an online impedance-internal temperature prediction model to achieve internal temperature sensing based on single-frequency impedance. They also developed a battery overcharge thermal runaway early warning device based on dynamic impedance measurements, enabling low-cost and accurate early warning of thermal runaway in LIBs, which demonstrates high practicality.

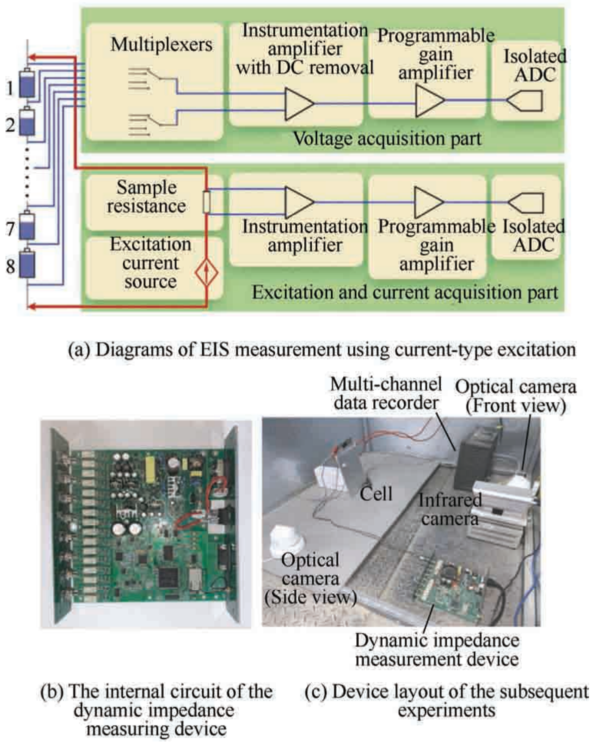

Fig. 5 Temperature-impedance early warning implementation scheme [15]

3.2 Ultrasonic signals-based warning method

The propagation of sound waves in batteries varies according to the properties of the battery material. Ultrasonic waves can accurately monitor the material performance, internal damage, and structural integrity in real-time when propagated through a test object.

Therefore, ultrasonic inspection can detect potential changes in the material properties inside a battery, thereby providing early indications of faults. This has recently been shown to be an additional technique for battery measurements [16-19]. The corresponding models established for ultrasonic technology reflect the relationship between material changes in cyclic engineering and ultrasonic wave reflections, enabling state of charge (SOC) evaluation through sound wave propagation time [20]. Thus, ultrasonic technology can be used for SOC and state of health assessments in LIBs [17, 21-22]. Moreover, they play a significant role in detecting battery-safety faults.

Owing to the unreliability of current BMS for detecting and warning battery faults, Wu et al. [23] utilized ultrasonic sensing data for data fusion analysis to construct a new battery health indicator, thereby expanding the traditional BMS functionality to improve early fault-warning reliability. This study proposes a new battery failure indicator, the ultrasonic time of flight, and verifies its correlation with battery expansion. By combining temperature and ultrasonic sensor data, they established a health indicator based on data fusion, referred to as Mahalanobis Distance (MD). The implementation of this approach is illustrated in Fig. 6. The experimental results demonstrate that the MD value gradually increases with battery aging and can directly determine battery degradation, offering the advantages of earlier catastrophic fault warning and extended fault-prevention time. Integrating the MD indicator into an existing BMS enables real-time monitoring of battery status. However, further research is required on batteries with different chemical compositions, sizes, and shapes.

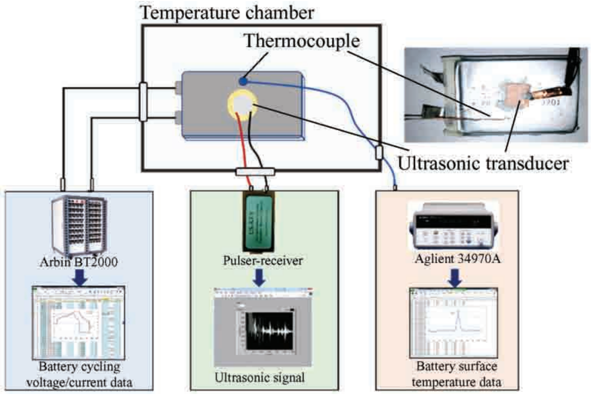

Fig. 6 Ultrasound signal battery failure warning [23]

Appleberry et al. [24] directly detected the battery status using ultrasonic waves to monitor changes in the properties of battery components. This study performed cyclic constant current and voltage overcharging and extracted ultrasonic signal features. Two conditions for identifying faults were defined: a warning at the onset of excessive charging, and an emergency stop (E-stop) that immediately ceases battery usage. By utilizing the changes in the ultrasonic signal features, consistent warning and stop classifications were applied to all the failure experiments. On average, a warning notification was issued after 15% of the overcharging time, and an E-stop was triggered after 35% of the total overcharging time before the occurrence of a fault. Further testing demonstrates that responding to intermediate warning notifications before an immediate E-stop can prevent thermal runaway. The experimental data demonstrated the effectiveness of the ultrasonic feature-based warning system. However, for this technology to be applied economically in practice, further considerations must be given to sensor design.

3.3 Gases signal-based warning method

In the early stages of thermal runaway in LIBs, changes in parameters such as voltage and current were relatively slow, and the increase in battery temperature was not significant. However, during thermal runaway, the internal electrochemical reactions of LIBs release a large amount of gas. Therefore, placing gas sensors around the energy-storage battery module to detect released gases is an effective means of providing early warning [25]. The types and concentrations of gases produced at different stages of battery thermal runaway vary. Fernandes et al. [26] conducted overcharging thermal runaway experiments on a lithium-iron-phosphate battery module using high-precision gas-detection devices. They monitored the temperature changes and gas diffusion behavior of the battery module from normal operation to the occurrence of thermal runaway. After multiple experiments, they found that large amounts of carbon dioxide (CO_2), carbon monoxide (CO), ethylene carbonate (EMC), dimethyl carbonate (DMC), methane (CH_4), and other gases were generated in the early stages of battery module thermal runaway. During this time, the battery module casing remained intact and there was no noticeable increase in the battery temperature. After a certain period, the battery casing begins to rupture and the electrochemical reactions of the battery generate a large amount of gas, resulting in an increased gas generation rate and a sharp rise in the temperature of the battery module. Gas detectors detect harmful gases, such as dimethyl ether (CH_3OCH_3), methyl formate ($HCOOCH_3$), and ethylene (C_2H_4). Tab. 1 presents the results of the analysis.

Tab. 1 Battery failure gas composition

References	Failure mode	Gas composition
Ohsaki et al. [7] (2005)	Overcharge	CO_2-CO-CH_4-C_2H_4-C_2H_6-H_2
Doughty et al. [27] (2005)	Thermal (ARC)	CO_2-CO-CH_4-C_2H_4-C_2H_5F-C_3H_6-C_3H_8-H_2
Roth [28] (2008)	Thermal (ARC)	CO_2-CO-CH_4-C_2H_4-C_2H_5F-C_2H_6-C_3H_6-C_3H_8-C_5H_{12}-H_2
Somandepalli et al. [29] (2014)	Overcharge	CO_2-CO-CH_4-C_2H_4-C_2H_6-C_3H_6-C_3H_8-C_4H_8-C_4H_{10}-C_5H_{12}-C_6H_6-C_6H_{14}-C_7H_8-C_8H_{10}-H_2
Golubkov et al. [30] (2014)	Overheated	CO_2-CO-CH_4-C_2H_4-C_2H_6-H_2
Golubkov et al. [31] (2015)	Overheated	CO_2-CO-CH_4-C_2H_4-C_2H_6-H_2
Zheng et al. [32] (2016)	Overdischarge	CO-CH_4-C_2H_2-C_2H_4-C_2H_6-C_3H_8-H_2
Lammer et al. [33] (2017)	Overheated	CO_2-CO-CH_4-C_2H_2-C_2H_4-C_2H_6-H_2
Qin et al. [34] (2022)	Overheated	CO_2-CO-CH_4-C_2H_4-C_2H_6-H_2
Yang et al. [35] (2022)	Overheated	CO_2-CO-CH_4-C_2H_2-C_2H_4-C_2H_6-H_2
…	…	…

Jin et al. [36] studied a $LiFePO_4$ battery module used in grid energy storage. They found that the concentration of hydrogen gas varied most sensitively during the battery thermal runaway process, indicating its potential as an early warning gas for battery thermal runaway. Experimental tests on battery-overcharge-induced thermal runaway were conducted in an actual energy-storage chamber. An indoor experimental platform was set up with gas detectors for in situ detection and gas chromatography analysis of the battery thermal runaway process. The results showed that lithium dendrites and hydrogen gas were generated in the early stages of battery overcharging, revealing the mechanism of hydrogen gas generation during battery TR, as illustrated in Fig. 7. Based on these findings, a novel method for lithium dendrite growth detection and early warning of battery thermal runaway is proposed. This method can be applied to ultra-early safety warnings of LIBs.

Based on this research, the team introduced a power battery early safety-warning device based on hydrogen gas detection. The hydrogen gas sensors were placed inside a lithium-ion battery module chamber and connected to a data processing unit. The device determines the normal operating state of the battery based on the hydrogen gas concentration inside the chamber, enabling early safety warnings for battery thermal runaway and preventing accidents, such as fires and explosions.

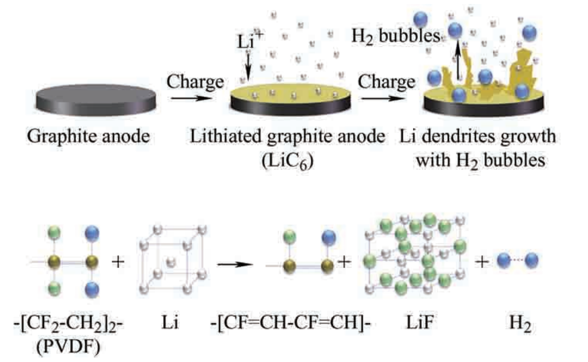

Fig. 7 Mechanism of H_2 generation inside the battery [36]

Owing to the complex diffusion behavior of characteristic gases caused by the dense stacking of cooling systems and batteries in energy-storage systems, the installation position of the detectors significantly affects the gas-detection time. Building on the aforementioned research, Shi et al. [37] further optimized the installation position of the sensors. Through experiments and simulations of the gas diffusion behavior, it was found that sensors installed at the top of the energy-storage chamber could effectively issue warnings 145 s before thermal runaway. Optimal monitoring was achieved by installing 3-5 gas sensors inside the chamber. In addition, the detection time of the three sensors was 116.43 s earlier than that of the single sensor. The H_2 signal warning intentions are illustrated in Fig. 8. These experimental results provide valuable guidance for the timeliness of gas warnings for thermal runaway.

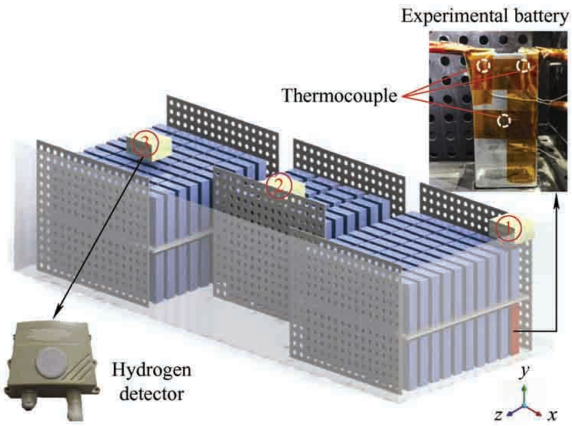

Fig. 8 H_2 gas signal warning intention [37]

CO_2 accounts for the largest proportion of the gas released during early thermal runaway, as confirmed in previous studies [26, 33, 38]. The presence of CO_2 has been observed under various battery abuse conditions, making it suitable for early safety warnings of thermal runaway. Cai et al. [39] compared different types of sensors and selected a Non Dispersive InfraRed sensor for CO_2 detection. Overcharging experiments demonstrated that the sensor emitted a rapid and clear signal upon gas release, proving the effectiveness of the CO_2 warning system for battery thermal runaway. Furthermore, the article indicates that in battery failures involving gas release, the gas detection and warning system based on carbon dioxide does not require specific positioning of the faulty battery. This was sufficient to install a gas sensor at the exhaust outlet to ensure its effectiveness.

3.4 Pressure signal-based warning method

Monitoring the internal pressure of the battery can also serve as a basis for identifying thermal runaway. Typically, an internal pressure sensor is embedded in a battery module to monitor its internal pressure. The battery pack utilizes a vent valve on the battery casing to maintain internal and external pressure balance. Under normal operating conditions, the internal pressure of the battery should be consistent with atmospheric pressure. However, during thermal runaway, various chemical reactions, such as SEI decomposition [40], negative electrode-electrolyte reactions [41], positive electrode-electrolyte reactions [42], separator melting [43], and electrolyte decomposition, generate a significant amount of gas and heat, leading to battery expansion [44] and a rapid increase in the internal pressure exceeding atmospheric pressure. Changes in the internal pressure detected by the pressure sensor can serve as an early warning signal for thermal runaway [45].

Experimental studies have shown that the false negative rate of thermal runaway warnings based on internal pressure is extremely low. When the pressure sensor detects a rapid increase in the internal pressure, it is highly likely that thermal runaway has occurred. Koch et al. [25] used different types of sensors to detect thermal runaway in pouch-type LIBs. The experimental results showed that the pressure sensor detected thermal runaway 5 s earlier than the temperature sensor. Chen et al. [46] investigated the thermal runaway process induced by the overheating of 18650 LIBs. They found that pressure monitoring effectively warned of thermal runaway because the pressure release exhibited strong oscillations.

However, this method has a relatively high false-positive rate. This is because the individual battery capacity, volume, and other factors may limit the amount of gas produced during thermal runaway, which may not reach the predetermined pressure threshold required to trigger a thermal runaway warning. Additionally, the peak time of the pressure changes caused by thermal runaway in batteries is short, typically approximately 100 ms. Subsequently, the rapid increase in pressure leads to the opening of the pressure relief valves, causing the internal pressure of the battery to rapidly decrease. Depending on factors such as the sampling frequency of the pressure sensor, it is not possible to detect rapid changes in the internal pressure in a timely manner, thereby failing to trigger a warning [47].

The pressure signals can also be detected in the environment surrounding the battery. In a battery module, when individual cells release gas owing to overcharging and overheating, there are noticeable changes in the internal pressure of the module. As shown in Fig. 9. Song et al. [48] conducted experiments in sealed and ventilated modules to verify the effectiveness of pressure-change signals for early warnings. The experimental results showed that under the conditions of 13 A (1*C*) overcharge-induced thermal runaway, the pressure in the sealed and ventilated module spaces increased by 19.3 hPa and 3.05 hPa, respectively, compared to normal conditions. Under the conditions of 6.5 A (0.5*C*) overcharge-induced thermal runaway, the pressure in the sealed module space increased by 14.43 hPa. Under conditions of overheating-induced thermal runaway, the pressure in the sealed module space increased by 6.52 hPa. Upon detecting the pressure-change signal, immediate measures, such as stopping charging, were taken to effectively prevent battery thermal runaway. The average time interval from the alarm signal to the battery thermal runaway was 473 s.

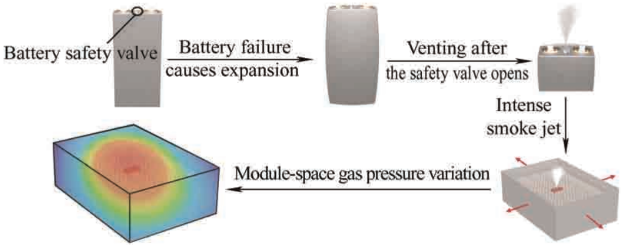

Fig. 9 Module air pressure change during thermal runaway [48]

Pressure-based warning methods at the module level offer the advantages of cost-effectiveness and do not require complex models. In addition, they enable simultaneous safety warnings for multiple individual battery cells within a module, thereby making them suitable for scalable applications. However, it is important to note that this method is limited to battery modules.

3.5 Acoustic signal-based warning method

Utilizing acoustic signals from battery exhaust for thermal runaway early warning is cutting-edge academic research that has not been fully industrialized. Su et al. [49] proposed a method for the early warning of TR in megawatt-scale energy-storage systems based on acoustic signals. To validate the effectiveness of this method, they conducted overcharge-induced thermal runaway experiments using commercial battery cells and modules in an actual energy-storage chamber. Considering the presence of noise in the operational environment of the energy-storage chamber, a spectral subtraction method was employed to denoise the acoustic signals from the battery exhaust. The results showed that spectral subtraction effectively suppressed noise while preserving the target signal.

By extracting Mel Frequency Cepstral Coefficients (MFCC) as features from the signals, a 40-dimensional MFCC feature coefficient matrix was obtained, forming an effective feature set for identification. Based on the extreme Gradient Boosting (XGBoost) model, the team constructed a pattern recognition classifier for exhaust sound signals, achieving an accuracy of 92.31% with a small amount of data, thereby validating the effectiveness of the XGBoost model for sound signal recognition. After capturing the battery exhaust sound signal, the system promptly cuts off the power, effectively preventing the spread of thermal runaway. Acoustic signals are easy to detect, and can be used in a wide range of applications. This method offers advantages, such as fast implementation, high sensitivity, and low cost. However, it currently only enables the recognition of battery exhaust sound signals and cannot precisely locate faulty cells that cause thermal runaway.

Based on the aforementioned achievements, Lyu et al. [50] proposed a battery fault alarm and localization method based on acoustic signals, as shown in Fig. 10, which depicts the schematic of an acoustic sensor warning. This method requires the installation of only four acoustic sensors at the corners of an energy-storage chamber. When a battery failure occurs, acoustic sensors capture the exhaust sound signal and calculate the spatial position of the battery.

The results demonstrate that the combination of the basic frequency-domain-cross-correlation algorithm and spatial modeling algorithm achieves satisfactory localization accuracy, with a maximum localization error of 0.1 m. Considering that the effective range of firefighting facilities is significantly larger than 0.1 m, such localization error is acceptable. Furthermore, the team proposed a wavelet transform-based-anti-misjudgment method to ensure the reliability of fault warning and localization, thereby providing a nonintrusive, timely, and effective solution for ensuring the safety of battery energy-storage systems.

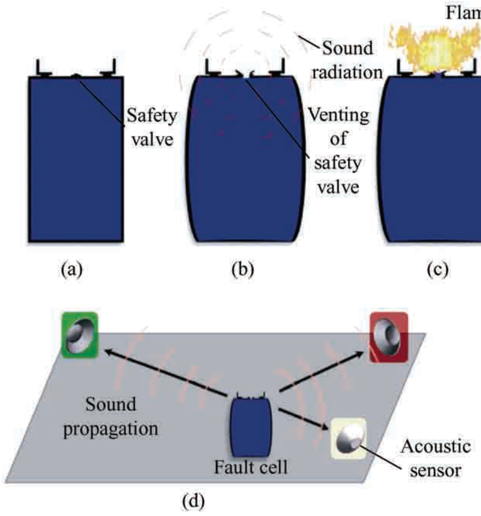

Fig. 10 Acoustic signal warning diagram [50]

4 Comparative analysis

4.1 Same-dimensional analysis

The characteristic signals summarized in this study include internal temperature, ultrasonic features, gas features, pressure signals, and acoustic signals. In addition, common battery fault detection methods include BMS warnings and surface temperature-based warnings.

In a BMS, a voltage detection method is commonly used to record the real-time voltage of each battery cell. Significant voltage changes occur during battery faults such as overcharging, which leads to voltages exceeding the normal range, over-discharging, and internal short circuits. This in turn causes the voltage to drop below the normal range. When the voltage exceeds the normal range, a battery fault warning is issued [51]. However, this method relies on monitoring all cells in the compartment, which complicates wiring and increases the potential risks.

Surface temperature detection senses the incremental surface temperature of the battery cells during a fault [52]. It relies on temperature sensors installed on the surfaces of all the battery cells. However, this method involves complex wiring and is expensive, limiting its applicability. In addition, owing to thermal conduction, the surface temperature lags behind the internal temperature [14]. After a battery fault occurs for a certain duration, the surface temperature increases, thereby reducing the effectiveness of the warning system. Compared with the surface-mounted temperature sensor method mentioned above, infrared cameras do not require complex wiring. However, infrared cameras can only observe the temperature on the surface of the modules and cannot promptly detect anomalies inside the modules. Moreover, the field of view of the infrared cameras is limited. Having too few infrared cameras hinders effective warnings and significantly increases the cost of the warning systems.

In internal temperature-based predictive methods, the use of embedded sensors [13] allows for precise temperature measurements within the battery. However, this approach requires alterations to the internal structure of the battery, which poses a challenge when applied to commercial batteries. In addition, the application of an impedance phase shift [14] requires precise measurement equipment, which incurs relatively high costs. In contrast, the transition in the slope of the dynamic impedance [15] allows ease of monitoring and lowers associated costs, making it a favorable temperature-based predictive method.

Ultrasonic signal-based predictive methods detect the status of batteries by monitoring subtle internal changes. The application of this method entails higher costs, making it more suitable for microlevel experimental validation than for practical production applications.

In gas-signal-based detection, both H_2 and CO_2 gas detection can be used to provide an early warning of thermal runaway events. H_2 can propagate more quickly and easily in the surrounding air because of its tendency to be generated earlier in the event of thermal runaway and its lower molecular mass. However, the effectiveness of the warning system is influenced by the sensor placement. However, for effective detection, CO_2 warning systems require sensors to be fixed at the exhaust outlet.

In pressure-signal-based predictive methods, pressure monitoring points can be categorized into internal and battery module pressures, with distinctions between their respective application scenarios.

4.2 Multidimensional comparative analysis

Owing to the variations in sensing principles and hardware design among warning methods, it is possible to analyze these methods in terms of warning costs and the difficulty of large-scale equipment deployment. Acoustic signal warning methods offer advantages, such as low warning costs and simple equipment installation, making them highly valuable for practical applications. Conversely, ultrasound characteristic signal warning devices may present challenges in terms of scalability for online detection, coupled with higher warning costs, rendering them less suitable for production applications.

In addition, gas signal, pressure signal, and internal temperature warning methods share the advantages of being cost-effective and suitable for large-scale applications. Gas signal warning methods were applied at this scale.

Regarding the lifespan of these warning methods, internal temperature warnings based on optical fiber sensors and pressure warnings may have limited lifespans, because they require embedding within the battery. After an individual battery experiences a thermal runaway warning, there is a possibility of sensor hardware failure. By contrast, sensing methods that do not require embedding within the battery and are suitable for large-scale applications, such as acoustic signals, gas signals, and internal temperature warnings based on battery impedance, tend to have longer lifespans.

This paper introduces fault detection methods based on characteristic signals, which start from the essence of thermal runaway faults in batteries, and extracts and utilizes characteristic signals based on observed phenomena during the process. A comparison of engineering applications is shown in Fig. 11 and Fig. 12. However, different characteristic signals have their own advantages and limitations, as listed in Tab. 2. In practical production processes, a combination of multiple characteristic signals can be comprehensively employed for multi-angle fault warning.

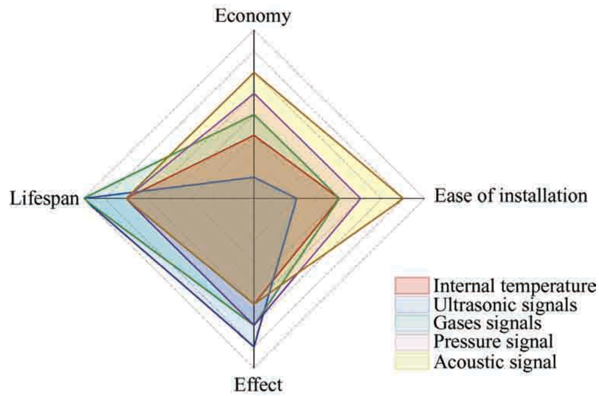

Fig. 11 Comparison of engineering applications

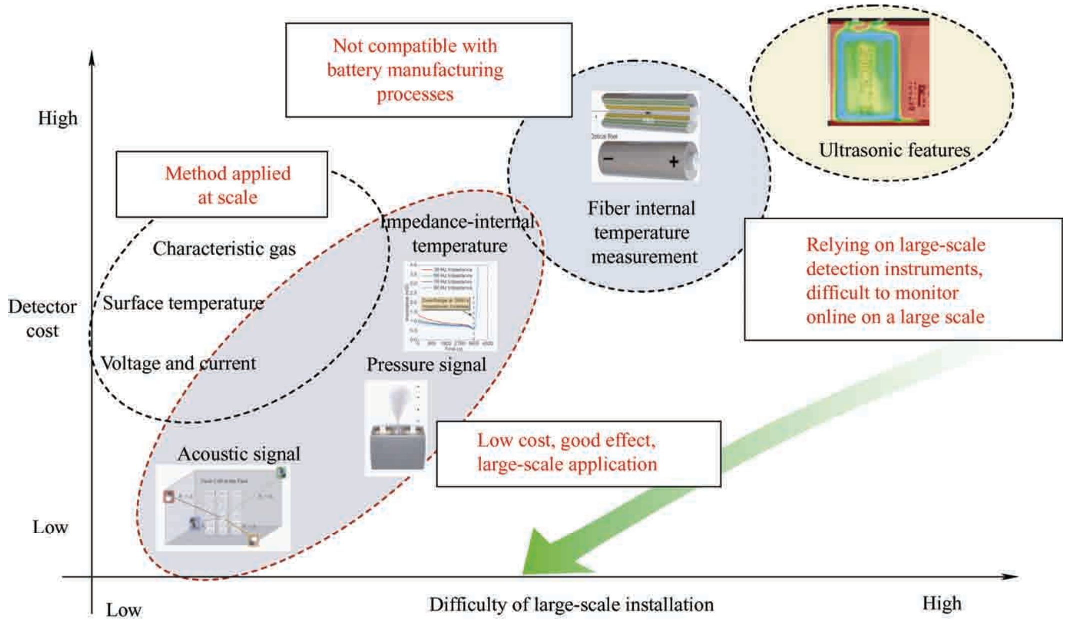

Fig. 12 Fault-warning comparison

Tab. 2 Fault-warning comparison

Warning methodology	Reference	Characteristics signal	Advantage	Disadvantage
Internal temperature	[12-15]	Internal temperature exceeds the normal value, corresponding to the positive and negative change of impedance slope	Visually determine the internal safety condition of the battery	Complex models or additional excitation devices
Ultrasound features	[16-24]	Abnormal ultrasound signal amplitude	Early and reliable detection of battery failure	Not convenient for large cells and module-level cells; high cost
Gases signal	[7, 25-39]	Signal acquisition of characteristic gases such as H_2 and CO_2	Proven and effective method with high economy	Gas diffusion behavior is complex and vulnerable to environmental influences
Pressure signal	[25, 40-48]	Dramatic changes in internal battery or ambient air pressure	Reliable, effective and easy to implement, economical and high	Different air pressure thresholds limited by single cell capacity, volume and other factors, high leakage rate
Acoustic signal	[49-50]	High duty cycle high frequency component, high decibel acoustic signal	Non-invasive and efficient detection	Different types of battery modules have different acoustic signal characteristics
BMS	[2-4, 51]	Voltage, current, SOC	Mature market and high economics	Low reliability
Surface temperature	[14, 52]	Abnormal change in surface temperature	Convenient and easy to implement	Large difference between internal temperature and surface temperature, low warning effectiveness

5 Summary and prospecting

This article summarizes the types and distribution of characteristic signals during the thermal runaway of LIBs and provides a comprehensive overview of multiphysical dimensions, including electrical, thermal, acoustic, and pressure signals for thermal runaway warning methods. In terms of the overall safety of lithium batteries, in addition to preventing accidents through pre-warnings before thermal runaway, the stability of battery thermal runaway can be improved through the design of structural materials. Additionally, measures taken after an accident are crucial, and the selection of efficient fire suppression devices can begin with the material composition of the fire extinguishing agents.

Currently, there is still a significant amount of ongoing research on thermal runaway warning methods, and more efficient and effective measures will be discovered [53]. The primary challenges that must be addressed include enhancing the accuracy of thermal runaway prediction by integrating multidimensional predictive methods to reduce the accident risk. Simultaneously, efforts should focus on improving the cost-effectiveness of predictive methods to lower overall warning system expenses.

The TR mechanism of thermal runaway still has unresolved issues that require further research by the scientific community [54]. Several methods for detecting thermal runaway in LIBs have been proposed: ① finding suitable detection methods to prewarn regarding the diffusion and overflow of electrolytes during thermal runaway, ② using impedance detection to prevent internal short circuits that cause thermal runaway through lithium dendrite growth, and ③ applying safety detection methods for lithium batteries to emerging solid-state battery-safety detection.

References

[1] Q Wang, P Ping, X Zhao, et al. Thermal runaway caused fire and explosion of lithium ion battery. *Journal of Power Sources*, 2012, 208: 210-224.

[2] M Ouyang, M Zhang, X Feng, et al. Internal shortcircuit detection for battery pack using equivalent parameter and consistency method. *Journal of Power Sources*, 2015, 294: 272-283.

[3] L Lu, X Han, J Li, et al. A review on the key issues for lithium-ion battery management in electric vehicles. *Journal of Power Sources*, 2013, 226: 272-288.

[4] Q Wang, B Mao, S I Stoliarov, et al. A review of lithiumion battery failure mechanisms and fire prevention strategies. *Progress in Energy and Combustion Science*, 2019, 73: 95-131.

[5] D Belov, M H Yang. Investigation of the kinetic mechanism in overcharge process for Li-ion battery. *Solid State Ionics*, 2008, 179(27): 1816-1821.

[6] H Wang, A Tang, K Wang. Thermal behavior investigation of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$-based Li-ion battery under overcharged test. *Chinese Journal of Chemistry*, 2011,

29(1): 27-32.

[7] T Ohsaki, T Kishi, T Kuboki, et al. Overcharge reaction of lithium-ion batteries. *Journal of Power Sources*, 2005, 146(1): 97-100.

[8] D Ouyang, Y He, M Chen, et al. Experimental study on the thermal behaviors of lithium-ion batteries under discharge and overcharge conditions. *Journal of Thermal Analysis and Calorimetry*, 2018, 132(1): 65-75.

[9] D Wang, L L Zheng, X C Li, et al. Effects of overdischarge rate on thermal runaway of NCM811 Li-ion batteries. *Energies*, 2020, 13(15): 15.

[10] C H Mccoy. System and methods for detection of internal shorts in batteries, 20140266229. [2014-09-18].

[11] H Maleki, J N Howard. Effects of overdischarge on performance and thermal stability of a Li-ion cell. *Journal of Power Sources*, 2006, 160(2): 1395-1402.

[12] A Ganguli, B Saha, A Raghavan, et al. Embedded fiber-optic sensing for accurate internal monitoring of cell state in advanced battery management systems part 2: Internal cell signals and utility for state estimation. *Journal of Power Sources*, 2017, 341: 474-482.

[13] A Raghavan, P Kiesel, L W Sommer, et al. Embedded fiber-optic sensing for accurate internal monitoring of cell state in advanced battery management systems part 1: Cell embedding method and performance. *Journal of Power Sources*, 2017, 341: 466-473.

[14] R Srinivasan, P A Demirev, B G Carkhuff. Rapid monitoring of impedance phase shifts in lithium-ion batteries for hazard prevention. *Journal of Power Sources*, 2018, 405: 30-36.

[15] N Lyu, Y Jin, R Xiong, et al. Real-time overcharge warning and early thermal runaway prediction of Li-ion battery by online impedance measurement. *IEEE Transactions on Industrial Electronics*, 2022, 69(2): 1929-1936.

[16] K Rhodes, N Dudney, E Lara-Curzio, et al. Understanding the degradation of silicon electrodes for lithium-ion batteries using acoustic emission. *Journal of the Electrochemical Society*, 2010, 157(12): A1354.

[17] G Davies, K W Knehr, B V Tassell, et al. State of charge and state of health estimation using electrochemical acoustic timeofflight analysis. *Journal of the Electrochemical Society*, 2017, 164(12): A2746.

[18] C Bommier, W Chang, J Li, et al. Operando acoustic monitoring of SEI formation and long-term cycling in NMC/SiGr composite pouch cells. *Journal of the Electrochemical Society*, 2020, 167(2): 020517.

[19] T Hodson, S Patil, D A Steingart. An initial exploration of coupled transient mechanical and electrochemical behaviors in lithiumion batteries. *Journal of the Electrochemical Society*, 2021, 168(7): 070515.

[20] R J Copley, D Cumming, Y Wu, et al. Measurements and modelling of the response of an ultrasonic pulse to a lithium-ion battery as a precursor for stateofcharge estimation. *Journal of Energy Storage*, 2021, 36: 102406.

[21] P Ladpli, F Kopsaftopoulos, F K Chang. Estimating state of charge and health of lithium-ion batteries with guided waves using built-in piezoelectric sensors/actuators. *Journal of Power Sources*, 2018, 384: 342-354.

[22] A G Hsieh, S Bhadra, B J Hertzberg, et al. Electrochemical-acoustic time of flight: In operando correlation of physical dynamics with battery charge and health. *Energy & Environmental Science*, 2015, 8(5): 1569-1577.

[23] Y Wu, Y Wang, W K C Yung, et al. Ultrasonic health monitoring of lithium-ion batteries. *Electronics*, 2019, 8(7): 7.

[24] M C Appleberry, J A Kowalski, S A Africk, et al. Avoiding thermal runaway in lithium-ion batteries using ultrasound detection of early failure mechanisms. *Journal of Power Sources*, 2022, 535: 231423.

[25] S Koch, K P Birke, R Kuhn. Fast thermal runaway detection for lithium-ion cells in largescale traction batteries. *Batteries*, 2018, 4(2): 16.

[26] Y Fernandes, A Bry, S de Persis. Identification and quantification of gases emitted during abuse tests by overcharge of a commercial Li-ion battery. *Journal of Power Sources*, 2018, 389: 106-119.

[27] D H Doughty, E P Roth, C C Crafts, et al. Effects of additives on thermal stability of Li-ion cells. *Journal of Power Sources*, 2005, 146(1): 116-120.

[28] E P Roth. Abuse response of 18650 Li-ion cells with different cathodes using EC:EMC/$LiPF_6$ and EC:PC:DMC/$LiPF_6$ electrolytes. *ECS Transactions*, 2008, 11(19): 19.

[29] V Somandepalli, K Marr, Q Horn. Quantification of combustion hazards of thermal runaway failures in lithium-ion batteries. *SAE International Journal of Alternative Powertrains*, 2014, 3(1): 98-104.

[30] A W Golubkov, D Fuchs, J Wagner, et al. Thermal-runaway experiments on consumer Li-ion batteries with metal-oxide and olivin-type cathodes. *RSC Advances*,

2013, 4(7): 3633-3642.

[31] A W Golubkov, S Scheikl, R Planteu, et al. Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes - impact of state of charge and overcharge. *RSC Advances*, 2015, 5(70): 57171-57186.

[32] Y Zheng, K Qian, D Luo, et al. Influence of over-discharge on the lifetime and performance of $LiFePO_4$/graphite batteries. *RSC Advances*, 2016, 6(36): 30474-30483.

[33] M Lammer, A Königseder, V Hacker. Holistic methodology for characterisation of the thermally induced failure of commercially available 18650 lithiumion cells. *RSC Advances*, 2017, 7(39): 24425-24429.

[34] P Qin, Z Z Jia, J Y Wu, et al. The thermal runaway analysis on $LiFePO_4$ electrical energy storage packs with different venting areas and void volumes. *Applied Energy*, 2022, 313: 118767.

[35] X Yang, H Wang, M Li, et al. Experimental study on thermal runaway behavior of lithium-ion battery and analysis of combustible limit of gas production. *Batteries*, 2022, 8(11): 11.

[36] Y Jin, Z Zheng, D Hui, et al. Detection of micro-scale Li dendrite via H_2 gas capture for early safety warning. *Joule*, 2020, 4(8): 1714-1729.

[37] S Shi, N Lyu, X Jiang, et al. Hydrogen gas diffusion behavior and detector installation optimization of lithiumion battery energy-storage cabin. *Journal of Energy Storage*, 2023, 67: 107510.

[38] A O Said, C Lee, S I Stoliarov, et al. Comprehensive analysis of dynamics and hazards associated with cascading failure in 18650 lithium ion cell arrays. *Applied Energy*, 2019, 248: 415-428.

[39] T Cai, P Valecha, V Tran, et al. Detection of Li-ion battery failure and venting with carbon dioxide sensors. *eTransportation*, 2021, 7: 100100.

[40] S K Heiskanen, J Kim, B L Lucht. Generation and evolution of the solid electrolyte interphase of lithium-ion batteries. *Joule*, 2019, 3(10): 2322-2333.

[41] C Forestier, S Grugeon, C Davoisne, et al. Graphite electrode thermal behavior and solid electrolyte interphase investigations: Role of state-of-the-art binders, carbonate additives and lithium bis (fluorosulfonyl) imide salt. *Journal of Power Sources*, 2016, 330: 186-194.

[42] H Bian, Z Wang, J Jiang, et al. Thermal runaway hazard characteristics and influencing factors of Li-ion battery packs under high-rate charge condition. *Fire and Materials*, 2020, 44(2): 189-201.

[43] C Zhang, L Hui, S Wang, et al. A polyethylene microsphere-coated separator with rapid thermal shutdown function for lithium-ion batteries. *Journal of Energy Chemistry*, 2020, 44: 33-40.

[44] P Xu, J Li, N Lei, et al. An experimental study on the mechanical characteristics of Li-ion battery during overcharge-induced thermal runaway. *International Journal of Energy Research*, 2021, 45(14): 19985-20000.

[45] P Qin, J Sun, Q Wang. A new method to explore thermal and venting behavior of lithium-ion battery thermal runaway. *Journal of Power Sources*, 2021, 486: 229357.

[46] S Chen, Z Wang, W Yan, et al. Investigation of impact pressure during thermal runaway of lithiumion battery in a semi-closed space. *Applied Thermal Engineering*, 2020, 175: 115429.

[47] P T Coman, S Rayman, R E White. A lumped model of venting during thermal runaway in a cylindrical lithium cobalt oxide lithium-ion cell. *Journal of Power Sources*, 2016, 307: 56-62.

[48] Y Song, N Lyu, S Shi, et al. Safety warning for lithium-ion batteries by module-space air-pressure variation under thermal runaway conditions. *Journal of Energy Storage*, 2022, 56: 105911.

[49] T Su, N Lyu, Z Zhao, et al. Safety warning of lithium-ion battery energy storage station via venting acoustic signal detection for grid application. *Journal of Energy Storage*, 2021, 38: 102498.

[50] N Lyu, Y Jin, S Miao, et al. Fault warning and location in battery energy storage systems via venting acoustic signal. *IEEE Journal of Emerging and Selected Topics in Power Electronics*, 2023, 11(1): 100-108.

[51] J Hong, Z Wang, Y Yao. Fault prognosis of battery system based on accurate voltage abnormity prognosis using long short-term memory neural networks. *Applied Energy*, 2019, 251: 113381.

[52] J Chen, J E, S Kang, et al. Modeling and characterization of the mass transfer and thermal mechanics of the power lithium manganate battery under charging process. *Energy*, 2019, 187: 115924.

[53] F Sun. Green energy and intelligent transportation: Promoting green and intelligent mobility. *Green Energy and Intelligent Transportation*, 2022, 1(1): 100017.

[54] R Xiong, J Kim, W Shen, et al. Key technologies for electric vehicles. *Green Energy and Intelligent Transportation*, 2022, 1(2): 100041.

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