Fire Safety of Battery Electric Vehicles: Hazard Identification, Detection, and Mitigation

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Abstract

Battery electric vehicles (EVs) bring significant benefits in reducing the carbon footprint of fossil fuels and new opportunities for adopting renewable energy. Because of their high-energy density and long cycle life, lithium-ion batteries (LIBs) are dominating the battery market, and the consumer demand for LIB-powered EVs is expected to continue to boom in the next decade. However, the chemistry used in LIBs is still vulnerable to experiencing thermal runaway, especially in harsh working conditions. Furthermore, as LIB technology moves to larger scales of power and energy, the safety issues turn out to be the most intolerable pain point of its application in EVs. Its failure could result in the release of toxic gases, fire, and even explosions, causing catastrophic damage to life and property. Vehicle fires are an often-overlooked part of the fire problem. Fire protection and EV safety fall into different disciplines. To bridge the gap between these two disciplines and summarize the state-of-the-art knowledge of fire safety issues of EVs, this review article will provide a comprehensive overview of their fire hazard identification, detection, and mitigation strategies. This article also highlights the failure mechanisms of LIBs in EVs, which establish the basis for understanding the LIB fire safety issues in EVs. The aim of this review article is to provide a general and basic understanding of the fire hazards of EVs from different scales to both engineers and researchers. This review article can also be used as educational material for the public and emergency responders to increase their awareness of the fire safety of modern EVs.

This article is part of a focus issue on Fire Safety of Electrified Vehicles: Past, Present, and Future.

1. Introduction

Since the start of the 21st century, there has been a fast-ongoing trend of road vehicle electrification worldwide, which brings significant benefits in reducing the carbon footprint of fossil fuels and new opportunities for adopting renewable energy. In the U.S., electric vehicle (EV) sales have increased significantly from a mere 0.2% of total car sales in 2011 to 4.6% in 2021. Based on the estimation of S&P Global Mobility, 40% of all passenger cars will be EVs by 2030, and more pessimistic estimates even project that EVs will account for 50% of all passenger cars by that year [1]. In the worldwide, the global EV market is estimated to rise to $93.1 billion by 2025 [2]. Over the decade from 2021 to 2031, many factors will contribute to continuously driving consumer demand for EVs, including environmental concerns, more EV purchase options in the market, increased battery capacity, and cost savings [1]. However, vehicle fires are an often-overlooked part of the fire problem, and the wide application of EVs in the automobile industry may bring new problems and challenges in terms of fire safety to occupants and emergency responders. On one hand, vehicle fires play a significant role in the total fire loss. For instance, in 2021, vehicle fires were responsible for 14% of direct property damage, 18% of all recorded civilian fire deaths, 10% of all reported civilian fire injuries, and 15% of all fires that were reported to U.S. fire departments [3]. On the other hand, EVs are rapidly gaining market share but as a technology that is still under development, the fire hazards of EVs haven't been fully studied and the public still lacks a complete understanding of the fire risk of EVs. Any fire incidents involving EVs would gather broad attention from the media and the public, which could substantially undermine consumer confidence in EV safety [4].

Compared to internal combustion engine (ICE) vehicles, energy is stored in the batteries of EVs, and they can convert chemical energy into electrical energy to propel the vehicle and provide all the necessary electrical functions [5]. A variety of vehicle batteries and technologies have been developed and employed. Lead-acid, nickel–cadmium (NiCd), and nickel–metal hydride (NiMH) are some examples of conventional battery technologies used in EVs before. However, their energy density, capacity, rate of charging, and rate of discharge are not high enough, which limits their applications for modern EVs. The lithium-ion battery (LIB) is a technology that was invented in 1980 and commercialized in 1991. Since then, the LIB has gained popularity in usage in almost all kinds of electrical devices. The LIB technology even brought new possibilities to EVs. In the past decade, the LIB dominated the battery market, and it enabled the broad introduction of EVs to commercial applications. And this trend is expected to continue in the next few decades [6]. The main reason is that battery technologies before lithium and battery technologies beyond lithium, so-called "post-lithium" technologies, such as sodium-ion batteries (SIBs), mainly suffer from significantly lower energy density and specific energy compared to state-of-the-art LIBs [7]. Additionally, longer cycle life and lower weight make the LIB most suitable for vehicles as it can promote transportation efficiency. However, compared to ICEs, which have been continuously developed and used over the past century, the LIB-powered EVs are still far from mature and the LIBs still have drawbacks. Faced with harsh working conditions, including vibration and shock, and under the most abusive circumstances, they may experience overload, overheating, short circuits, collisions, or nail punctures, and the chemistry used in LIBs is vulnerable to experiencing thermal runaway [8]. To meet the needs for power and energy, a battery pack in an EV typically consists of hundreds or even thousands of cells connected in parallel and/or series. However, such a huge amount of energy stored in the battery pack could result in fire and even explosions, causing catastrophic damage to life and property when a severe safety issue occurs [9].

Recently, many studies have been performed to investigate the fire hazards of EVs involving LIBs. To improve the fire safety of EVs, researchers are making strenuous efforts to develop and optimize thermal safety management systems for controlling the battery pack within safe working conditions and enhancing the capability of early warning and protection before thermal runaway. In the meantime, many EV fire detection and suppression methods/techniques are being developed to reduce the occurrence and mitigate the consequences of battery thermal runaways and related fire incidents. There are already many excellent review papers existing in the open literature. However, these review papers may just focus on one specific topic of LIBs and EVs and have deep discussions on it. Furthermore, fire protection and EV safety fall into different disciplines. To bridge the gap between these two disciplines and summarize the state-of-the-art technical knowledge of fire safety of EVs from both academia and the industry, this review article will provide a comprehensive overview of their fire hazard identification, detection, and mitigation strategies. This article also highlights the failure mechanisms of LIB in EVs, which establishes the basis for understanding the LIB fire detection and mitigation methods in EVs. The main aim of this review article is to provide a general and basic understanding of the fire hazards of EVs from different scales to both engineers and researchers, which they can use as a starting point for their work on the fire safety of LIBs and EVs. This review article is also aimed to be used as educational material for the public to increase their awareness of the fire safety of modern EVs. Section 2 discusses the fire risks of LIB-powered EVs, including the working principle of LIBs, battery packs, thermal management systems, and failure mechanisms of LIBs in EVs. In Section 3, the safety hazards of EV fires are reviewed, focusing on thermal runaway and thermal propagation mechanisms, EV fire energy release, toxic gases, smoke, and detection and mitigation of fire hazards of EVs. A summary and conclusions are provided in Section 4.

2. Fire Risks of LIB-Powered EVs

An increasing amount of polymers and other combustible materials are used in the construction of modern vehicles.

These materials frequently burn more furiously and/or longer than legacy materials, ignite more easily, and contain more chemical energy per unit volume [10]. LIB-powered EVs present certain different fire risks from ICEs. LIB-powered EVs do not have an exhaust system with hot surfaces. Additionally, unlike traditional vehicles, they don't have an engine compartment containing combustible fluids or a gasoline tank [11]. However, the battery pack adds risks that are unique to EVs. The primary fire safety concern with LIB-powered EVs originates from the individual battery cells of LIB that makeup the battery pack [12]. As a result, if one cell in the pack experiences thermal runaway, the failure and fire could spread throughout the pack, with potentially disastrous consequences. To understand the thermal runaway and thermal propagation process, the working principles of LIBs need to be examined first and their susceptibility to fire safety will be characterized.

2.1. Working Principle of LIBs

The four primary functional components of a rechargeable practical LIB cell are the negative electrode (anode), positive electrode (cathode), separator, and electrolyte. Using $LiCoO_2$ (cathode) and carbon (anode) as an example, the general working principle of typical LIBs is shown in Figure 1 [13]. Cathodes and anodes are the active materials to allow Li^+ to intercalate into them during charging and discharging, contributing to LIB energy storage and release. The separator, which is a porous membrane, physically isolates the two electrodes from each other to prevent internal short circuits while allowing Li^+ flow. The electrolyte is an ion-conducting media, through which ions, including Li^+, could migrate back and forth between cathodes and anodes.

FIGURE 1 Schematic of the general working principle of LIBs.

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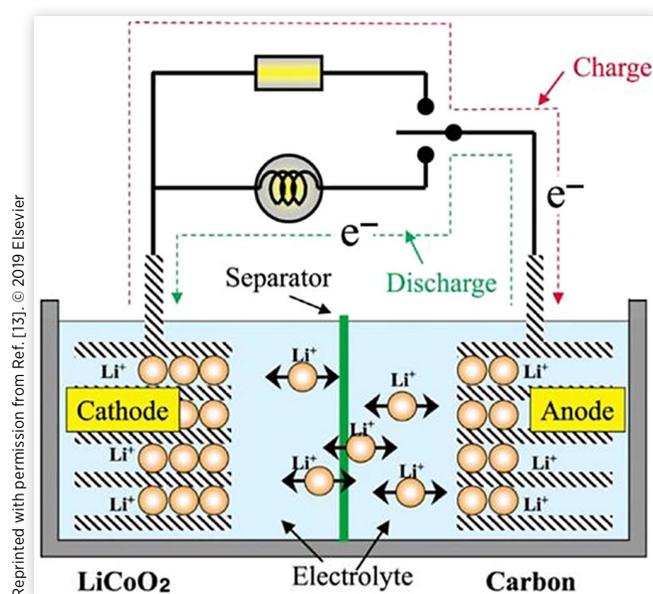
Most commonly, the cathode is made of transition metal oxides in different structures, in which Li^+ is deintercalated and intercalated during the charging and discharging process. Some examples of cathodes are lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt oxide doped with alumina (NCA), lithium manganese oxide (LMO), and lithium iron phosphate (LFP). These cathode materials themselves are not combustible but they are not thermally stable. With increasing temperature, these materials decompose under the formation of new phases and the generation of free oxygen [14]. Lithium iron phosphate (LFP) is a more stable cathode material than the mainly cobalt-based lithium oxides that are commonly used in consumer LIBs. The most common anode material is some form of carbon, usually graphite, in powder form, combined with binder material. However, these graphite anodes have certain drawbacks, including decreased rate capacity, low specific capacity, as well as safety risks, because of the formation of lithium dendrites as a result of the slow working potential of carbon and the sustained deposition of lithium ions [15]. Porous polyethylene (PE), polypropylene (PP), or composite PE/PP films are the most typical types of LIB cell separators. These films are normally around 20 μm thick. When the temperatures are high (often in the range of 130 to 170 °C), these polyolefin separators start breaking down and changing dimensions [16]. Commonly used electrolytes consist of organic solvents and salts dissolved in the solvents, such as lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate monohydrate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), and lithium tetrafluoroborate ($LiBF_4$). These commonly used liquid electrolytes are still flammable and they are more dangerous in the presence of oxygen [13].

The malfunction of these functional components, together or individually, can negatively affect LIB safety and they have the potential to self-heat and enter a thermal runaway, which would result in a rapid uncontrolled rise in temperature and pressure inside the cell. Additionally, even in normal operation, during the charge and discharge process, a large amount of heat will be released from those electrochemical reactions in the cell and lead to the battery temperature rising [17]. Currently, these functional components are still very sensitive to temperature, and their thermal stability is not good enough. If heat generation and dissipation cannot be properly controlled, the battery temperature can go beyond its design operational range, thus triggering thermal runaway of functional components and leading to fire or even explosion.

Furthermore, the development of EVs has increased the demand for fast-charging batteries. High-current charge and nonstandard environmental conditions lead to greater pressure on the anode. The lithium intercalation kinetics in the graphite material is the main limitation factor to the high-power performance of batteries. Lithium dendrites result from the transport speed of Li^+ at the interface, which exceeds its diffusion speed in the electrode. However, over-polarization of the battery with a high charge rate will lead to a negative potential of the anode, which provides favorable conditions for the deposition of lithium metal (Figure 2) [18].

FIGURE 2   Lithium charging insertion process and lithium deposition process during LIB fast charging.

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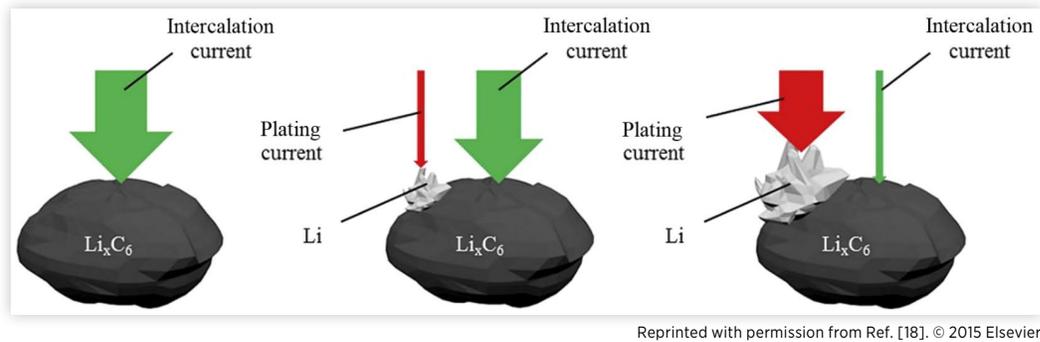
2.2. Battery Pack and Thermal Management System

The LIB cell's electrochemical components are protected by packaging. Packaging comes in a variety of materials and forms. Three different battery cell types are employed in EV applications: small solid cylindrical cells, larger solid prismatic cells, and larger soft pouch or polymer cells. The three types, presented in Figure 3, mainly differ in size, geometry, and individual cell parameters such as capacity and supplied power [19]. Coin cells are small and typically used for laboratory material testing. In cylindrical cells, the anode, separator, and cathode are rolled up in a steel can as a "jelly roll." Cylindrical steel case can withstand high internal pressures without deforming. Cylindrical cells have different sizes, and 18,650 and 26,650 are the two most common sizes. Prismatic cells are rigid and in rectangular shape, and they also have different sizes. Prismatic cells are contained in a prismatic container made of aluminum or steel. Pouch cells are more flexible in both shapes and sizes and often there is no industry-wide standard size for them. In pouch cells, electrodes are stacked and sealed by aluminum laminated film, which can save weight and increase energy density. Different battery cell types are used in EVs by different manufacturers. These LIB cells are normally connected together in series and/or parallel, to form a module for EV applications. To provide the necessary level of energy and power, the battery modules are connected to form battery packs, which contain incredible power currently that scales up from 17 to 100 kWh [20]. For the battery packs of EVs, the specific number of cells in an EV varies greatly based on the cell format. On average, EVs with cylindrical cells have between 5,000 and 9,000 cells. This is in stark contrast with pouch cells, which only have a few hundred cells, and an even lower number in prismatic cells.

FIGURE 3   Four basic cell formats of LIBs: (a) cylindrical, (b) prismatic, (c) pouch, and (d) coin.

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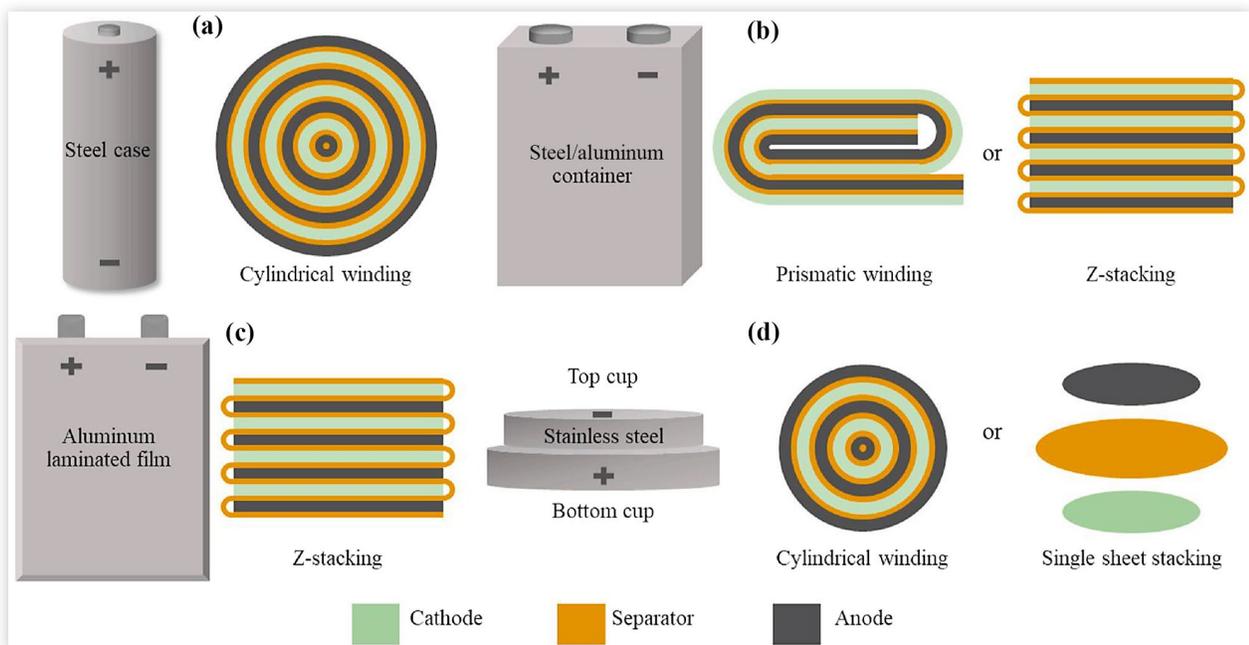
Given the high voltage (300–1,000 V) and a large amount of energy stored (up to 100 kWh), the battery pack in EVs presents a significant safety hazard to both occupants and emergency responders in an incident. Therefore, the battery pack geometry, its position, and the structural design of the vehicle are all design parameters that need to be considered to ensure the safety of EVs [21]. Installing the battery pack inside reinforced and stiffened compartments or other places that are less likely to be damaged in crashes is a typical strategy. This area is sometimes referred to as the "safe zone" of a vehicle. The region between the wheel shafts in the middle of the chassis is considered a safe zone for EVs. This space is utilized by the battery pack in three different ways for passenger cars. The "Floor" and "T" configurations, as depicted in Figure 4(a) and 4(b), are the most popular ones. The "safe zone" is fully utilized by the "Floor" configuration, in which the entire battery pack is installed under the passenger compartment. This configuration not only provides additional interior space for passengers and luggage but also enables high-energy storage. However, this configuration also has some disadvantages, including a lower ground clearance and a larger target for ground debris. In comparison, the "T" configuration provides a larger clearance between the ground and the battery pack, which is achieved by reducing the passenger area. Its main body is rather narrow and can usually be protected by the front axle of the vehicle. This feature can protect the battery pack against frontal collision and side impact. The "Rear" configuration is usually utilized in small vehicles or hybrids, as they require less storage capacity and a smaller battery pack is needed, as shown in Figure 4(c). Compared with passenger cars, different configurations are used in buses. Instead of integrating the battery pack underneath the chassis, bus manufacturers prefer to mount some of their vehicles' battery packs on the top as illustrated in Figure 4(d). This design

requires less modification to the structure of existing buses. Furthermore, putting the battery pack on top of the vehicle makes it easier to be exposed to air and allows for a better cooling effect on the battery, as well as being more easily accessible for various charging methods. Additionally, the greatest amount of space is made available to passengers. However, the higher center of gravity is a drawback.

The temperature has a significant impact on the battery pack's capacity, cycle life, and safety performance [22]. At low temperatures, the viscosity of electrolytes and the internal resistance increase. Due to the lithium plating at a high rate of charging and discharging, the battery capacity will be severely reduced if the temperature is too low. The battery's side reactions and deterioration will be accelerated by the high temperatures. During some extreme conditions, the battery may even suffer a thermal runaway, during which the battery's temperature increases uncontrollably due to a self-reinforcing reaction. For the best performance, LIBs need to be operated within a constrained temperature range of 15–35 °C as shown in Figure 5, and the maximum temperature difference among cells should be less than 5 °C under a wide range of C-rates [23]. When LIBs operate in temperatures outside their operating ranges, their safety, performance, and lifespan will all be impacted. However, in actual applications, terrible environmental circumstances, such as very high or exceedingly low temperatures, are unavoidable. Given the bigger size of the battery pack and higher energy convention rate during the normal operation of EVs, a significant amount of heat will be generated to raise the temperature of the LIB cell due to electrochemical reactions and resistive (or Joule) heating during charging and discharging cycles [24]. Therefore, in order to maintain optimal performance and prolong the lifespan of the battery pack, an efficient battery thermal management system (BTMS) is essential to

FIGURE 4 The battery pack geometry and position in passenger EVs: (a) "Floor" solution, (b) "T" solution, and (c) "Rear" solution; (d) battery packs in electric buses.
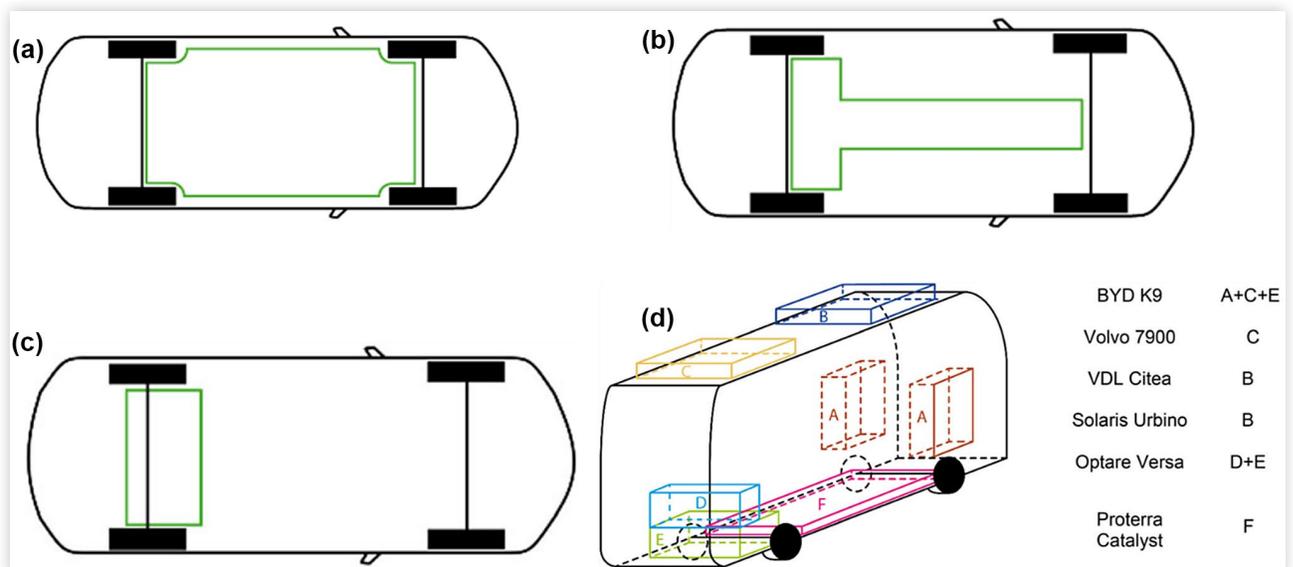
FIGURE 5   Optimal operating temperature range of LIBs.
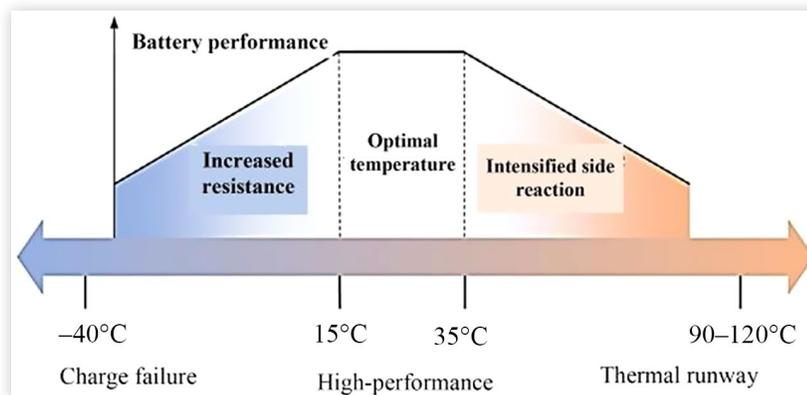
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keep battery temperature within the proper range and to decrease the temperature variance between cells [25, 26]. The heating techniques for LIBs can be categorized into the following groups based on the diverse heating forms: electric heating, air heating, liquid heating, phase change material (PCM) heating, and other heating techniques (such as the Peltier effect and heat pipe). Similarly, a variety of techniques have also been developed to regulate the high temperature of LIBs in EVs, including air cooling, liquid cooling, and PCM cooling technologies. Fans, air ducts, and other accessories are necessary for the air heating/cooling system. However, the heat transfer efficiency of air is relatively low, and thus a quite huge system is needed to achieve the required performance. Hence, air cooling might not be appropriate for next-generation EVs with battery packs of higher energy capacity, but it still has a promising prospect in large-scale energy storage systems. Liquid cooling includes both indirect liquid cooling and immersion cooling. In an indirect cooling system, the liquid coolant flows along channels of pipes or cooling plates and transports the heat out of the battery pack. In an immersion cooling system, the cells come into direct contact with a working fluid that is electrically insulating. The benefit of this method is that exceptionally high rates of heat transfer can be achieved by direct contact between the cells and the immersion fluid. Another benefit is that many immersion fluids can act as fire suppressants to reduce the likelihood and severity of thermal runaway. Nevertheless, there is always a significant risk of liquid leakage in liquid cooling systems. Electric heating has become the most popular type of heating since it is both a reasonably simple and effective method. However, using electric heating, the temperature may not be very uniform throughout the battery packs, which can shorten their lifespan. PCMs are also a good choice for the thermal management of LIBs, for both winter heating and summer cooling if appropriate PCMs are employed. Besides the thermal performance, a variety of other factors need to be considered for the design of BTMS, including scalability, practicability, energy consumption, compatibility, and system cost. It is generally accepted that BTMS should not take over 20% of the weight of the whole

battery pack in EVs [23]. Furthermore, other parts like cables, bus bars, and pack shells shouldn't be interfered with by the thermal management structures.

2.3. Failure Mechanisms of LIBs in EVs

LIBs are quite stable themselves. Depending on the quality of the manufacturing, their failure rate is estimated to be between 1 in 10 million on the high end and 1 in 40 million on the low end, when they are stored and operated within manufacturer-recommended conditions [13]. However, with the big number of LIB cells in the pack, unpredictable circumstances may further substantially increase their failure probability [27]. The components used in current LIBs are a combination of flammable fuel, potential oxidizers, and heat generation during usage. They also have narrow operational temperature ranges and charge/discharge rates. When LIBs are subjected to conditions outside of their design window, the thermal runaway and total failure of LIB cells may happen following some form of abuse as shown in Figure 6 [13]. Possible forms of abuse for LIBs in EVs are classified as [24]:

- Mechanical abuse: Mechanical deformation by external force and penetration by metal objects.

- Electronic abuse: Battery management system failure and hence overcharge and over-discharge, rapid charging.

- Thermal abuse: Poor ventilation, high/low ambient temperatures, heat from cells in thermal runaway, and BTMS failure.

The most common types of mechanical abuse are penetration and collision caused by an external force. They can lead to internal short circuits in battery cells or bus-bar short circuits [28]. Electrical abuse is when a battery is in an overcharge or over-discharge state or is undergoing an external short circuit. Electrical abuse may result in an internal short circuit because of lithium plating, lithium dendrite formation,

FIGURE 6   Schematic of the causes of LIB thermal runaway and fire accidents.

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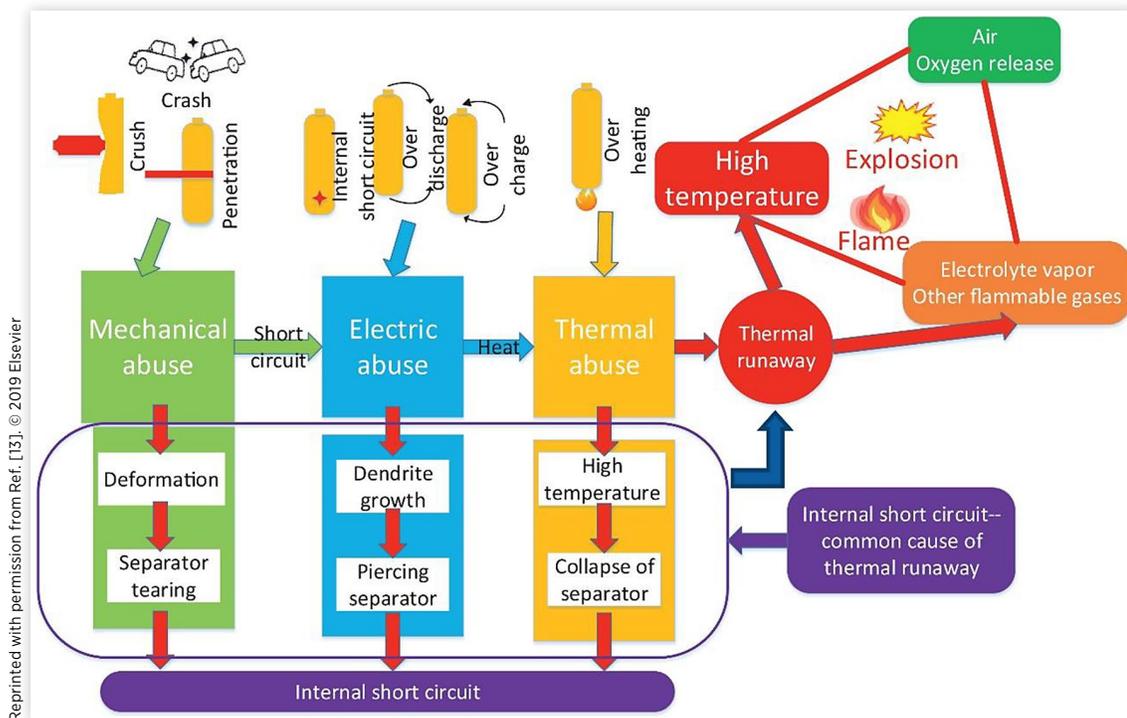
and trigger chain secondary exothermic side reactions. High ambient temperatures and/or insufficient thermal management are the main factors that lead to thermal abuse. Heat accumulation and local overheating during the charging and discharging of batteries are the main causes of thermal runaway, in which LIBs operate outside of their ideal operating temperature range and/or the temperature difference within battery modules is more than 5 °C [29]. These abuse conditions are related to each other. Mechanical abuse can result in a short circuit, which is electrical abuse. Thermal abuse is caused by Joule heating brought on by electrical abuse, leading to increased cell temperatures.

Instead of abuse conditions, statistics on EVs' safety show that self-ignition is the most frequent cause, accounting for 80% of EV fires [30]. The self-ignition might be due to arson or sustained abuse, for example, fire during the charging process, self-ignition while driving, and fire after a traffic accident such as a high-speed collision. Therefore, the propensity of self-ignition during typical charging, parking, and driving situations makes EV fires unique and quite distinct from fires in ICEs. The causes of self-ignition remain unclear, but defects in design and/or manufacture (e.g., battery pack seal failure in wet weather or the introduction of contaminants during manufacture) are commonly postulated [24]. Internal cell defects could be introduced during the manufacturing stage or develop inside individual cells over time, causing the initiation of thermal runaway and ultimately leading to self-ignition. Manufacturing defects can also be induced at the module and pack levels and these defects might not be detected

until the unit is powered up and the battery management system (BMS) identifies a resistance issue (assuming a BMS has this capability) [31]. Failures attributed to manufacturing defects are by far the most worrying as these are very difficult to detect, even with the extensive efforts carried out by battery manufacturers [30]. Thus, internal cell defects and internal faults that develop inside individual cells over time, causing the initiation of thermal runaway, are a major concern for all industries that demand methods and tools to reliably identify them. However, so far, compared with different abuse conditions, there are limited studies on the effects of internal failures of LIBs on thermal runaways of LIBs.

In summary, based on these internal defects and external abuse conditions, EV fires can occur under the following circumstances [32]:

1. A stationary vehicle: extreme temperatures, high humidity, internal cell failure, and abuse of LIB can all cause EV fires.

2. In the charging/discharging process due to overcharge/over-discharge or problems with the charging stations or cables.

3. After a traffic crash or other abuse results in sufficient damage to cause ignition during or immediately after the crash.

4. The re-ignition of the LIB fire after an initial fire has been handled.

5. Due to external factors, such as arson or other fires (wildland, structure, or other vehicles) nearby.

3. Safety Hazards of EV Fires

LIB-powered EV fires pose different hazards from ICE fires in terms of initiation, spread, duration, toxicity, and extinction. The main risks with LIBs are thermal runaway, hazardous gas emissions, and LIB fire re-ignition after extinguishment [33]. As discussed earlier, most LIBs contain both highly energetic materials and flammable electrolyte solutions and separators. Their electrochemical reactions and stability are sensitive to temperatures. When they operate beyond their thermal or electrochemical stability temperature, thermal runaway occurs, and the corresponding temperature increases irreversibly. In that situation, from the intimal thermal degradation reactions all the way to the thermal runaway, LIBs can produce a substantial amount of gases, and smoke, ultimately leading to cell overheating, overpressure, gas and particulate emissions, fire, and even explosion [34]. As reported in both media and literature, there are many examples of EV fires re-igniting hours, days, or even weeks after the initial incident. Besides the danger of re-ignition, LIBs that appear to have been extinguished may still retain toxic gases. Additionally, there is a risk of electrical shock and arc flash due to stranded electrical energy that could be present in the LIBs [24].

3.1. Thermal Runaway and Thermal Propagation

The chain reactions shown in Figure 7 can be used to comprehend the mechanism of thermal runaway of LIBs [35]. If the temperature is high, chemical side reactions will take place one after another inside the battery cell and start a chain reaction. The heat–temperature loop is the root cause of chain reactions. In particular, the abnormal heat accumulation increases the battery's temperature and triggers adverse events such as the solid electrolyte interface (SEI) layer decomposition, the reaction between the cathode and the electrolyte, shrinkage and collapse of separator, decomposition of cathode, and reaction with electrolyte. A heat–temperature loop is created by the side reactions as they continue to emit heat. Up until the battery loses control, the heat–temperature reaction loop circulates to extremely high temperatures [36].

In addition to the aforementioned chemical side reactions, the increase in temperature also causes the electrolyte to evaporate and undergo decomposition. As a result, when exposed to high temperatures, the internal pressure quickly rises, and expansion is frequently the first change in LIB cell. If the cell contains a safety valve, it will open when the pressure exceeds the critical level and release flammable gases and aerosols. Otherwise, the seam cracks under intense internal pressure for pouch cells without a safety valve. The flammable gases and aerosols include H_2, CO, CH_4, C_2H_4, and C_2H_6, as well as organic electrolyte solvents. Depending on the materials used in LIB cells and the state of charge (SOC), the specific compositions of these flammable gases and aerosols

FIGURE 7 The chain reactions during the thermal runaway of LIB.

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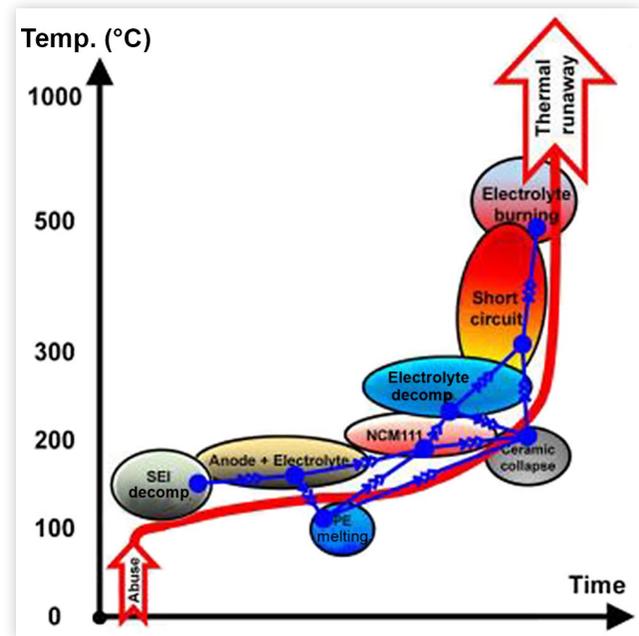
may vary. When they mix air, the combustible mixture can be ignited by sparks and hot surfaces quite easily to initiate a jet fire or explosion [37]. The jet and injection can cause the propagation of thermal runaway to other cells, leading to continuous deterioration of thermal hazard.

When a LIB cell undergoes thermal runaway, a situation known as thermal runaway propagation can happen where single battery cell failure spreads to neighboring cells [38]. The greater the number of cells involved, the more gas and energy will be released. Thus, the energy released by a cell in a thermal runaway is relatively limited, but the thermal runaway propagation can result in the release of the whole energy stored in the battery pack, leading to a large-scale fire or even explosion [35]. Therefore, considering the large number of LIB cells in the battery pack of EVs, there is an increasingly higher risk of fire propagation. However, despite this risk, because of space constraints and the requirement for high-energy density in the packs, there is typically no or very little space between cells and modules. This provides the pathway for fast thermal runaway propagation between cells, in which heat transfer plays a more dominant role in the mechanism. There are three different ways that heat can transfer between cells: conduction through the battery shell and the pole connection tab, convection through the air, and radiation from a flame or a hot battery body as shown in Figure 8(a) [13, 39]. The burst-out electrolyte can catch fire on the top of the battery and Figure 8(b) shows the calculation method for the heat flow transferred between two adjacent battery cells through the three paths, where R_x is the thermal resistance between the temperature nodes TC_y and TC_z [13, 39]. The form factor of the cells (such as cylindrical, prismatic, and pouch) affects the heat transfer modes between cells. Thus,

FIGURE 8 The heat transfer and thermal runaway propagation in battery and battery pack: (a) heat transfer paths during thermal runaway propagation; (b) thermal resistance network representation; and (c) thermal runaway propagation in battery pack.
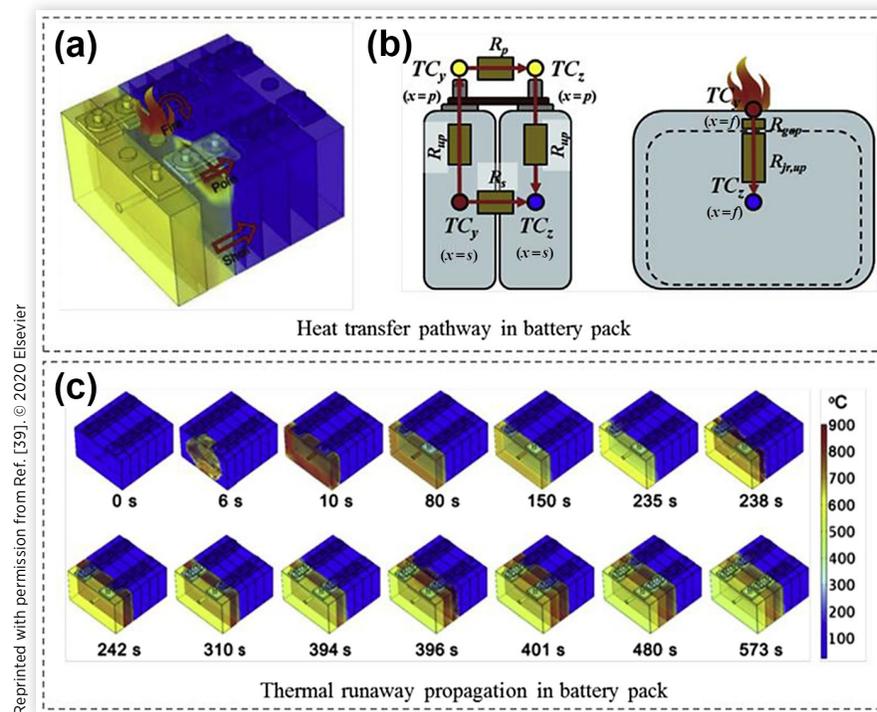
they also influence the thermal runaway propagation dynamics within the battery pack as shown in Figure 8(c). With minimal physical contact between adjacent cylindrical cells and the significant air gaps around them, conduction and convection are insignificant, and thermal radiation is the main heat transfer path. It was found that the cylindrical cell module was less vulnerable to thermal runaway propagation, while the electrical connectivity will impel the propagation of thermal runaway in the single battery cell. As for pouch cells, shell contact between nearby pouch cells will contribute to a faster heat transfer within the pack. The heat transfer in prismatic battery pack mainly consists of three parts, i.e., heat transfer through the cell shell, pole connector, and fire spread. The heat transfer by cell shell is the principal thermal propagation process, and heat transfer by pole connector is about 1/10 of that. The fire is mainly caused by the burst-out electrolyte, and the ceiling jet fire in the battery pack can scorch adjacent batteries, but fire spread is also not the main heat transfer path for thermal runaway propagation for prismatic battery packs [39]. However, some researchers also pointed out that if combustion occurs in a large LIB pack, the ceiling jet can scorch the surrounding cells directly. Therefore, the effect of the flame on the thermal runaway propagation should be given attention and needs further investigation, especially for large LIB packs [13]. Another factor that affects thermal runaway propagation is the charged state of the battery cell. In general, charged cells release energy at a rate that is far higher than discharged cells. Currently, small modules are mainly used

for studies on thermal runaway propagation. Fire spread within large packs is largely different from that in small modules. Future research should focus on large-scale LIB pack fires, including modeling and experimentation [37]. Additionally, besides the BTMS, thermal barriers can be used to delay or prevent thermal propagation between cells. Two main characteristics of the thermal barrier are crucial for this functionality: (1) a strong endothermic behavior after exceeding the failure onset temperature and (2) a high thermal resistance to avoid a fast heat transfer between the cells [40]. Depending on cell size, cell format, and module integration, different materials, such as aerogel and PCM, have been applied as thermal barriers in battery packs. Some commercial products have been developed for this purpose. For example, 3M™ Thermal Barrier 5000 Series is a dispensable, light-weight silicone-based solution that helps protect neighboring cells from the heat from a failed cell by creating a fire retardant, electrically and thermally insulating barrier layer.

3.2. EV Fires and Energy Release

Both ICEs and EVs contain a significant amount of combustible materials, and they mainly consist of flammable plastic parts, as well as the power system or fuel (liquid petroleum fuel or battery). In an average modern vehicle weighing 1,500 kg, 12–15% of the total weight is plastic material (around 200

kg), which is higher than that of gasoline (less than 50 kg) [41]. For common petroleum-based polymers used in modern vehicles, such as polyethylene and polystyrene, their heat of combustion is very close to that of gasoline. The total heat released from burning plastic components may have a major contribution to the vehicle fire, especially if the gasoline tank is not full. There is no major difference between ICE and EV in terms of plastic components. Therefore, the difference in their power system and the fuels will lead to different fire behaviors between them [6].

As discussed earlier, LIB cell and pack include many different combustible components, and their chemistry, packing, capacity, and SOC affect their thermal runaway and subsequent fire behaviors. The heat of combustion is a measure of the amount of energy released in the form of heat by the complete burning of a substance, which is an important parameter to evaluate the fire behavior of a material [42]. For instance, the heat of combustion for a 2.9 Ah (11 Wh) commercial pouch-type LIB was approximately 4 MJ/kg, compared to approximately 2 MJ/kg for an 18650 cylindrical battery cell [43, 44]. The heat of combustion for gasoline is roughly 47 MJ/kg in comparison. In general, LIB has a lower heat of combustion than gasoline by an order of magnitude. However, the weight of the EV battery pack is at least an order of magnitude greater than gasoline for ICE due to the battery's low (chemical or electrical) energy density. Additionally, besides the electrical energy stored in the battery, the thermochemical energy can also be released from the battery fire, including both the thermal runaway heat inside the battery (i.e., the internal heat) and flame sustained by the flammable gases injected from the battery (i.e., the flame heat). It was reported that battery fire can release 5–10 times more energy than the stored electrical energy (or kinetic energy), depending on SOC [6]. Overall, under the same driving range, it was estimated that the fuel load or the fire heat release of the LIB pack is about twice that of a full gasoline tank. Furthermore, while driving, the amount of gasoline in the tank will be consumed gradually. However, in this process, the total mass of the LIB pack will not change and the potential heat release of burning LIB does not vary significantly in the SOC range of 20–100% [6]. Kang et al. conducted full-scale fire testing of battery EVs (BEVs) and compared their characteristics with conventional passenger cars. The LIB pack (64 kWh) and BEV body fires generated 1.54 and 7.81 MW of pHRR (peak heat release rate) and 1.30 and 7.53 GJ of THR (total heat release), respectively. The BEV with the 64-kWh pack resulted in the fire with 7.25 MW of pHRR and 9.03 GJ of THR, respectively. The THR of the BEV fire was comparable with the sum of the individual THRs of the pack and body (8.83 GJ). This observation led to the conclusion that a larger contribution of BEV fires came from the BEV body than the LIB pack in terms of pHRR and THR [45]. As seen in Figure 9, the BEV fire that started in the LIB pack developed more quickly than the ICE and fuel cell electric vehicle (FCEV) fires. All these behaviors show that EV fire has a higher hazard and requires more stringent risk-mitigating efforts.

Overall, EV fires are characterized by a large heat release rate, a fast temperature rise rate, and a long-elevated
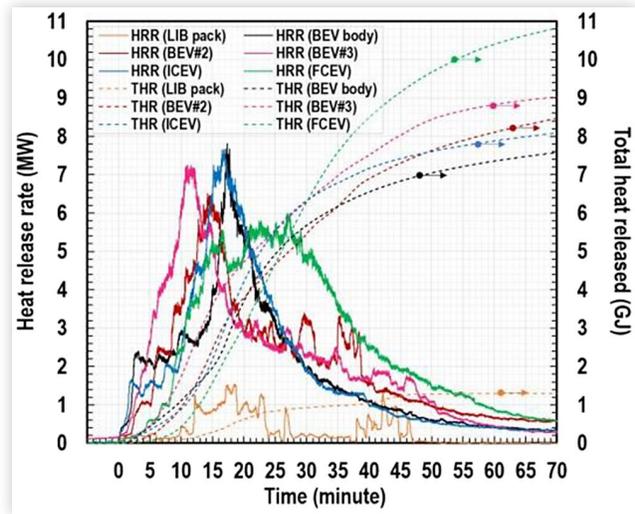
temperature duration. The main hazards of EV fires are high temperature, jet fire, and explosion [2]. LIBs under thermal runaway produce a lot of gases inside its shell, and the buildup of the gases not only results in high pressure but could also result in the formation of a jet flame when it is released and comes into contact with a heat source [46]. The maximum height of jet flame of the 18650-type LIB was 0.31 m [47]. For prismatic LIBs under lengthwise and transversal placements, the peak jet velocity was 42.05 m/s occurring at the moment when the safety valve opens [48]. The jet flame height of a 50 Ah LIB module is 0.96 m [49]. The temperature rise rate can exceed 100°C/s and the flame temperature was over 900°C, which has the potential to harm occupants and set off nearby flammable materials, leading to a more serious fire. It was found that the jet flame released from the LIB pack can cause the rapid spread of the EV fire. Although the jet fire originating from the LIB pack accelerated the ignition and combustion of other EV components, the jet flame was not the primary contributing factor to the HRR and THR. Rather, the majority of the heat released at an instant (i.e., pHRR) was governed by the flames created from the conventional combustion of the organic–polymer components of the vehicle [45]. There are a few full-scale testing of EV fires. Nevertheless, the intensity of the jet flame and whether the gas phase explosion occurs are unknown in BEV fires. Most of the EVs used in the existing fire tests are rebuilt or old models, making it challenging to explore the fire patterns of modern EVs.

3.3. Toxic Gases and Smoke

Besides the heat released, another strong concern related to burning EVs containing LIB packs is the release of toxic gas and smoke. The significant amount of plastics contained in modern vehicles may serve as a source of various toxic gases, such as carbon monoxide, hydrogen cyanide, organic irritants, and

carcinogenic organic compounds. Additionally, some plastics can be a source of substances such as hydrogen chloride (HCl) and hydrogen fluoride (HF), for example [37]. Furthermore, after thermal runaway, the cell or its safety valve will rupture and discharge more toxic gases. In a fire, the combustion of electrolytes is the main source of toxic gases and smoke [50]. The lithium hexafluorophosphate ($LiPF_6$) in the electrolyte as well as other fluorine-containing compounds have the ability to emit HF when heated and burned [51]. Phosphorous oxyfluoride (POF_3), which is even more hazardous than HF, can also be produced by the fluorine present inside the LIB cell [6]. The chemistry and SOC of LIBs can have a significant impact on the composition of toxic gases and smoke emissions, depending on the EV manufacturers and the particular type of LIBs used as shown in Table 1. The quantity of gas varies with the battery size, its SOC, and chemistry. Depending on battery types and test scenarios, there are large variations in the quantity and composition of toxic gases measured. These gases can be inhaled and cause symptoms such as headaches, comas, loss of consciousness, and even death. There are few studies on metal residues associated with airborne particles from EV fires, but one earlier study found shockingly high quantities of cobalt (Co), lithium (Li), and manganese (Mn) from battery fire testing [50]. Heavy metals can be extremely harmful, and the composition is anticipated to change as a result of the input from EV batteries.

If the EV fire happens in a confined space with poor ventilation, such as a parking garage, a large quantity of toxic gases and smoke may accumulate in that space with a low oxygen concentration. Therefore, even after extinguishing, forced ventilation is highly recommended to protect first responders from continued exposure to toxic and flammable gas emissions [52].

3.4. Detection and Mitigation of Fire Hazards of EV

3.4.1. Detection of Thermal Runaway and EV Fires
With the increasing demand for high capacity, the LIB packs become progressively larger and higher in energy density. The fire propagation through the pack can cause significant, potentially catastrophic damage. The initial failure of LIB can

FIGURE 10 The general process of thermal runaway prediction and early warning method of LIBs.
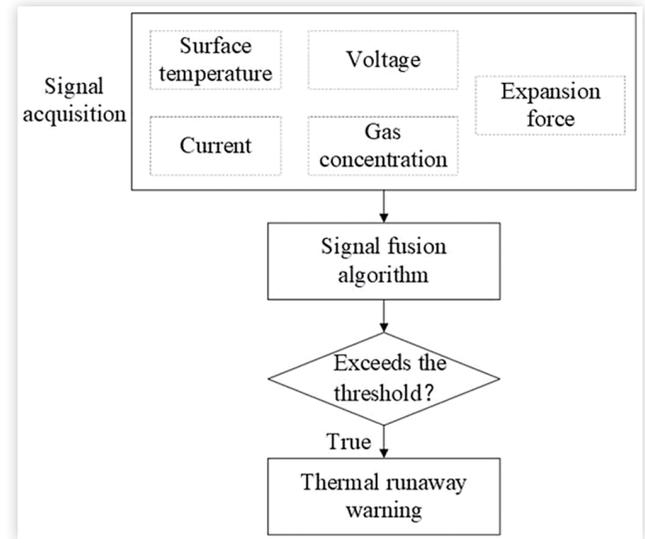
Reprinted from Ref. [53] and licensed under the Creative Commons Attribution 4.0 International License

happen quickly, after a cell is damaged, or slowly over a long period of time, resulting in delayed failure that happens a considerable time after the damage is first caused. The time in between is usually referred to as the incubation period which can last from several hours to years, depending on the cause and failure mechanism [30]. Since LIB failure processes are time-dependent, early detection of failure, thermal runaway, or fire is crucial. An ideal early thermal runaway and fire detection and warning system should have a perfect balance between the avoidance of false alarms and the speed of the early warning response, which so far is still changeling to achieve. In general, the current thermal runaway and fire detection and warning methods can be divided into two categories.

The first category is developed based on the internal electrochemical mechanism of the battery, such as heat generation calculation, gas generation monitoring, expansion force monitoring, and electrochemical impedance spectroscopy (EIS) testing as shown in Figure 10 [53]. They can be summarized in five different methods: (i) terminal voltage using the BMS;

TABLE 1 Composition of the gases generated from thermal runaway of commercial LIBs.

Graphite-based 18650 cells at 100% SOC with different cathode materials				7.7 Wh LIB cells (LCO/graphite) at different SOCs			
mol%	$LiCoO_2$/ $LiNiMnCoO_2$ (LCO/NMC)	$LiNiMnCoO_2$ (NMC)	$LiFePO_4$ (LFP)	vol.%	50% SOC	100% SOC	150% SOC
H_2	30.0	30.8	30.9	H_2	30	27.7	29.7
CO_2	24.9	41.2	53.0	CO_2	32	30	20.9
CO	27.6	13.0	4.8	CO	3.61	22.9	24.5
CH_4	8.6	6.8	4.1	Hydrocarbons	34	19.3	24
C_2H_4	7.7	8.2	6.8				
C_2H_6	1.2	-	0.3				

Data taken from Ref. [37]. © Ruiqing Shen, Yufeng Quan, James D. McIntosh, Asad Salem, Qingsheng Wang

(ii) unusual gases emitted; (iii) internal battery temperature; (iv) current variations as an indication of short circuits; and (v) mechanical deformation using strain gauge sensors [30]. The most widely used method for detection is a mix of terminal voltage (i) and temperature (iii). The BMS has built-in sensors, which can be used to monitor the surface temperature and voltage of each cell within the battery. When any abnormal signal is detected, the BMS triggers a warning. However, the BMS does not respond fast enough to detect the initial stages leading to thermal runaway. Internal temperatures measured *via* dedicated embedded sensors have a higher accuracy than surface temperature measurements to predict thermal runaway, but they add a high cost as well as complexity to the pack. In EVs, it is common with just one temperature sensor per module as the number of sensors in a LIB module is typically minimized to reduce the cost, weight, and volume of the module. Therefore, it is highly likely for an individual cell to overheat and vent without timely detection if a temperature sensor is not located near enough to the cell. Gas sensors can be used to detect the start of thermal runaway. They can act faster than voltage or temperature methods because the accumulation of initial gases often precedes any significant changes in the voltage or temperature signals. However, it makes the system more complex and costs more. Its faults could trigger false alarms. With these advantages and disadvantages, heat, smoke, and gas detectors all can find their appropriate applications in battery industries. For example, gas detectors are recommended for stationary energy storage systems in enclosures, where they are able to give a warning before flammable gases build up [30]. For EVs, fixed fire detection systems are widely used to protect engine compartments on heavy vehicles, but they are not common in passenger vehicles [11].

The second category is the methods established based on artificial intelligence (AI) algorithms with battery big data [30, 53]. A large amount of historical data such as the current, voltage, and temperature of battery packs in EVs have been collected and stored in data centers, which can be used to train the battery thermal runaway model for early thermal runaway and fire detection and warning. On one hand, the model uses information including but not limited to correlation coefficients between voltages, thresholds, sample entropy, and the like to analyze the abnormal performance of voltages in massive real-vehicle data. On the other hand, some models use machine learning methods to directly predict whether the battery is abnormal or even thermal runaway occurs, which is mostly based on experimental data and real data. However, most of the novel methods can only be verified for specific experimental datasets or data that are difficult to collect by simple sensors, while for thermal runaway of real vehicles, most of them perform post-mortem analysis on the data collected by a BMS. Generally, methods based on big data have the potential to improve their generalization performance with further development in the near future.

3.4.2. Suppression of EV Fires
LIB fire is not a typical fire because at least a portion of it consists of direct reactions between battery components. In LIB fire, heat causes the decomposition of the lithium metal oxide cathode material and results in the release of oxygen [54]. Thus, their combustion reactions do not necessarily depend on the external oxygen supply. On the other hand, the battery pack arrangement is tight to increase the volumetric energy density. This makes it hard for the fire-extinguishing agents to access the inner of the battery pack. Even if the fire is extinguished initially, due to cascading cell thermal runaway reactions, the temperature of the battery is still high, and the violent chemical reaction is still ongoing inside the battery. LIB fires still have the potential for re-ignition. Moreover, due to the electrical nature of battery packs, conductive suppression agents may not be a good choice. The risks of electric shock and battery re-ignition/fire arising from the energy that remains in a damaged battery (also known as stranded energy) are safety concerns for not only occupants but also emergency responders [55].

There are four basic approaches to the suppression of a typical fire: isolation method, smothering method, cooling method, and chemical suppression method. Isolation of LIB module or pack from the LIB cell undergoing thermal runaway, and from other hot combustion products is important in mitigating the fire hazards, which, however, is hard to achieve in the limited space of EVs. Because of the self-supported nature of LIB thermal runaway and fire, the smothering approach is not very effective to suppress LIB fires by controlling the supply of external oxygen. Cooling the battery with a continuous water mist is a promising approach for the suppression of LIB fires. However, it can also have an impact on the integrity of the electrical circuits, as water can cause an external short circuit and further ignition or thermal runaway propagation [30]. Additionally, the salt in the electrolyte, for example, $LiPF_6$, can react with water to release a large amount of HF, which is toxic and harmful to people [56]. Besides, lithium can react with water to form highly flammable hydrogen. Conventional fire-extinguishing agents are not suitable to stop the thermal runaway reactions inside LIBs. They have only been proven effective to extinguish open flames external to the battery as the battery's surface temperature decreases. The performances of eleven common fire-extinguishing agents are shown in radar plots in Figure 11, in which their viscosity, biodegradable capability, heat capacity, wettability, insulativity, smoke adsorption, and cost are compared [54]. So far, despite its disadvantages, water is still the most used fire-extinguishing agent by emergency responders to control EV fire, because of its high heat of vaporization and heat capacity [57]. It may not only help suppress flaming combustion but also may be able to slow down or stop the propagation of the thermal runaway. In this case, long extinguishing time and large volumes of water may be required to avoid glowing and re-ignition problems of EV fires. The NFPA emergency field guide states that large, sustained volumes of water are required to extinguish a high-voltage battery fire: "it could require over 2,600 gallons, depending on the size and location of the battery" [55]. The NFPA also advises firefighters to continue applying water (even after they can no longer see a flame) to sufficiently cool the battery pack—it could take an hour or more—so as to reduce the risk of re-ignition [55]. Some research has been performed to improve the fire-extinguishing efficiency of water using additives to change its physical and

FIGURE 11 Radar plots of the performances of (a) halons, (b) carbon dioxide, (c) heptafluoropropane, (d) Novec 1230, (e) dry powders, (f) water, (g) water sprinkler, (h) water mist, (i) F-500, (j) foams, and (k) aerosol.
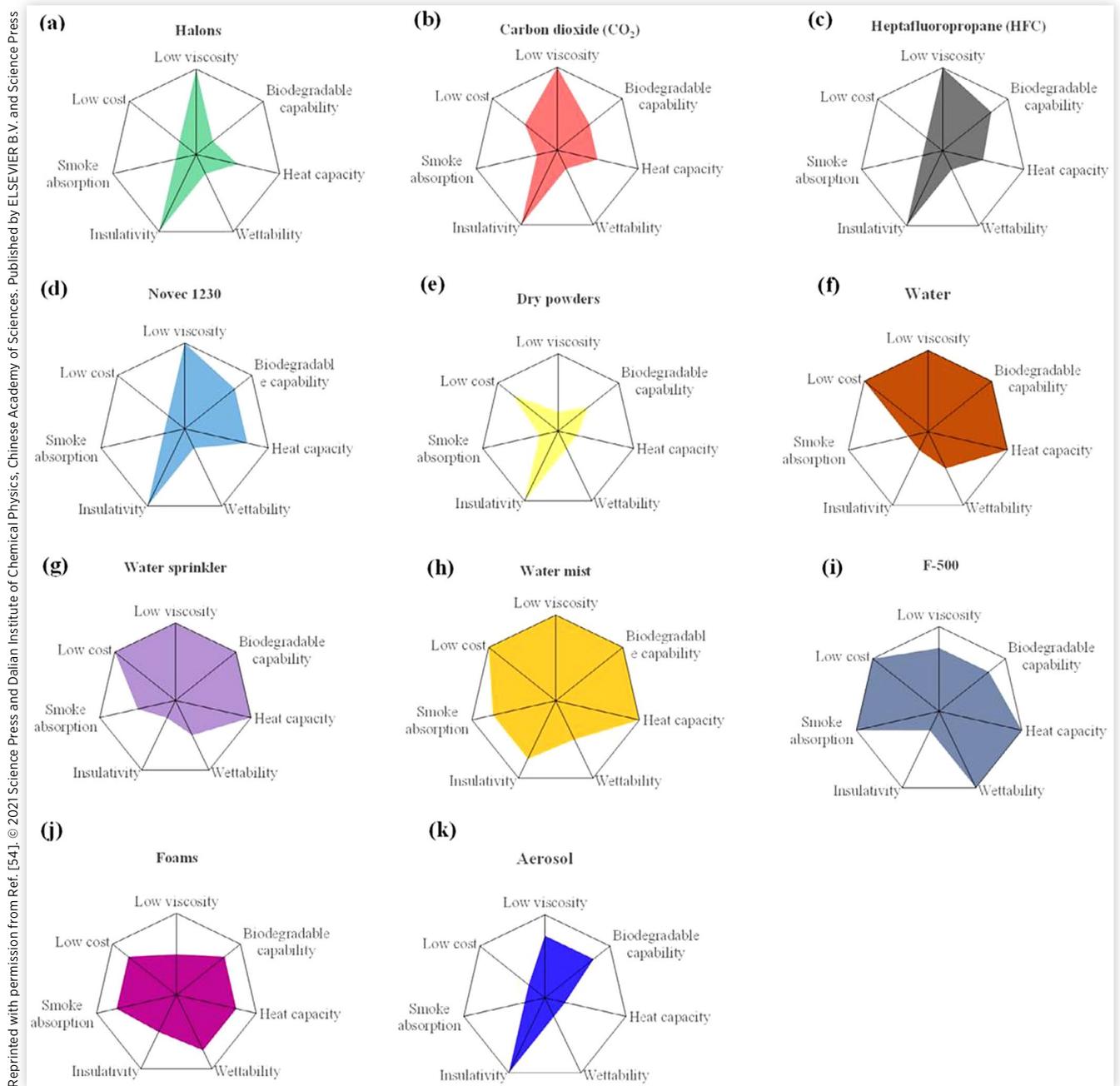
chemical properties [58, 59, 60]. The physical properties can contribute to improving cooling capacity. Furthermore, physical additives can adjust the surface tension of droplets and hence enhance their penetration into the LIB pack. Some chemical additives can even react with toxic gases and smoke to decrease their concentration. It should be noted that the research on suppression methods for battery fires is at an early stage and it is far from reaching an optimal solution to effectively and safely extinguish battery fires.

4. Conclusions

LIBs have emerged as an important energy storage technology for the present and future to reduce and eliminate greenhouse gas emissions. However, even with significant advancement, currently, the functional components used in traditional LIBs are still very sensitive to temperature, and their thermal stability is not good enough. Furthermore, LIBs in EVs are subjected to harsh working conditions and there are external

abuse conditions and internal defects that may trigger the thermal runaway of LIBs. Because of the large number of LIB cells in the battery pack of EVs, there is an increasingly higher risk of fire propagation, leading to catastrophic consequences such as the release of hazardous gases, fire, and even explosions. Compared with conventional vehicle fires, EV fires are characterized by a large heat release rate, a fast temperature rise rate, and a long-elevated temperature duration. The main hazards of EV fires include high temperature, jet fire, and explosion. Since LIB failure processes are time-dependent, early detection of failure, thermal runaway, or fire is crucial. The avoidance of false alarms and the speed of the early warning response are two key parameters to evaluate the performance of early thermal runaway and fire detection and warning systems in EVs. The common system is developed based on the internal electrochemical mechanism of the battery, such as heat generation calculation, gas generation monitoring, expansion force monitoring, and EIS testing. Additionally, AI is also emerging as a novel strategy to monitor LIB packs and detect their thermal runaway and fire. The fire suppression of EV fire is still a challenging issue because of its reactive chemistry and tight configuration. There is a risk of electrical shock and arc flash to emergency responders due to stranded electrical energy that could be present in the battery. So far, despite its disadvantages, water is still the most used fire-extinguishing agent to control EV fire, with its high heat of vaporization and heat capacity. In this case, long extinguishing time and large volumes of water may be required to avoid glowing and re-ignition problems of EV fires.

Both the technologies of LIBs and EVs are fast developing. The safety of EVs is a subject that is continuously evolving with new materials, new technology, new systems, new applications, new standards, and the like. It is beyond the scope of this review article, but it is necessary to mention that there have been tremendous efforts to improve the thermal stability and control reactivity of LIBs in the material aspects from the lab to the industry. Intelligent manufacturing and Industry 4.0 are being incorporated into the LIB manufacturing process to reduce or even eliminate manufacturing defects and improve product quality. All these efforts are a part of the ongoing revolution in the automobile industry. The fire hazard identification, detection, and mitigation strategies in this review article are based on the current knowledge of fire protection and EV safety existing in the open literature. With more research and collaboration in the disciplines of both fire protection and EV safety, new improvement and integration on the fire safety of EVs will emerge, which will continuously support the safe evolution of the automobile industry.

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