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Review article

A review of safety strategies of a Li-ion battery

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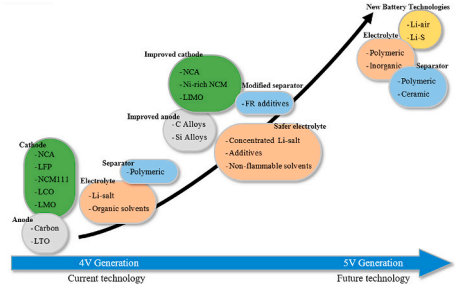
HIGHLIGHTS

- Overcharge and overheat are the ultimate initiator of the thermal runaway.
- Battery additives and material modification enhance safety at a cost of performance.
- Improved heat transfer and cutting-off thermal cascading failure secure pack safety.
- The ability to stop fire and cool the battery define the best suppressing agent.
- The promising materials and technology govern the development of futuristic battery.

GRAPHICAL ABSTRACT



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ABSTRACT

Since the burst of sales of electric vehicles in the world market, there have been frequently reported fire accidents throughout the globe. These accidents have led into the demise of occupants and vehicles which demoralize end-users. Herein, an extensive review of the thermal hazards of Li-ion battery and effective safety strategies toward eradicating the danger of thermal runaway is elucidated. First, the mechanism of thermal runaway (TR) and its associated chain reactions such as the breakdown of SEI layer, a reaction between anode/electrolyte, breakdown of electrolyte, a reaction between electrodes, etc. which in turn, generates enormous heat energy and variety species of flammable gases, is explained. In pack level, the main concern is the propagation of TR to the adjacent batteries inside the module and between modules. The propagation events transmit thermic consequences to adjacent batteries and, finally, catastrophically damage the battery pack. Thus, to reduce the thermal hazard of Lithium-ion battery, adequate measures have been reviewed, such as usage of thermally protective separators, safety devices, flame retardants, passive cooling devices, and fire suppressants. To conclude, the main goal here is to provide a better understanding of the TR mechanism and safety strategies toward enhancing the safety of Lithium-ion battery.

1. Introduction

The transition in the road transport sector from using conventional vehicles to alternative efficient vehicles is assisted by Lithium-ion battery technology. The superior attributes of the Lithium-ion battery, compared to other battery technologies, include higher current, voltage,

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power and energy density, reduced cost, weight and pollution, lack of memory effect, excellent stability, low self-discharge rate and prolonged life cycle [1,2]. These features make Lithium-ion useful in propelling energy-efficient traction vehicles. However, during daily usage it is often for Lithium-ion battery to experience different forms of mistreatment such as overcharge/over-discharge due to variations in cell capacity resulted from manufacturing processes [3]; over-temperature affected by failure of battery management system (BMS), cooling system, elevated ambient temperature or nearby glowing fire; and due to physical activities like vibrations, rollover, etc. Noteworthy, the final result from any of these forms is the rise in internal battery temperature, which when not well drawn to the surrounding it can steeply raise battery temperature and trigger an exothermic reaction. Consequently, a loop of exceedingly self-induced temperature termed as thermal runaway, emerges that ends to catastrophic damage [4].

The safety and reliability of the Li-ion battery are paramount to the end-users. However, the dreadful fire accidents emerged in EVs, some led into demises, for example, Tesla Model S in West Hollywood [5], Tesla Model S in California [6], Tesla Model S in Zurich [7], Tesla Model S in Florida [8], BYD e6 in Shenzhen [9], Tesla Model S in Indianapolis [10], Tesla Model S in Amsterdam [11], Tesla Model X in Mountain View-CA [12], and Tesla Model S in Florida [13]; are significantly featured by reactions of internal chemical substances of Li-ion battery. To date, there are certain advancements from the conventional Lithium-ion to new technologies such as solid-state-electrolyte Lithium-ion battery and an all-solid-state Lithium-ion battery. However, new technologies of Lithium-ion battery are still immature to rectify the existing problems. In recent studies of conventional Lithium-ion battery, the root-cause of this intrinsic damage is the chemistry of electrode-separator-electrolyte [14–16] whereas low-temperature margin acts as a chief source [4].

Lithium (Li) is the third-smallest element having tiny space to carry a positive charge which leads to higher energy density [17]. So, the first principle for selecting electrode materials is a high concentration of Lithium-ions in the intercalation/de-intercalation process. When electrodes are soaked into the electrolyte, below 25 °C, a lithium plating is formed. Beyond that, a thin passivation layer is formed from the interaction between anode and electrolyte, called solid electrolyte interphase (SEI). At normal temperatures, the SEI layer prevents oxidation, lowers chemical reaction, reduce self-discharge and capacity fade. However, the SEI layer grows with temperature and becomes crucial over a long time. In regular use of Lithium-ion battery, the recommended peak operating temperature is 40 °C [18–20]. In that manner, a battery to decompose at elevated temperature has to pass several stages. Whenever abused such as overcharge/over-discharge, short-circuit, or exposed to high external temperature, the internal battery temperature raises abruptly. Wang, Sun and Chu [21] reported more chemical reactions to occur beyond 66.5 °C whereby decomposition of SEI layer for some special electrolytes were reported to occur below 68 °C [16,22–24], 90–130 °C [25], 90–120 °C [26], 100 °C [27] and120 °C [28]. As temperature exceeds 100 °C, it further breaks down the SEI layer, causing interaction between lithiated anode and electrolyte, after that decompose electrolyte to generate flammable hydrocarbon gases such as ethane and methane [16]. At a temperature of 135 °C for polyethylene (PE) [29,30] or 165 °C for polypropylene (PP) [30] separator melts resulting into high resistance, increase in battery temperature and melt-out of metal oxide cathode [28]. Consequently, cathode releases oxygen (O_2) beyond 145 °C [28], followed by a significant amount of hydrogen fluoride (HF), phosphorus pentafluoride (PF_5) and phosphoryl fluoride (POF_3) from the breakdown of polyvinylidene fluoride (PVdF) binder and electrolyte mainly at 200–300 °C [31,32]. At this moment, temperature becomes exceedingly and uncontrolled, termed as thermal runaway. Eventually, temperature due to exothermic reaction and pressure from generated gases raise rapidly and turns the battery a pressure vessel [33]. Thus, if pressure and gases are not well relieved in a proper way, cell rupture, fire ignition and explosion are inevitable [21].

To avoid the risk of catastrophic failure not to propagate in the module or pack, safety strategies are adopted depending on their outcome. In Ref. [34], these strategies are mentioned as preventive, fail-safe and extinguishing measures. Herein, a critical review on the safety of Lithium-ion battery with advanced technologies is given.

2. Mechanism of thermal runaway

The occurrence of thermal runaway is very tricky and unforeseeable in real applications. Abuse conditions are the chief sources of TR formation such as mechanical abuse (crush, penetration, drop, immersion, rollover, etc.), electrochemical abuse (forced overcharge, over-discharge, short-circuit, etc. [28]), and thermal abuse (fire, thermal shock, overheat, etc. [35]), see the left side of Fig. 1. When the abuse is beyond tolerance, harmful battery's internal reaction is triggered and raise the battery temperature. Nevertheless, state of charge (SOC), electrode materials, electrolyte and separator have great influence in the rate of rising of temperature. The Lithium plating results whenever the battery is overcharged at low temperature (particularly below 25 °C) whereas all forms of a mechanical abuse trigger an internal short-circuit. Thus, at elevated temperature, a series of incidents inside the battery are initiated such as decomposition of the SEI layer, anode – electrolyte reaction, electrolyte decomposition, pressure build-up, separator melt-down, and cathode breakdown. Eventually, these incidents increase battery's internal temperature that later triggers TR. At that moment, TR adds up more heat which in turn burns the electrolyte and ignites fire. The incidents outside the battery include gas evolution flowing through the vent holes with an increasing hissing sound effectuated by the burning of internal battery materials. At high internal pressure, the safety vent cracks to release the gases produced, releases more gases that triggers fire and later explosion.

Charging describes the transfer of electrical energy to the chemical energy of the battery while overcharging is to exceedingly continue to charge the battery beyond its working voltage or applying higher voltage than the specified charging voltage. Ouyang et al. [36] reported that Lithium-ion battery, to some extent, may endure overcharge or over-discharge due to inevitable capacity differences between batteries in the pack, subsequently leading into pitfall to maintain homogeneous SOC of each battery. Alternatively, overcharging may be caused by applying high current densities or aggressive charging profiles [37] through electrodes. Dendritic lithium is the primary outcome emerging on the anode surface influenced by the charging process resulting in damage of the separator and later internal short-circuits. Orsini et al. [38] reported a close agreement between charging current and dendritic formation. In addition to that, larger current densities contributed to the aggressive dendrite formation. The concomitant of dendrite growth was observed to cause domino events such as accumulation of Lithium metal on the anode, decomposition of electrolyte and cathode material leading to a generation of flammable gases. Further, Dolle et al. [41] reported that dendrite grows around and toward the polymer insulator, covers the surface of the polymer and subsequently leads to short-circuits between electrodes. Dendrites are claimed to take place through electro-deposition and electro-dissolution that describe their expansion or shrinkage [42]. With the analytical model developed in Ref. [42], four unique patterns were observed such as suppression (impeded growth), permeable (dendrite covers separator's surface), penetration (growth within separator's layer) and short-circuit (linkage between electrodes). Brissot et al. [43] observed two regimes, effectuated by current densities: dendrites formed on the anode at zero ionic concentrations and high current density, whereas at low current density, local heterogeneities was a key factor. Recent technologies to address the dendrite problem include solid state electrolyte, electrolyte additives to improve SEI layer, and modified current collector [44]. Solid state electrolyte is a futuristic approach as it gets rid of organic and flammable electrolyte, although, low ionic conductivity and production hinder its application. Another alternative is to use a multifunctional electrolyte to enhance the

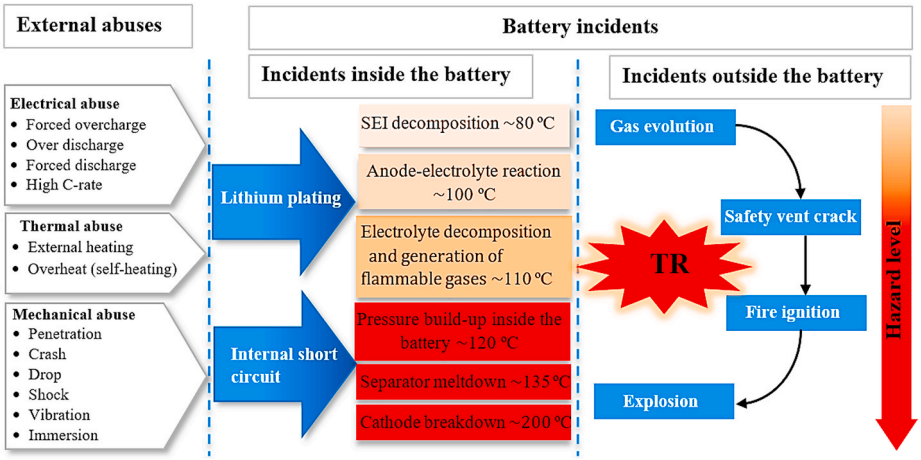

Fig. 1. A chain of reactions after abusing a Lithium-ion battery.

battery safety. Li et al. [44] employed 5% wt additive – (trifluoroethoxy)pentafluorocyclotriphosphazene (TFPN) to developed a multifunctional electrolyte that can suppress dendrite growth and retard a flame. The TFPN additive formed a LiF-rich solid electrolyte layer (SEI) that hampered dendrite growth, improved a reversible and capacity retention of the Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811)/Li full battery. Furthermore, the findings were suggested for the development of future non-aqueous battery.

Overheating is another factor leading to thermal runaway. It is primarily caused by overcharging; external short-circuit as a result of defective wiring; internal short-circuit from defective cells or flaws, and elevated ambient temperature [28]. Ouyang et al. [45] observed a drastic increase in battery internal resistance during overcharging of Lithium-ion battery which led into an increase in surface temperature, triggered thermal runaway and explosion. Similar results were found in Ref. [46–49]. Randolph et al. [50] overcharged a 1Ah prismatic Lithium-ion battery at 12 V, 1 C constant current and the voltage suddenly overshoot to the peak limit when reached 5.5 V and finally exploded when attained 376 K. In Ref. [51], a 100 Wh Lithium-ion battery was charged at 10 V, 1 C constant current and current quickly declined at 368 K. A 6 Ah Lithium-ion battery was charged at 1 C constant current for 5 h ended with explosion [52]. Leising et al. [53] employed 1.5 Ah prismatic Lithium-ion battery to observe the influence of overcharge. They found a separator temperature to reach approximately 132 °C. Moreover, their conclusion agreed with [54] that lower C-rates (<C/5) does not trigger thermal runaway compared to higher C-rates (in cell level). In Ref. [55], a 45 Ah pouch cell was charged at 2 C-rate and immediately exploded 5 min after reaching 115% SOC.

Internal short-circuit is another phenomenon that leads to excessive self-heating and finally triggers thermal runaway. The main causes of internal short-circuit are flaws or penetrations. In Ref. [56] a 2.6 Ah NCM-LCO blend Lithium-ion battery with 25% SOC was revealed to reach a peak surface temperature of 142 °C followed by thermal runaway after a nail penetration test. Noteworthy, at SOC beyond 25%, peak temperatures were lessening, but internal pressures were increasing due to remarkable gas generation. Larsson et al. [55] did an external short-circuit through 7 Ah pouch battery and, within a few minutes, observed swelling, the maximum discharge current of 900 A (128 C) and surface temperature of 100 °C which is crucial for thermal runaway.

Lei et al. [57] used 18650 LMO battery with 100% SOC in external heating tests and found three key stages: gas evolution at ca. 90 °C; onset of a thermal runaway at 110 °C; and exothermic reaction between cathode and electrolyte at 200 °C.

Once TR is onset, the process is accompanied by the formation of flammable gases such H_2, CO, CO_2, CH_4, C_2H_6, C_3H_6, C_3H_8 [39] and O_2 [37,40]. The electrolytic oxidation on the cathode surface leads to CO_2 due to O_2 generation from over-delithiated cathode electrode [58] whereas CO, CH_4, C_2H_4, C_2H_6 are due to reduction on the anode surface [28]. Furthermore, at elevated temperatures from abuse conditions, a severe amount of toxic compounds may be generated such as hydrogen fluoride (HF), phosphorus pentafluoride (PF_5), phosphoryl fluoride (POF_3) due to electrolyte and polyvinylidene fluoride binder decomposition [59]. Other toxic gases are alkyl fluoride, fluorinated phosphorous compounds, alkyl difluorophosphate (OPF_2OR) and dialkyldifluorophosphate ($OPF(OR)_2$) from autocatalytic reaction [60]. Nonetheless, the gas formation may greatly depend on the electrode materials, temperature and state of operation (charge, discharge, overcharge, over-discharge).

Once a battery failure occurs, the uncontrolled heat energy may propagate to neighbouring batteries (thermal propagation) and can cause critical failure to the overall system if there is no proper countermeasure equipped. Normally, Lithium-ion batteries are voltage and temperature-dependent products. In the growth of Lithium-ion technology, there is an evolution of several chemistries which will exhibit different incidental temperatures during their decomposition. Fig. 2 shows the voltage-temperature characteristics of some selected chemistries. From Fig. 2, the effects of overcharge, over-discharge at low and high temperature are depicted. $LiCoO_2$ and $LiFePO_4$ are the unique chemistries having the lowest and highest temperatures for cathode decomposition.

To mitigate the catastrophic damage of the battery as an outcome of thermal runaway, numerous strategies are developed, and some are already utilized to enhance safety. The section below discusses strategies used to improve the thermal stability of the Lithium-ion battery.

3. Safety strategies for suppressing the occurrence of thermal runaway

3.1. Overcharge protection additives

Overcharge is one of the inevitable abuse in EVs. To control this, the battery management system (BMS) maintains the external control of charging and discharging voltage and current of each cell in the pack. However, in large EVs, BMS contributes to enhanced volume, weight, and cost of the EVs. In some moments, BMS malfunctions and introduces thermic effects to the battery pack. Apart from that, BMS cannot control the internal chemical changes inside the battery that effectuate electrical and thermal behaviours. For that case, it is untrustworthy to depend on BMS to provide external protection against overcharge [28].

The redox shuttle additive is an alternative way to enhance battery safety by avoiding internal voltage overcharge. It is a typical electrolyte

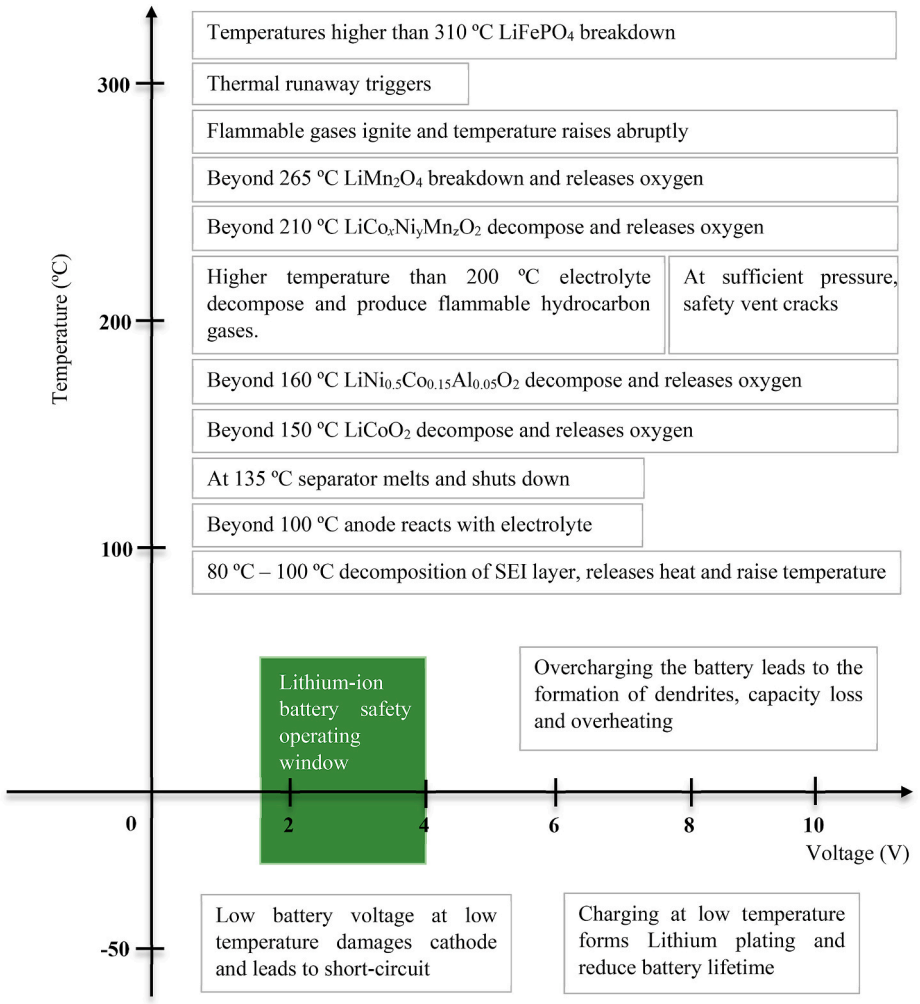

Fig. 2. Operating windows and incidental temperatures of some Lithium-ion chemistries.

additive which halts a charging process at a defined voltage. Redox shuttle can reversibly be oxidized/reduced between electrodes at a certain voltage a bit higher than the end-of-charge voltage and provide inherent overcharge protection. At lower or normal voltage, molecules of the redox shuttle additive become inactive and do not interfere with the internal battery reaction. When the redox voltage is reached, a redox shuttle molecule (A) oxidation start to emerge on the cathode and forms a radical cation ($A^{\cdot+}$), see equation (1). Then, the radical cation diffuses to the anode through the electrolyte and reduces to the initial state A, see equation (2), and transfer back to the cathode for the next redox cycle to complete a reversible reaction. Thus, the electrochemical cycle becomes "oxidation →diffusion→reduction →diffusion", see in Fig. 3. During overcharge, the cathode voltage raises, triggers the redox shuttle reaction, and finally, the cathode voltage latches at the oxidation

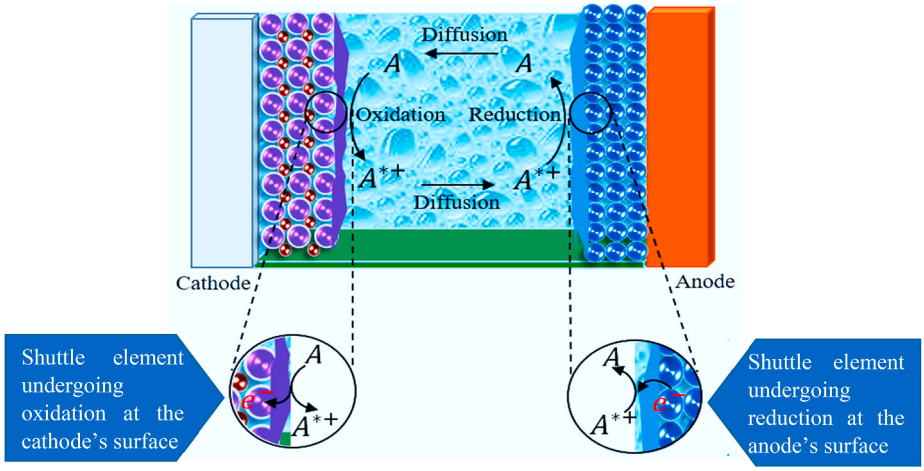

Fig. 3. Operating principle of the redox shuttle for overcharge protection.

voltage of the redox shuttle molecule.

At the cathode:

$$A \rightarrow A^{*+} + e^{-} \quad (1)$$

At the anode:

$$A^{*+} + e^{-} \rightarrow A \quad (2)$$

To acquire efficient performance of the redox shuttle protection [28], suggested the following techniques: (i) deploying a redox shuttle with a slight higher voltage (about 0.3 V–0.4 V [61]) than the end-of-charge voltage but lower than decomposition voltage of electrolyte, (ii) redox shuttle reaction should be reversible in both electrodes' surface, (iii) shuttle molecules should have high coefficient of diffusion and solubility, (iv) shuttle molecule should provide good chemical and electrochemical stability to give a prolonged overcharge protection.

Efforts have been undertaken to find for suitable redox shuttle additives that can sustain at higher voltages. Examples of redox shuttle additives are phenothiazines, triphenylamine, organometallic metallocenes, dimethoxybenzene and their derivatives [61], see Table 1. Currently, the commercialization of 4 V class Lithium-ion battery has effectuated research works to focus on higher potential redox shuttles. Consequently, cathode materials like $LiCoO_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ are claimed to require a higher voltage for redox shuttles to provide proper overcharge protection [62]. In Refs. [62,63], fluorinated redox shuttles 2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole (PFPTFBB) versus Li^+/Li exhibited onset potentials of about 4.3V and 4.43V respectively which found suitable for many 4V class Lithium-ion battery. Alternatively, instead of adding redox shuttles in the electrolyte, Wen et al. [64] proposed a novel method that used a $LiCoO_2$/CuO (95:5 by weight) as a composite cathode for overcharge protection and exhibited a high-potential (up to 5 V vs Li^+/Li) with better anti-overcharge performance. However, Liu et al. [37] suggested tailoring of molecular structures of redox additives to enhance oxidation potentials beyond 4V and make them appropriate for high voltage Lithium-ion battery. Despite that, the failure to respond in heat generation inside the battery is the only bottleneck of redox shuttle since they are triggered at high charging voltage [16].

Table 1
Some redox shuttle additives and their derivatives from published research works.

Abbreviation	Full name of redox shuttle additives	Onset oxidation potential for overcharge protection (V)	Deployed battery chemistry	Ref
TEMPO	2,2,6,6-tetramethylpiperidinyl-oxide	3.52	LFP	[67]
MPT	10-methylphenothiazine	3.74	LFP	[68]
BODTB	1,4-bis(2-methoxyethoxy)-2,5-di-tert-butylbenzene	3.80	LFP	[69]
DBBB	2,5-di-tert-butyl-1,4-bis (2-methoxyethoxy) benzene	3.90	LFP	[70]
DBDB	2,5-di-terbutyl-1.4-dimethoxybenzene	3.96	LFP	[71–73]
TDTN	1,2,3,4-tetrahydro-6,7-dimethoxy-1,1,4,4-tetramethyl-naphthalene	4.05	4V cathodes	[74]
PFPTFBB	2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole	4.30	4V cathodes	[71]
PFPTFBB, 1	2-(pentafluorophenyl)-tetrafluoro-1,3,2-benzodioxaborole	4.43	4V cathodes	[75]
TEDBPDP	Tetraethyl-2,5-di-tert-butyl-1,4-phenylene diphosphate	4.80	LCO, LMO	[76]
$Li_2B_{12}F_xH_{12-x}$	lithium fluorododecaborates	4.90	LMO	[28]

Contrary to redox shuttles, shutdown overcharge additives are irreversible additives that permanently suspend battery operation once triggered in higher voltage. Shutdown overcharge additives perform dual protections: release gas at higher potentials which later operates current interrupting device (CID) that isolates the external circuit; and polymerizing at higher potential onto the surface of the cathode to terminate battery overcharge prior to catastrophic damage [28,37,65]. Examples of shutdown overcharge additives include xylene, cyclohexylbenzene, biphenyl, 3-thiopheneacetonitrile, 2,2-diphenylpropane [28,37,65] and so on. However, shortening of the battery calendar life due to their irreversible oxidation is the major drawback of these compounds.

To sum up, the redox additives are reported to be effective at low current overcharge and for providing a voltage balance between cells in the module whereas shutdown overcharge additives are suitable at higher current overcharging [66]. To date, more researches have based on the technologies of multifunctional battery components such as multifunctional separators (protects separator and overvoltage, see Ref. [107,108]), electrolyte improvers (provide both overcharge protection and flame retardancy, see Ref. [130]), etc. In the future, for better operation in the 5V generation batteries, the redox shuttles should have higher redox potential; high solubility and diffusion; be electrochemically stable with electrodes; have reversible oxidation; higher overcharge protection performance; and be a multifunctional redox compound.

3.2. Overheating protection

3.2.1. Improving cathode materials

The safety of the Lithium-ion battery originates from the materials such as an electrode, binder, electrolyte, separator, and so on. The material science, their chemistry and engineering design of Lithium-ion result in complex activities inside the battery that sometimes lead to thermal runaway [2]. To that end, countermeasures should be initiated to suppress the detrimental internal activities (cut off chain reactions) as a way to enhance battery safety [2,16]. Numerous works have been performed to improve the thermal performance of the cathode materials. Two primary techniques are employed: element substitution and a protective coating.

Element substitution can effectively improve the thermal performance of the layered oxide materials by stabilizing the crystal structure [37]. Researchers have drawn interest on Al to substitute the transition metal like Co, Ni and Mn [2]. Likewise, cations metals such as Co, Mn, and Mg can be employed to partially substitute Ni or Mn in $LiNiO_2$ or $Li_{1.05}Mn_{1.95}O_4$ to enhance their thermal performance [77]. In Ref. [78], Co in a coin $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ was partially substituted by Ni and Al to form $Li(Ni_{(0.33+0.07)}Mn_{0.33}Co_{(0.33-0.2)}Al_{0.13})O_2$. Introduction of Al enhanced better thermal performance when that positive electrode was energized. Liu et al. [37] reported that by employing doping and alloying elements like Ni and Mn in $LiCoO_2$ can significantly enhance decomposition onset temperature and avoid deleterious reactions in elevated temperatures. Consequently, redundant in battery specific capacity was claimed to be a major drawback.

The second method to improve the thermal performance of the cathode material is to apply a protective coating on its outer surface. This protective coat is a thin layer and Li^+ conducting compound which primarily protects cathode's surface from direct contact with an electrolyte, thereby preventing side reactions, phase transition, enhance structural stability, and reduces the disorder of cations in the crystal sites [2,16,37]. Thus, incorporation of protective coat leads into reduced heat generation. The materials for coating the cathode can either be

chemical or inert thermal. Example of chemical inert materials are inorganic films [MgO, Mg_2TiO_4, ZnO, ZrO_2, ZrFx, ZrP_2O_7, Li_2ZrO_3, SiO_2, SnO_2, TiO_2, TiP_2O_7, $NaAlO_2$, Al_2O_3, $AlPO_4$, AlF_3, FeF_3, etc.], organic films [poly(diallyldimethylammonium chloride)], and protective film [2,37,79]. Fluoride coating materials have good performance due to their inertness which reduces heat generation. For example, in Ref. [80] the onset thermal runaway temperature of AlF_3-NCM was delayed by 20 °C. Likewise, solid oxides materials have better trends in protecting the cathode. The deployment of SiO_2 in Ni-rich $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode materials showed a reduction in heat generation by 35% and lessened degradation of active core material [81]. Phosphate coating materials are the promising materials due to their strong covalent bonds which enhance thermal stability. In Refs. [82], cycling tests were undertaken with $Ni_3(PO_4)_2$-coated $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ at 55 °C. Results showed a reduction in chemical attacks by hydrogen fluoride (HF) on the coated cathode and serrated on the pristine cathode.

Thermal-sensitive coating materials are currently considered as promising materials to protect the cathode electrode. These coating materials have a positive temperature coefficient which stops electrochemical reactions, side reactions and shut-down the battery circuit at elevated temperatures via polymerization. Examples of recently utilized thermal inert materials are poly(3-decylthiohene) (P3DT) and poly(3-octylthiopene) (P3OT) [83]. Noteworthy, the better thermal performance of these thermal-sensitive materials have been reported in LCO only. The P3OT used by Ji et al. [83], inserted between Al and $LiCoO_2$ layer to form a sandwiched Al/P3OT/$LiCoO_2$ showed a strong positive temperature coefficient behaviour and capability to shut-down the electrochemical reactions at 90–100 °C before thermal runaway. Xia et al. [84] claimed that P3DT-coated $LiCoO_2$ could stop the electrochemical reaction at temperature ca. 110 °C. (P3DT)-modified separator with self-actuating overcharge protection mechanism for $LiFePO_4$ –based lithium-ion battery.

Electrode partition is also regarded as a promising technology in protecting electrodes from an internal short circuit in moments such as vehicles crash accidents. In this technology, battery electrodes are designed to break and separate into parts after indentation, which results in electrical isolation. The exciting innovation is that the broken part of the electrode remains without electricity before puncturing the separator. Therefore, it reduces the risk of internal short circuit and onset of thermal runaway once it reaches to the opposite electrode [85]. In summary, enhancing cathode safety is crucial for the battery performance and protection. Element substitution, coating and electrode partition are the promising strategies employed for enhancing the safety of cathode. These strategies may open a new avenue for suppressing the TR, however, the presence of their side reactions should be well investigated.

3.2.2. Improving anode materials

SEI layer plays crucial roles in the performance of anode. Its thermal decomposition can aggravate the safety of the anode and battery system as a whole. So, recently, the goal has been set to develop artificial SEI layer to improve the mechanical and thermal performance of the SEI layer. These enhancements lead to minimizing the irreversible capacity by mitigating electrochemical reactivity with electrolyte [86]. Mild oxidation, deposition of metals, and polymerization (or coating) are among the recent techniques employed to improve the SEI layer. Ding et al. [87] found that an AlF_3-coated graphite anode has higher initial discharge capacity, better cycle life, higher capacity retention and improved rate performance when compared to an uncoated graphite anode. They argued that a more stable and conductive SEI layer is formed on AlF_3-coated graphite particles, which improves the performance of graphite anode. However, $Li_4Ti_5O_{12}$ (LTO) is considered as a promising coating material for the producing artificial SEI layer in various anode materials. For example, LTO-coated meso-carbon microbeads (LTO-MCMB) [88], LTO-coated graphite (LTO-G) [89,90], LTO-coated carbon microbeads (LTO-CMB) composites [91], LTO-coated carbon nanotubes (LTO-CNTs) [92], a composite of LTO and multilayered carbon nanotubes (CNTs) co-doped with nitrogen (N) and boron (B) (B,N-CNT), denoted as N–B–C-LTO [93], LTO/carbon nanotubes/graphene (LTO-CNT-G) [94] etc. By modifying the surface structure of anode, Kim, et al. [95] used oxygen-deficient black titanium oxide (TiO_{2-x}) to modify the surface of graphite to achieve better performance at fast charging. With $LiCoO_2$, the artificial SEI revealed a better cycling and capacity retention at 5C fast charging, which seems to be a futuristic strategy to mitigate thermal runaway. Overall, SEI layer play an important role in the electrochemical performance of anode electrode. So, in the wide use of Lithium-ion battery with a liquid electrolyte, enhancing the mechanical and thermal performance of an artificial SEI layer could provide a better way to a safer anode and battery as a whole.

3.2.3. Thermally protective separators

Separator is the vital element in the function and safety of the Lithium-ion battery. Conventional separator materials include paper, gel, or polymer, whereby polymer is the most used separator material. The unique attributes that favour polymer to be used in Lithium-ion battery include their micro-thickness (20–25 μm) that provide lower internal resistance, higher current, power and energy densities; small pore size (<1 μm) to block penetration of electrode active materials and conducting additives; sufficient pore density or porosity (40–60%) to reserve sufficient liquid electrolyte to provide enough ionic conductivity; and excellent mechanical and chemical stability [96]. So, to characterize an effective separator, a set of parameters need to be effectively utilized. See Table 2 for the selected list of parameters according to the United States Advanced Battery Consortium [97].

In the function of a Lithium-ion battery, separator prevents a direct electrical connection between electrodes by providing mechanical separation and high electrical resistance during battery operations. However, in all kinds of batteries, there exists a small leakage current passing through a separator, called “self-discharge”. A self-discharge varies greatly with battery chemistry, age, cycling, and storage temperature. On the other side, the separator serves as a medium for transfer of Li^+ between electrodes due to its porous structure which reserves sufficient liquid electrolyte and provides enough ionic conductivity. When the battery temperature rises close to the separator melting point, separator pores tend to shut down, a process known as “separator shutdown”. The temperature that triggers separator shutdown depends on the melting point of separators, e.g. 165 °C for PE and 135 °C PP [98]. During the separator shutdown, the medium for ionic conductivity and electrochemical reactions are partially blocked. Hence, the battery temperature does not drastically drop. Consequently, the separator must maintain its mechanical integrity; otherwise, a separator may shrink, collapse, and cause internal short-circuit that generates enormous heat energy and finally result in a battery explosion. Therefore, minimizing separator shrinkage and delaying the collapse at elevated temperature are the

Table 2
Selected parameters of separator materials, adopted from Ref. [97].

Parameter	Goals
Sales Price	1.00 US$/m^2
Thickness	<25 μm
Pore size	<1 μm
Puncture strength	>300 g/25.4 μm
Permeability (MacMullin Number)	<11
Gurley	<35 s/10 cm^3
Thermal stability	<5% shrinkage after 60 min at 90 °C
Purity	<50 ppm H_2O
Tensile strength	<2% offset at 1000 psi
Moisture Content	<50 ppm
Skew	<2 mm/m
Shut down temperature	100–110 °C
Structural stability	≥200 °C
Chemical Stability	Stable in the battery for 10 years

goals of every researcher.

New designs such as triple-layered polymer separators whereas the PE layer is sandwiched between two PP layers (PP/PE/PP developed by Celgard LLC) have already commercialized. This design extends the time between separator shutdown and shrinkage. At temperatures ca. 135 °C, PE partially melts and undergoes separator shutdown whereas PP maintains mechanical integrity to avoid internal short-circuit. Despite that advantage, PP/PE/PP has a narrow temperature margin, i.e. collapse temperature is similar to that of PP [2]. Alternative materials with higher thermal stability such as ceramic [99], polyethylene terephthalate (PET) [100], polyimide (PI) [101], non-woven membrane [102], polymer electrolyte employed as a separator [103], etc. are still under research, although, they are challenged by high cost and inefficiency manufacturing efficiency [104].

In recent years demand of higher capacity lithium-ion batteries has shown an uptrend following the steady growth in portable electronics and electric vehicles. A common strategy employed to achieve higher capacity is by lowering the thickness of separators. This has led to the fabrication of separators with 16 and 20 μm used in higher capacity cylindrical cells (>2.0 Ah), and 9 μm in lithium-ion gel polymer cells [105]. Unfortunately, reduction of separator's thickness introduces safety challenges. Typical properties of some manufactured separators and manufacturers are listed in Table 3.

Thermal protective material like paraffin wax microspheres can be used to protect anode and separator by producing a protective polymer layer between anode and separator when a battery temperature reaches a critical value and shutdown the battery permanently [108]. Researchers have gained much interest in studies of separators with thermal-triggered flame-retardant behaviours [109–111]. The flame retardants are enclosed in a polymer separator to avoid direct decomposition of the retardants into the electrolyte and adverse effects on battery performance. At elevated temperatures in the lithium-ion battery, the polymer separator melts, releases flame retardants, and finally halts the burning of the flammable electrolyte.

A multi-functional separator is another technique to avoid overstressing a separator. Ai et al. [112] and Li et al. [113] soaked an electroactive poly(3-decylthiophene) (P3DT) polymer into a commercial porous separator (Celgrad 2500) and use it as a potential switch to reversibly protect overcharging of a lithium-ion battery. The P3DT-modified separator showed an onset-voltage of 3.7 V with LFP battery and effective protection of voltage runaway up to 3C overcharging without hampering charge-discharge performance. Nonetheless, the existing commercialized separators still have the remaining challenges, such as withstanding voltage and current. It should be noted that most of these separators were firstly designed to work under low voltage (<20 V) and low system current (<10 A). Thus, if these separators need to be used in larger batteries with higher voltage and current, the tolerance and separator shutdown function may or may not function.

3.2.4. Flame retardants additives

In the early stages of the thermal runaway, the heat-releasing reaction is triggered, which, in turn, generates gas inside the battery and causes the internal pressure to increase. Electrolyte is the most thermally sensitive component of the Lithium-ion battery formed by a solution of Lithium salt such as $LiFPO_4$, $LiClO_4$, $LiPF_3(CF_2CF_3)_3$, $LiPF_6$, $LiAsF_6$, $LiBF_4$ [16], $LiSO_3CF_3$, $LiN(SO_2CF_3)_2$, $LiC(SO_2CF_3)_3$, and $LiPF_3(C_2F_5)_3$, [114]; and organic solvent like dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), or diethyl carbonate (DEC) ethylene carbonate (EC), ethyl-methyl carbonate (EMC) [28], and propylene carbonate [21]. Concerns such as poison ($LiAsF_6$), explosion ($LiClO_4$), expensive ($LiPF_3(C_2F_5)_3$), problematic on the anode ($LiBF_4$) and cathode ($LiC(SO_2CF_3)_3$), poor conductivity ($LiSO_3CF_3$), have made a $LiPF_6$ a compromise [114]. Traditional electrolyte employs alkyl carbonates as solvents and $LiPF_6$ as Li-salt. However, the low-temperature performance of organic solvents presents a serious concern. For example, the flashpoints of DMC, EMC and EMC are 15 °C, 22 °C and 33 °C respectively [115]. Immediately after the onset of thermal runaway, exceedingly temperature is generated that decomposes electrolyte into flammable and toxic gases (HF, POF_5 and POF_3) which in turn degrade cathode and produce more oxygen. At sufficient amounts of temperature, oxygen and flammable gases, the battery becomes prone to ignite and violently explode.

To overcome this problem, the thermal stability of the electrolyte needs to be chemically improved via additives, modifying the molecular structure of existing compounds or using alternative solvents with higher thermal stability. The former method employs flame retardant additives (FR) to lower the flammability of the electrolyte. The principal characteristics of the FR additive include higher flash point than organic solvents, inert, not impede the battery performance [4], electrochemically stable in both electrodes [4,16] and more efficient in retarding the electrolytic flame [16]. So far, researches of FR additives employed in liquid electrolyte focus on organic phosphorus compounds or halogenated compounds. But halogens are dangerous to human health and environment friendliness, making organic phosphorus compounds the futuristic candidates. Examples of organic phosphorus compounds are trimethyl phosphate (TMP), dimethyl methyl phosphate (DMMP), 4-isopropyl phenyl diphenyl phosphate (IPPP), tris(2,2,2-trifluoroethyl) phosphite (TTFP), triphenyl phosphate (TPP), cresyl diphenyl phosphate (CDP), diphenyloctyl phosphate (DPOF), alkyl phosphate,

Table 3
Typical properties of some commercialized separators.

Manufacturer	Materials	Layers	Properties					Trade name	Ref
			Melt temperature, (°C)	Thickness, (μm)	Gurley, (s)	Ionic resistivity, (Ω cm^2)	Porosity, (%)		
Celgard LLC	PE [a]	Single	135	20	22	2.23	43	Celgard	[106]
	PP [b]	Single	165	25	24	2.55	40	Celgard	
	PP/PE/PP [c]	Multiple	135/165	20	20	1.36	42	Celgard	
	PP/PE/PP [d]	Multiple	135/165	25	23	1.85	42	Celgard	
Asahi Kasai	PE	Single	138	25	21	2.66	40	Hipore	[106]
Tonen	PE	Single	137	25	26	2.56	41	Setela	[106]
Entek membranes	PE	Single	135	25	–	–	38	Teklon	[106]
Degussa	PE/Al_2O_3	Multiple	–	25	–	–	–	Separion	[97]
	Ceramic/PET/ Ceramic	Multiple	220	25	–	–	>40	Degussa	[107]
Exxon	PE	Single	135	25	–	–	36	Tonen	[107]

[a] Celgard 2730.
[b] Celgard 2400.
[c] Celgard 2320.
[d] Celgard 2325.

hexamethylphosphoramide (HMPA), tributylphosphate (TBP), tris(2,2,2-trifluoroethyl) phosphate (TFP) [12], bis(2-methoxyethoxy) methylallylphosphonate, (ethoxy)pentafluoro cyclotriphosphazene, ethylene ethyl phosphate [37], hexamethylcyclophosphazene (HMPN), triethyl phosphate (TEP) [4], etc. The flame retardation mechanism of organic phosphorus compound lies on the chemical scavenging process, whereas phosphorus-containing free-radical species are produced during combustion [37] and act in the gas phase. Then, the *H and *OH radicals produced from the burning electrolyte inside the battery necessary for supporting combustion can be blocked by the phosphorus-containing free-radical species such as *PO and *PO_2 [108]. Thus, the chain reactions of the oxidation of HC in the gas phase are interrupted and minimizes heat generation, which is termed as flame retardation [116]. For example, equation (3) shows the introduction of TPP as an FR additive and generation of *PO free radicals, and their reactions with *H and *OH radicals in (4) and (5), respectively [37].

Introduction of TPP as FR additive:

$$TPP \ \ heat \rightarrow *PO \tag{3}$$

Reaction of *PO with *H:

$$*PO + *H \rightarrow HPO \tag{4}$$

Reaction of *PO with *OH:

$$*PO + *OH \rightarrow HPO_2 \tag{5}$$

For better cycling performance and enhanced thermal stability, the weight percentage of FR in the electrolyte is recommended to less than 20% [4]. For example, 10 wt% DMMP [28], 10 wt% CDP [117,118], 0.5–10 vol% tris(trimethylsilyl) phosphite (TMSP) [119], 10 wt% ethylene ethyl phosphate (EEP) [120], etc. Unfortunately, the addition of FR in the electrolyte comes at the expense of battery performance, such as reduced ionic conductivity and battery cycling. One of the strategies used to minimize this is to confine the FR into the separator where they can only be released into electrolyte once a certain temperature is reached. In Ref. [109], a nonwoven electrospun microfiber separator was confined with TPP flame retardant and binded by poly (vinylidene fluoride–hexafluoropropylene) (PVDF-HFP) shell. When the combustion temperature reached approximately 160 °C (melting point of TPP), TPP were then released in the electrolyte. This strategy showed no hampering on battery performance.

To further address the trade-offs of FR, researchers have focused on modifying the molecular structure of solvents through (i) partial fluorination of the alkyl phosphates to enhance flame retardancy, electrochemical stability of SEI layer, and ion conductivity of the formed electrolyte, examples of modified FRs are tris(2,2,2-trifluoroethyl) phosphate (TFP), bis(2,2,2-trifluoroethyl methylphosphate) (BMP), and (2,2,2- trifluoroethyl diethyl) phosphate (TDP) [122], (ii) utilizing multifunctional compounds capable of forming protective film and flame retardancy, for example, bis(2-methoxyethoxy) methylallylphosphonate can polymerize and form a stable SEI layer [37], ethylene ethyl phosphate (EEP) [120] and resorcinol bis(diphenyl phosphate) (RDP) [121] provide both overcharge protection and flame retardancy, triphenyl phosphate (TPP) captures particulate matters with high efficiency and extra-low pressure drop and retards a flame [123]. Another way to enhance the thermal stability of the electrolyte is to change salt and solvents with ones having better thermal performance and compatibility with electrodes. For example, new salts are: Li bis (oxalato) borate (LIBOB), $LiPF_3(C_2F_5)_3$ (LIFAP), Lithium trifluoromethanesulfonate (LiTf), Lithium bis(trifluoromethane sulfonimidate) (LiTFSI), Lithium bis(trifluoromethanesulfonimide) (LiBETI) [124], Lithium difluoro(oxalato)borate (LiDFOB) [125] and $LiN(SO_2F)_2$ [37]; the new and promising solvents under studies are: trimethyl phosphate (TMP) [126], 2,2,2-Trifluoroethyl N-caproate (TFENH) [127], esthers, for example, methyl acetate (MA), ethyl acetate (EA), ethyl proprionate (EP), ethyl butyrate (EB), methyl proprionate (MP), methyl butyrate (MB), propyl butyrate (PB), and butyl butyrate (BB) [128].

The new 'salt concentrated electrolyte' developed from alternative salt and FR is considered as a future fire suppressing inorganic electrolyte. For example, $LiN(SO_2F)_2$ as salt and TMP as a sole solvent [37]. Apart from being an alternative salt, $LiN(SO_2F)_2$ serves as an artificial SEI layer to stabilize the electrochemical performance. Thus, multifunctional electrolyte is a promising strategy to improve the performance and safety of the Lithium-ion battery. On the other hand, a proportion of FR of less than 10% is yet hindering the efficacy of FR. Hence, a future fire suppressing inorganic electrolyte should get rid of this challenge.

3.3. Battery management systems

The heat emerging in Lithium-ion battery during operation is generated as a result of internal resistance and electrochemical reactions. The primary battery operations are charging and discharging. Thus, in moments like overcharging more heat energy is generated and may tend to propagate to adjacent batteries inside the pack during dissipation. If not well managed, the accumulated heat can trigger thermal runaway and later can cause explosions. Battery management system (BMS) equipped inside the battery pack primarily serves to protect the battery against overcharging and over-discharging to extend the life cycle. Additionally, it monitors the SOC (remained charge inside the battery), state of health, state of function and state of safety (by checking defective insulation, loose connections, short circuit, and faulty battery to be replaced). BMS works in cell and pack level as well (see Fig. 4 for parameters in each activity). For a single battery, a BMS can be incorporated inside the battery. The secondary function of the BMS is to balance individual battery energy inside the pack, monitor temperature and provide real-time information to external devices such as electric motor, charger, displays and data loggers.

In the battery pack, under certain circumstances, some battery may experience overcharging or over-discharging during the charging/discharging process, respectively. This, when prolonged over time, makes some batteries weaker than others, introduces unbalanced batteries, limits the useable capacity of the battery pack, decreases energy and lessens the life cycle of the pack [129]. The passive technique is the simplest, cheapest and easiest for battery energy equalization whereby the excess energy is dissipated through shunt resistor without extending system run time. Active techniques such as outlier detection algorithm [129], shunt transistor equalization method [130], voltage based balancing strategy (VBBS), SOC based balancing strategy (SBBS), capacity-based balancing strategy (CBBS), hybrid-based balancing strategy (HBBS) [131], are seen to be promising for enhancing battery energy equalization. Active techniques are more sophisticated techniques, redistributes charge between batteries during cycling, increase system run time, and decrease the heat generated during energy equalization. Moreover, other challenges are temperature gradient, cost and reliability.

Monitoring of SOC in BMS is crucial for avoiding overcharge/over-discharge in the pack. Challenges and trade-offs in the estimation of SOC include the variety of battery chemistries which behave differently in models, variation in battery temperature, capacitance, internal resistance, ageing, loading, and frequent charging and discharging. For example, initial conditions for SOC estimation algorithms in electric vehicles are found while recharging the vehicle in stationary. However, in real applications, the battery is discharged and recharged (through regeneration) while in motion. This hinders availability of accurate initial conditions for SOC estimation algorithms [132], which in-turn introduces and accumulates errors over cycles. SOC estimation techniques are divided into three groups, i.e., data-driven, adaptive and hybrid methods. Data-driven techniques include Coulomb Counting (CC), Open circuit Voltage (OCV) and Impedance Method [133]. Adaptive techniques are Linear Kalman Filter(LKF) [134], Artificial

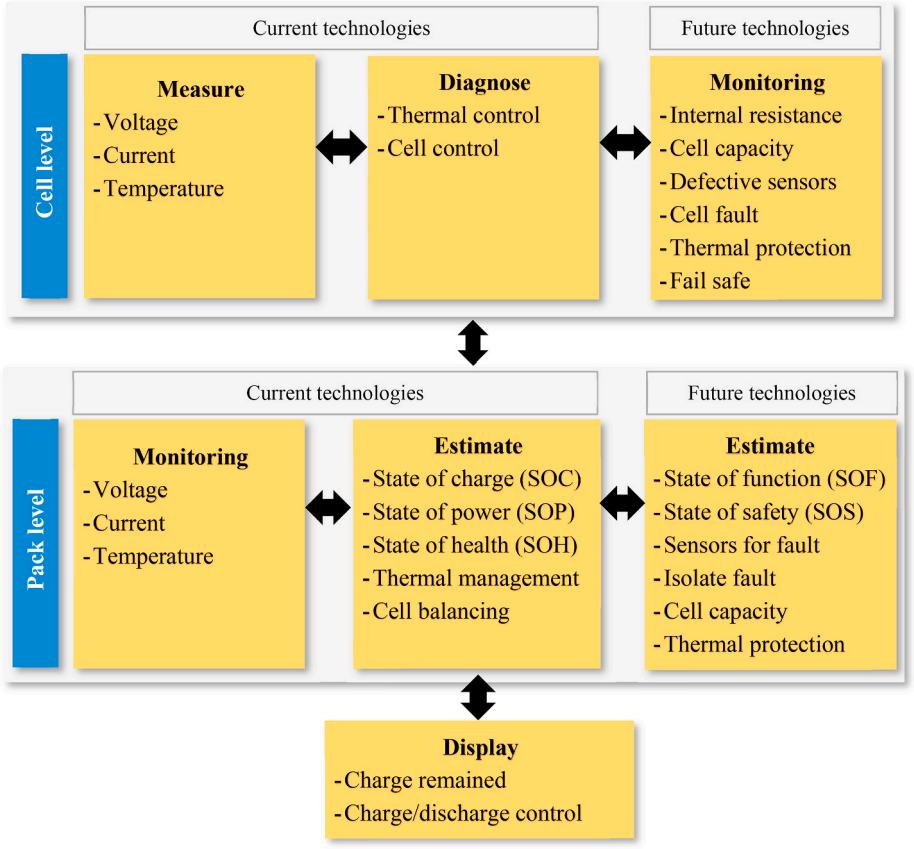

Fig. 4. Functions of the BMS in cell and pack level for the current and future technologies.

Neural Network (ANN), Fuzzy Logic Methods, and Support Vector Machine (SVM) [135]. Hybrids combine data-driven and adaptive techniques, are regarded as future methods to estimate SOC. These include Extended Kalman Filter (EKF).

Unscented Kalman Filter (UKF), Fading Kalman Filter algorithm (FKF), Strong Tracking Cubature Extended Kalman Filter (STCEKF), Particle Filter (PF), sliding mode observer (SMO), H-infinity observer, etc.

SOH describes the aging condition of a battery when compared to a fresh one [136]. Capacity degradation can lead to accident-proneness if not well monitored. So, BMS must estimate SOH to quantify the remaining usability of the battery. However, SOH estimation is very challenging due to its dependence on SOC and internal resistance. SOH can be estimated based on empirical models (Genetic Algorithm (GA), Recursive Least Square (RLS), and Multivariate Adaptive Regression Splines), electrochemical models, and data-driven models (support vector machines (SVMs), Bayesian Networks, Autoregressive Models, and Gaussian Process Regression (GPR)).

To sum up, BMS is a crucial element in the safe operation of the battery pack. Its reliability can ensure the excellent performance and longevity of the battery pack. The existing obstacles such as accurate estimation, the dependence of parameters and impact of real-time operation need proper addressing for safer usage of the battery pack. Moreover, in case battery temperature goes out of control (beyond onset of thermal runaway), currently, there is no proper measure to stop the fire such as to trigger fire extinguisher. BMS as the primary equipment for temperature measurement and control, could have the role of initiating fire extinguisher prior to the catastrophic failure. Moreover, the future technologies, both in cell and pack levels as illustrated in Fig. 4, could be key for the safety of the battery pack in the future.

3.4. Battery thermal management system

Battery thermal management system (BTMS) regulates the temperature within the battery pack in high and low-temperature environments to avoid overheating and improve the electrochemical performance of the battery, respectively [137–139]. In addition to battery cooling, BTMS ensures the temperature homogeneity and optimum operating temperature in the pack. Lowering the internal resistance can be an appropriate method to reduce battery heat generation. However, the heat generated from electrochemical reactions is unavoidable. So, battery thermal management system has been applied as a key and integral part to preserve the battery temperature in an optimal range. The main criteria for the BTMS to suit in the automotive application include low cost, lightweight, reliable, compact, easy packaging and maintenance. Based on the ambient temperature and desired conditions where BTMS need to be applied, the BTMS can either perform cooling (in hot weather beyond optimal temperature to avoid extreme damage or accelerated degradation), heating (in cold weather below optimal temperature to prevent damage due to fast charging), insulation (to reduce spike temperature difference between inside and outside the battery pack during hot or cold weather) and ventilation (to discharge the hazardous gases). It should be noted that most Lithium-ion batteries cannot be fast-charged at a temperature of less than 5 °C and cannot be charged at all at a temperature below 0 °C.

A conventional BTMS used for cooling employs air for natural cooling or fan/blower for forced air cooling [140–143], see Fig. 5 for air cooling. On the other hand, a liquid such as water, glycerol, mineral oil, refrigerants, oil, acetone, etc. have been used for direct contact [144] and indirect contact [145] cooling. Other techniques employed in liquid cooling are phase change materials [146,147], heat pipe [148,149] and combinations. Liquid cooling may involve tab or surface cooling. Fig. 5a and b are examples of surface cooling through indirect contact. In tab

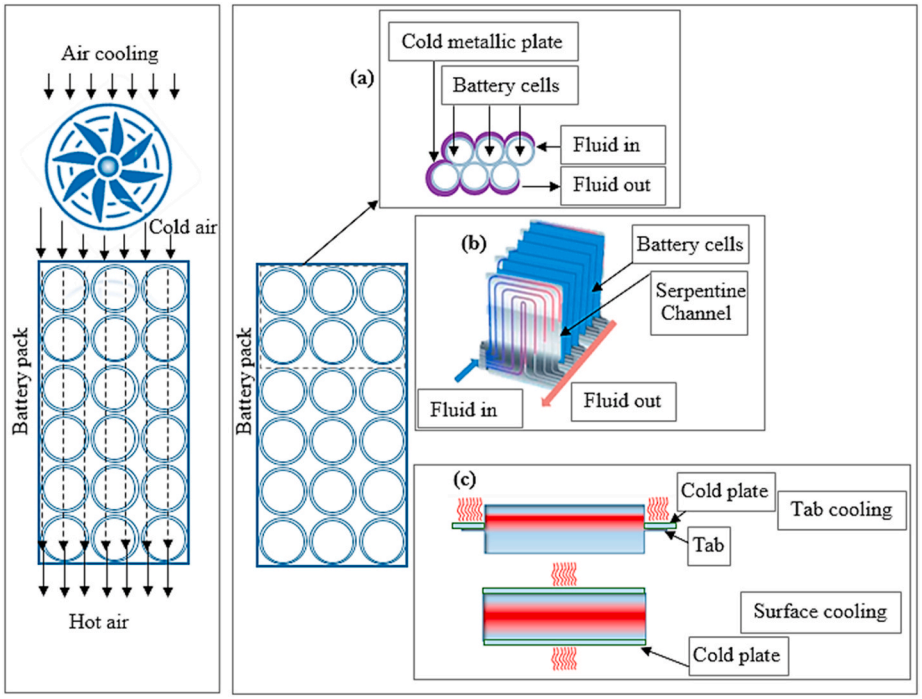

Fig. 5. Air and liquid thermal management systems (a) layout of the surface cooling by using a cold metallic plate for cylindrical batteries, (b) arrangement of serpentine channels in a pouch and prismatic batteries, and (c) tab and surface cooling of Lithium-ion battery.

cooling (Fig. 5c), there is a risk of coolant leakage, which may lead to external short circuit of batteries. Apart from the cooling media, BTMS also contains a controller and in-built algorithms to control the performance of the BTMS by adjusting the operational parameters. In air cooling, influencing parameters are air flow rate [141,150], battery spacing within a module, module-to-module spacing, module-to-enclosure spacing [151], and module spacing at the inlet and outlet, and optimal power consumption [152] and cost accrued.

Moreover, air path flow direction [153–155], enclosure design and battery layout [156] play a crucial role in the cooling performance of the BTMS. However, the low thermal conductivity of air hampers the performance of the BTMS to cool a battery pack in a hot environment, hence compromising the safety of the battery pack [157]. Alternatively, the battery pack can be cooled by circulating the liquid coolant via jackets, heat pipe or cold plate to utilize the advantages of higher heat capacity and thermal conductivity. Despite the higher heat capacity, thermal conductivity, efficiency (3500 times that of air cooling [157]) and lower parasitic power consumption (up to 40% [158]) of liquid media, the effectiveness depends on the liquid behaviour, technique and specific application. For example, a cold plate can be used in applications with limited space such as electric vehicles. Thus, to achieve better cooling with cold plate, critical parameters like channel geometry (square, rounded corners, diamond-shaped and elliptical) and channel configuration (the root of coolant such as serpentine, parallel and multi-channel) need to be optimized [157].

To date, air and liquid cooling systems have been commercialized and employed to cool battery packs in electric vehicles. Examples of electric vehicle models and their type of cooling systems are shown in Table 4. The direct immersion of battery in liquid coolant has been performed by XING Mobility whereby a 3 M Novec 7200 Engineered Fluid was used as a coolant [159]. The coolant was used for heat transfer, fire suppression and supercomputer cooling.

A few years ago, new approaches have emerged and studied including thermoelectric coolers, thermo-acoustic refrigeration, magnetic refrigeration, or by combining the advantages of several techniques, e.g., liquid and phase change materials, heat pipe; and phase change material. Currently, there are some cell-phones contain heat pipes with paraffin wax inserted inside. In normal condition, paraffin is semi-viscous solid. But in elevated temperatures, paraffin wax converts to liquid and flows into the heat pipe loop by gravity or capillary phenomenon. During the flow of paraffin wax, the heat absorbed from the battery is then dissipated by the condenser located away from the battery. Of great interest is that cell-phones' pouches and plastic packs with phase change materials have already commercialized and can be utilized in hot and extremely cold areas to cool and warm the battery, respectively.

Table 4
Examples of battery thermal management system used in electric vehicles, some examples are adopted from Ref. [159].

Model	Battery structure	Battery thermal management system and type of coolant
Nissan LEAF	Pouch	Air cooling
Toyota Prius	Prismatic	Air cooling
Volkswagen ID.3	Pouch	Air cooling
Tesla Model S	Cylindrical	Indirect liquid cooling through cooling metallic plate and water-glycol as coolant.
Porsche Boxster	Pouch	Indirect liquid cooling through cold-plate and water-glycol as coolant.
Chevrolet Volt	Pouch	Indirect liquid cooling through serpentine and water-glycol as coolant.
Fiat 500e	Prismatic	Indirect liquid cooling through a cold metallic plate
BMW i3	Prismatic	Indirect liquid cooling through bottom cold plate and refrigerant as coolant
Audi A3 e-tron	Prismatic	Indirect liquid cooling through bottom cold plate and refrigerant as coolant

3.5. Safety devices

3.5.1. Thermal fuse

A thermal fuse is a protective device comprised of a wire with specific alloys, resistance and thermal characteristics which is intended to melt when a pre-set current passes through it. For the thermal fuse to

melt, the current should exceed the pre-set value and abruptly pass through the fuse element. In most cases, this happens during a short-circuit where a huge amount of current suddenly flows out of the battery. Whenever short circuit current passes through the fuse element, excessive Joule heat is generated, which in turn melts the fuse element and shutdown the Lithium-ion battery. The melting temperature of most thermal fuses is 30–50 °C above the battery working temperature. However, the thermal fuse is incapable of mitigating the thermal runaway at high voltage [2].

3.5.2. Positive temperature coefficient (PTC)

Positive temperature coefficient (PTC) is the kind of protective device whose resistivity increases with temperature. The primary function of this device is to protect Lithium-ion battery against high currents due to external short-circuit or overcurrent and over-temperature, and hence, avoids thermal runaway. The device is made up of a ceramic PTC and a composite of polymer and conducting materials. Example of this PTC is polyswitch polymeric positive temperature coefficient (Polyswitch-PPTC) developed by Littelfuse attributed by a resettable, wide range of form-factors (strap, disc, surface-mount, weldable and reflowable), wide thermal cutoff temperature (72–90 °C) and high working voltage and currents from 6 A to 20 A at room temperature. Also, PolySwitch disc and metal hybrid polymer-thermal activated (MHP-TA) devices are nowadays equipped in cylindrical (18650) and prismatic Lithium-ion batteries. During normal operations of Lithium-ion battery, PPTC behaves like a low-value resistor that consumes little electrical power and slightly warm. Once a fault occurs, PPTC drastically raises its resistance and induces much heat from Joule's heat and opens the load circuit. After a short while, temperature and resistance drop and then PPTC restores the circuit, termed as automatic resettable. PPTC varies in holding voltage and carrying current from manufacturers, and unfortunately, this information is not indicated in battery specifications. Probably, mismatching of thresholding voltage, carrying current and operating voltage and current in PPTC could be the source of its failure. The report of National Aeronautics and Space Administration (NASA) [160] disclosed the effective protection of PTC in a single Lithium-ion battery and failure in certain series and parallel connections. That is, in a module with multiple batteries, once a PTC opens (say due to overcharging) the extreme load is imposed on the remaining batteries. In addition to that, materials and contact resistances between the Lithium-ion battery rolls, PTC and safety vents are the significant factors that accelerate Joule's heat in the positive terminal [161]. Consequently, thermal runaway can be triggered and cause catastrophic damage to the module. Alternatively, the battery management system (BMS) may provide sufficient protection by monitoring each battery voltage, although for large battery pack BMS becomes complicated and expensive.

3.5.3. Current interrupting device (CID)

A current interrupt device (CID) is typically used to protect by interrupting the battery circuit when undesired excessive internal pressure emerges inside a Lithium-ion battery. Whenever an adverse condition occurs (for example, over-temperature, short circuit and overcharge) a significant amount of internal gases, depending on the chemistry, capacity and abuse level, is generated which can compromise the safety of a Lithium-ion battery. For example, the CID employed in cylindrical 18650 LCO battery is comprised of six vent holes to allow passage of gases to the surrounding. This CID is placed and connected at the backside of the PTC by the welding point. The Aluminum sheet from the cathode layer is then linked at the bottom of CID to allow current to flow to the external circuit.

Limitations such as internal battery space, the material of the battery case, etc. have been hindering the usage of CID in configurations like pouch battery [162]. The soft case of the pouch, to some extent, have been utilized to safely release the internal pressure; however, the remaining challenge is how to protect the propagation of the damaged battery not to affect the adjacent battery. In cylindrical and prismatic Lithium-ion batteries, CIDs are widely used. Despite their usage, poor safety behaviour has been claimed from different works [163,164]. The work in Refs. [163] reported that CIDs failed to operate in multi-battery configurations under overcharge and external short circuit tests. The main reasons were internal battery heating, melting of a separator and softening of the battery seals due to burning of PTC before triggering of CID. Other factors are unclear rupture of the venting disc (partial interruption of the current path) and short circuit between high potential terminal and grounding system (through vibrations) [163]. Therefore, PTC or CID can interrupt the circuit during adverse conditions; however, they cannot cool the battery from local hot spots and elevated temperature from separator shut down (due to increased ohmic resistance) which, in turn, triggers thermal runaway. In future, analyses of materials and internal contact resistances, arc and vibration analysis, integration or usage of CID opening signal to trigger cooling system, protection in multi-battery configurations are essential. To eradicate the failure of CID in multi-battery configurations, the number of batteries, delivered current and voltage (as CID operation depends on current and voltage) should carefully be selected to avoid hazards.

3.5.4. Safety vent

Once the primary safety device such as PTC or CID fails to provide protection, the safety of the Lithium-ion battery is aggravated. So, the chain reactions such as a breakdown of the SEI layer, disruption of the electrolyte and electrodes and reactions between them, proceed faster, trigger thermal runaway [165] and generated enormous gas and pressure. Thus, a safety vent, designed to release dangerous internal gases and pressure before rupture of the steel can, is activated. Generally, a safety vent is made up of aluminum alloy such as Aluminum-Ferrum Alloy [166] due to its excellent corrosion resistance and elongation performance. Fig. 6a shows an example of a safety vent employed in a 18650 LCO battery. It is generally placed below the positive tab (the first picture in Fig. 6a) and comprises of an engraved area made to break in excessive pressure. In the bottom, it contains a welding point which attaches a CID. Based on the battery designs, for example, those employed in cell phones, the safety vent can be in the form of foil, edge, seam, or score [4] fabricated separately and later welded with the positive cap [167]. In a prismatic battery, a vent takes an oval shape of a metallic sheet with a trapezoidal notch along the edge of a gasket. The edge of the gasket contains the puncture film and a spike for rupturing the puncture film during dangerous pressures. Cylindrical batteries consist of engraved cylindrical metallic sheets. Typically, safety vents are designed to operate at designated battery core temperatures and pressures [165]. Fig. 6b shows an 18650 LCO battery failed during external heating, of which the Aluminum sheet melted and vented at the positive tab. For the cylindrical battery, the arrangement of the positive tab, PTC ring, safety vent and CID are shown in Fig. 6c. In a prismatic battery, a safety vent is mostly placed between the two electrodes, see Fig. 6d. In some cases, a sudden rise in pressure inside the battery can sometimes prevent proper functioning of the safety vent. For example, a plastic case of a, prismatic and cylindrical battery may swells and bulge, respectively, during sudden pressure rise [168]. Consequently, these problems lead to insufficient gas venting process blocked vent by the collapsed electrode becoming clogged, unclean rupture of venting disc (disc not rupturing at the notch), and short circuit between the opened disc and ground system through vibration. Thus, it is imperative to ensure that the performance of the safety vent is not compromised. However, neither UL 1642:1999 [169], IEEE Std. 1625:2004 [170], IEEE Std. 1725:2011 [171], nor IEC Std. 62133:2012 [172] has specified test requirements for safety vents. So, to study and enhance the performance of the safety vent researchers have been focused on the creep life cycle prediction [164], burst pressure [164,167,168,173], and introduction of the second vent at the base or anode [33]. Under the real conditions of battery operation, temperature, amount of gases and latter pressure grow slowly with time. In creep life cycle prediction, the

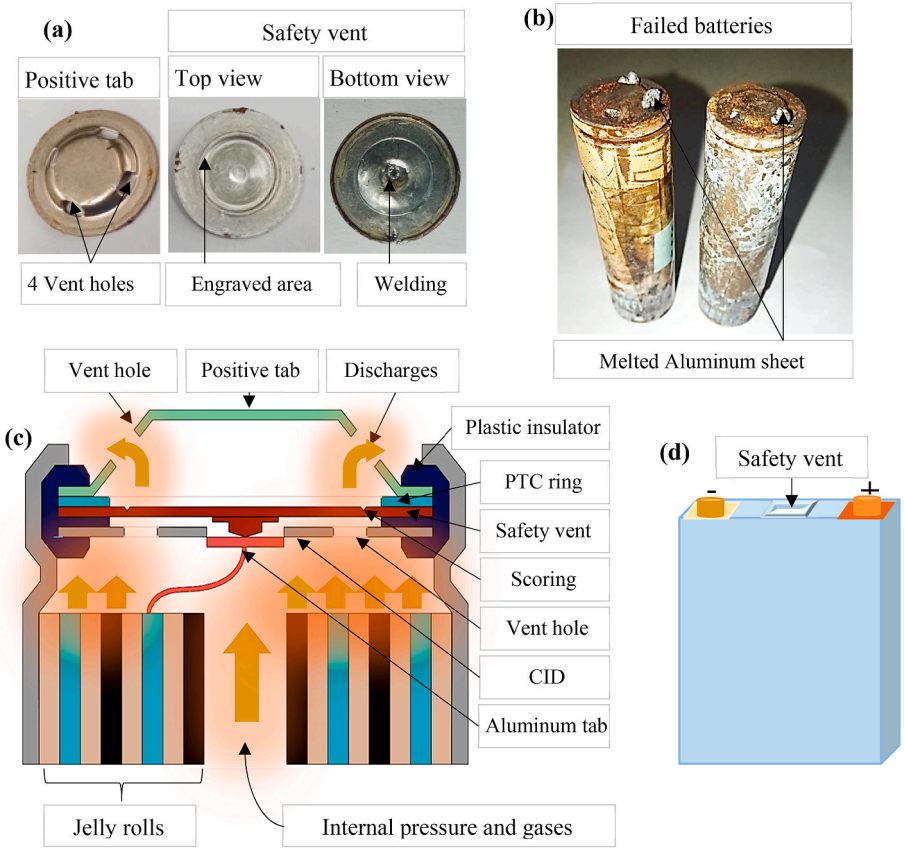

Fig. 6. (a) Example of safety vent used in cylindrical 18650 LCO battery, (b) a cross-section of 18650 Lithium-ion battery to show the arrangement of the safety vent, CID and PTC (c) location of the safety vent in a prismatic battery (d) failed battery showing a dry Aluminum after melting and vented during failure.

obstacle is the accurate representation of the slowly increasing internal pressure over time. On the other side, the discharged vents pressurize, corrode and overheat the battery enclosure. To eradicate the failure of the enclosure, a dual venting system in pack enclosure has been designed in some battery packs [174]. Moreover, a better design of the enclosure is needed to hold a big chemical fire over a certain burning time on the module or pack.

4. Preventing thermal runaway propagation across the battery pack

To meet most high power applications such as propulsion of electric vehicles, a large number of batteries stacked together in a confined space for economic manner is required. Unfortunately, these batteries contain reactive materials, in which, whenever thermal runaway goes exothermic, fire ignition becomes inescapable which later can propagate and massively destruct adjacent batteries.

Researchers have proposed various techniques to minimize thermal runaway propagation from a failed battery to adjacent batteries. Darcy

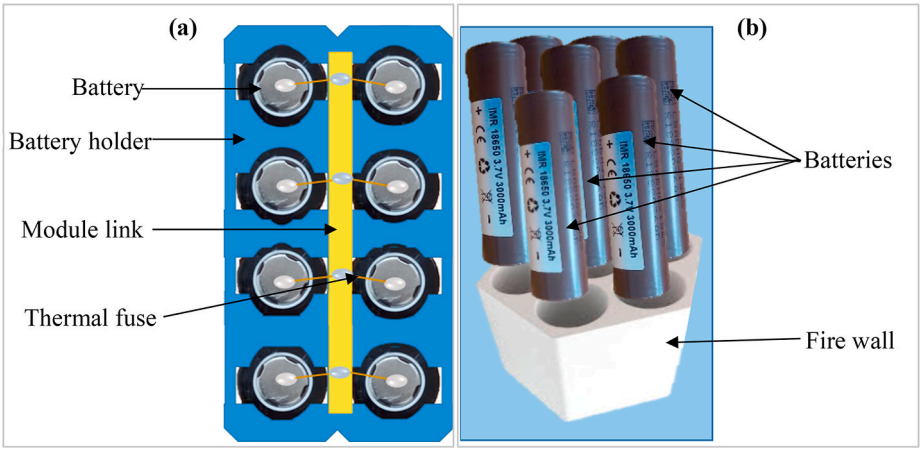

Fig. 7. Some measures to prevent thermal propagation in the battery pack (a) fusing individual parallel batteries in a battery module, (b) firewall to protect other batteries from a failing battery.

[175] proposed five measures toward mitigating thermal runaway propagation such as: to mitigate the risk of rupturing battery's steel can; provide adequate spacing and effective heat dissipation across batteries; fusing parallel-connected batteries individually (see Fig. 7a); protect the adjacent batteries from hot ejecta, Fig. 7b; and prevent flames and sparks from exiting the battery enclosures. Among the measures, heat dissipation or passive cooling has been widely employed as heat sinks of Lithium-ion battery pack through the use of metal plates or phase change materials.

Later, Darcy [175] developed LLB2 heat sinks with Alumina coating with 0.5 mm spacing between batteries within bank and 1.5 mm spacing between batteries of adjacent banks. After base-heating-to-thermal runaway, no battery side wall rupture, thermal propagation and substantial changes in adjacent terminal voltages were observed. Despite the lightweight, high thermal conductivity and specific heat of Aluminum, it is still very challenging to select the appropriate configuration of aluminum heat sinks to mitigate thermal runaway propagation.

Gao et al. [176] assessed the thermal runaway propagation regulation (TF5) developed by The Electrical Vehicle Safety - Global Technical Regulation (EVS-GTR) by exposing six different battery packs to thermal runaway through different heater powers. The heater power showed little implications to the maximum temperature but affected the propagation time. Noteworthy, factors such as ambient temperature, state of charge, overheating of the local area, uneven thermal contact within battery packs, and stacking form are critical for predicting the possibility and speed of the hazardous thermal runaway propagation [177]. Also, increasing the inter-battery spacing in a module and appropriate tab configuration exhibit a major impact on thermal runaway propagation [178]. In another way, Ouyang et al. [179] reported that triangular modular shape had better space utilization and lower propagation time compared to the line, rectangle, square, hexagon and parallelogram-shaped modules. Interesting results of Weng et al. [180] showed an easy occurrence of thermal failure propagation in transversal compared with the lengthwise array.

To gain better insight on the heat transfer inside the pack and its mitigation, Becher et al. [181] employed phase change materials between batteries to utilize its two major advantages: first as a thermal barrier to block the heat flows among adjacent batteries; and second option is to use phase change materials to absorb and transform thermal energy (endothermic). However, for the compact design, the amount of phase change material is lowered, which reduces its effectiveness [182]. Moreover, for the traditional phase change material, low thermal conductivity and diffusivity are the hampering factors that can aggravate thermal runaway propagation [183]. New material, for example, phase change composite material (PCC) [184] are seen to be futuristic material for mitigating thermal failure propagation.

Feng et al. [185] developed a lumped thermal model that can predict and help prevent thermal runaway propagation. Their study employed a six fully charged 25 Ah $LiNi_xCo_yMn_zO_2$ large format Lithium-ion battery connected through thermal resistances. Simulation results in Refs. [185, 186] proposed selection of parameters necessary to prevent rather than postponing thermal runaway propagation. To prevent thermal runaway propagation, the following were suggested: (i) enhancing the onset thermal runaway temperature to above 470 °C, (ii) reducing the electric energy released during internal short circuit, (iii) improving heat dissipation by upgrading heat dissipation coefficient to higher than 70 W/m^2K, (iv) adding additional thermal resistant layers between adjacent batteries with a thickness of 1 mm and a thermal conductivity less than 0.2 W/mK. Feng et al. [185] inserted thermal resistance between adjacent batteries as a measure to prevent propagation. Coman et al. [187] analyzed the heat propagation in a custom-made battery pack. The cylindrical Lithium-ion batteries were wrapped by a thermally and electrically insulating mica sleeve and insert into the Aluminum heat sink while allowing an air gap between the battery and the heat sink. Their findings revealed that by combining small insulating layers wrapped around the batteries, heat sink and air trapped between them can increase safety and provide good insulation which reduces the temperature to the adjacent batteries once thermal runaway is triggered.

5. Suppressing the fire of lithium-ion battery

The emerged fire of Lithium-ion battery seems to be a multi-class fire: an ordinary fire from plastics such as a burning of polymer separator (class A), a fire from liquid electrolyte and flammable gases (class B), and a fire from energized electrical component (class C), refer the classes of fire in Table 5. Previously, various fire suppressors have been employed in fire suppression such as dry powder, halons, carbon dioxide, etc. but cooling is another challenge of Lithium-ion battery fire due to the high temperature which could cause fire re-ignition.

Apart from electric vehicles, Lithium-ion batteries are also used in e-cigarettes, electronic products, smartphones, notebooks, hover boards, electric scooters, auxiliary power units (APUs) in airplanes, etc. In most of its real-world applications, there are some fire accidents which have been reported (see examples in Table 6). From Table 6, some challenges of extinguishing Lithium-ion fire can be observed, mainly are the time taken to extinguish the fire, efficiency of suppressant to cool down the battery temperature, and re-ignition and re-extinction time and frequency and spraying rate. In the electric vehicle's fire accident reportedin [203], carbon dioxide was used to extinguish, and it took several extinguishers to drop a temperature from 500 °C to 250 °C. The erupted Tesla Model S in Austria (2017) costed a group of five fire vehicles, thirty-five responders and copious amount of water to suppress the fire [199]. In a look of reported fire accidents, there are many scenarios where Lithium-ion batteries are stressed but are not yet clearly modelled and studied by researchers. Notably, charging or externally heating adds energy into the battery that worsens the failure, whereas discharge reduces the energy. In addition to mechanical stresses, the emerged fire hazards may become dangerous. So, the knowledge of burning phenomenon is crucial to understand the mechanism of fire triggering, fire hazards and later to propose suitable suppressing agents. Table 7 shows examples of simultaneous stresses that may occur in real-world usage of batteries.

To date, extensive studies have been undertaken to examine the effectiveness of these suppressants against Lithium-ion battery fires. Egelhaaf et al. [204] burned in an open space six pouch cells having a capacity of 17.6 kWh, 175 kg, and 95% SOC with n-heptane fire to examine the effectiveness of freshwater, water with 1% F-500 and water with 1.8% Firesorb additives. They quantified battery temperature, time to first extinction, time to re-ignition, time to re-extinction and volume of water consumed. Their findings showed that water could extinguish and drop off battery temperature while additives can reduce the volume of water, extinguishing time and stop re-ignition. Moreover, the use of water generated a large amount of white smoke [204] and toxic vapors

Table 5
Classification of fires and their suppressing agents.

Class	Description	Suppressing agent
A	Fires originated from ordinary combustible materials, e.g., wood paper, textiles, plastics, clothes and rubber.	Water, Foam, Dry powder, Wet chemical
B	Fires from flammable liquids, e.g., tars, oil paints, solvents, gasoline, grease, petroleum, lacquers, alcohols and flammable gases, e.g. butane and methane	Foam, Dry powder, CO_2
C	Fire involving energized electrical equipment, e.g., phone, computer, motor, generator, wiring, panel	Dry powder, CO_2
D	Fires in combustible metals, e.g., lithium, potassium, magnesium, aluminum, titanium, zirconium, and sodium	Dry powder, CO_2
K	Fires in deep fat fryers, e.g., chip pans, cooking oil, animal fats, and vegetable oil	Wet chemical

Table 6
Examples of Lithium-ion fire accidents, agents used for suppressing the fire and the emerged extinguishing challenges.

Device under accident	Description of the fire accident	Suppressant used and extinguishing challenges	Ref
Power bank	Went into a spectacular fire when carried-on the bag kept on the flight's overhead carriage in China Southern Airlines at Guangzhou City, 2018.	Extinguished by a soft drink. Not re-ignited	[188]
	Caught fire in Royal Brunei Airlines BI636 while boarding at Hong Kong City, 2019.	Extinguished by water and soft drink. Not re-ignited	[189]
Notebook's battery	Caught fire after being overcharged.	Extinguished by aerosol suppressant Spent up to 77 s for a 4 Li–Po stacked module. Could not stop propagation, all batteries were burned.	[190][a]
	Triggered into a fire during testing, 2013.	Suppressed by class D agent (Dry powder)	[191]
	Laptop exploded in LAX, 2007	Stopped by Dry powder, all batteries erupted.	[192]
Electric scooter	Suddenly caught fire while driving at high speed at Ganzhou City, Eastern China, 2018.	Extinguished by a dry chemical in 20 min. Reignited several times.	[193]
	Caught fire while charging in the parking lot, China, 2019.	Extinguished by water in a few minutes. No re-ignition.	[194]
	Burnt on the charge, Korea, 2019.	Extinguished by water. No re-ignition.	[195]
Tesla Model X	Went off-road and crashed a home and ignited in Lake Forest, CA, 2017	Water was used to put-off fire in more than 1.30 h. It reignited after 1 h. Spent more than 20 min to re-extinguish.	[196]
Tesla Model S	Hit palm tree and caught fire in Florida, 2017	Used a dry chemical to stop fire over the night. It took some hours to reignite. Reignited several times.	[197]
Tesla Model S	It was parked in the tow yard after caught fire and extinguished in the earlier day	Re-ignition occurred one day after being towed. Spent 5–6 h to re-extinguish with water.	[198]
Tesla Model S	Hit the concrete barrier and burst into flames, Austria, 2017	Used water for putting-off the fire. Spent several hours. Re-ignited several times before cutting power supply.	[199]
Tesla Model S	Collided tree and building, burst into flame, in Indianapolis, 2013.	Extinguished by dry powder and water. The fire stopped after several hours. Used copious amount of water.	[200]
Tesla Model S	Burnt in the supercharger, in Belgium, 2018	Extinguished by water.	[201]
Tesla Model S	Crashed roadblock, caught fire, Mountain View, 2017	Extinguished by carbon dioxide. Re-ignited after several days	[202]

[a] A commercial experiment performed to demonstrate the effectiveness of suppressants.

Table 7
Simultaneous stresses that may lead to a fire accident in Lithium-ion battery.

Device	Examples of simultaneous stresses leading to fire accident
Smartphone	Charging while discharging by various usages and temperatures. Charged overnight with temperature drop at night. Dropping or vibrating the phone while in-use.
Power bank	Storing at elevated altitude, lower temperature and pressure, e.g. in the airplane. Storing at high ambient temperature and vibrations, e.g. during shipping.
Notebook's battery	Prolonged charging or overcharging while in-use. Over discharged by various usages without plugging-in power. Dropping or vibrating the phone while in-use.
Electric scooter	Discharge or over-discharging at heavier loads and various ambient temperature, pressure and altitudes. Charging at fluctuating ambient temperature.
Electric vehicle	Rough discharging or prolonged discharging at fluctuating ambient temperature, pressure and altitude. High vibrations during discharging or regenerating. Discharging at fast weather fluctuation, e.g. fast driving from high temperature to low one or vice versa. Charging or discharging in cold weather Frequent discharging and regenerating at various temperatures.

such as sulfuric acid, oxide of carbon, nickel, lithium, copper and cobalt [199], electrocution to responders, and can cause a short circuit between the battery pack and ground system. Liu et al. [205] employed dodecafluoro-2-methylpentan-3-one ($C_6F_{12}O$) to study its suppressing efficiency on putting off the fire of a 4.2 V, 38 Ah, 100% SOC, NCM/graphite prismatic battery at 0, 0.5, 1.0, 1.5 and 2.0 kg dose. They found that as the dose of $C_6F_{12}O$ agent increased, the surface and base temperature of the battery first increased slowly and then decreased sharply. This was stated as a negative inhibitory effect, which distinctly grew with the dose. Wang et al. [206] investigated the efficiency of heptafluoropropane fire suppressing agent (HFC-227ea) on a heated-to-fire 2.3 V, 50 Ah, lithium titanate battery and observed that a single battery or small-scale battery pack fire could be extinguished by heptafluoropropane. However, they reported a danger of re-ignition due to violently internal reactions that generated enormous flammable gases. To further search for efficient suppressing agent, Federal Aviation Administration (FAA) [207] tested water and aqueous extinguishing agents such as water, AF-31, AF-21, Aqueous A-B-D, and Novec 1230 ($C_6F_{12}O$) and found that the cooling effectiveness from most effective to least effective was as follows: water, AF-31, AF-21, Aqueous A-B-D, Novec 1230. Further, Luo et al. [208] exploded an LFP battery to examine the extinguishing efficiency of pure water, 5% F-500 and 5% self-made solutions water mist containing additives. 5% F-500 and 5% self-made solution performed better than pure water.

To summarize, in the previous research of fire suppression, water effectively suppressed the fire and cooled the battery while water coupled with additives reduced the volume of water, extinguishing time, and avoided re-ignition. The typical characteristics of fire suppressing agent include short suppressing time, be able to stop the fire and cool the battery in a small volume, be environmentally benign, and be non-toxic or not form toxic species. However, some challenges still hinder the performance of suppressing agents such as unguaranteed uniformity of additives in water [208], generation of toxic species and electrocution to fire responders [199], the spray dose and cost of the suppressant [165], lack of firefighting guidelines for battery packs, and uncertain efficiencies of fire-extinguishing suppressants [4]. If vehicles could be fitted with fire extinguishers, issues such as limited space, allocation of the tank, synchronization with the in-vehicle control system, triggering signal, critical level to trigger extinguishing, spraying technology, and selection of suppressant need to be properly addressed.

6. Conclusion

To date, commercialized Lithium-ion batteries have brought a

breakthrough in areas of energy storage; however, their safety is still a big concern. With this challenge, much effort have been focusing on enhancing the safety of materials in current use or developing new ones. This review aims to provide a comprehensive analysis of the technologies employed to enhance the safety of Lithium-ion battery. As a first contribution, the review focuses on external factors that trigger TR, the TR formation inside the battery and its side reactions occurring inside and outside the battery. Here, the triggering conditions such as electrical abuse (overcharge, over-discharge) and thermal abuse (overheat) are discussed in detail. As a second contribution, the review elaborates the current and future strategies in suppression of TR in the form of overcharge protection (overcharge protection additives); overheat protection (improvement of cathode, anode, electrolyte's additive and separator materials); BMS; BTMS; and safety devices (PTC, CID and safety vent). As a third contribution, the review discusses the current and future strategies for mitigating thermal propagation across the battery pack including battery spacer and heat sink materials. As the fourth contribution, the review elaborates the characteristics, classification and performance of suppressing agents utilized in the recent applications. Challenges regarding the fire suppression, efficiency of suppressing agent and re-ignition have been elaborated from the real-world incidents and research experiments.

In summary, the current strategies, in cell level, have focused on improving the safety of materials. However, the battery performance and manufacturing cost of improvers are the twin-obstacles for enhancing the battery safety. On the other hand, breaking the cascading failure is also another challenge hindering the safety of the battery pack. Finally, the lack of an effective agent to suppress the fire, to the large extent, frightens end-users and lessen the penetration of products powered by Lithium-ion battery.

Overall, developing safer materials could be the utmost way to address the safety issues of Lithium-ion battery. Apart from materials, the impressing trend of other supporting devices such as safety devices and heat sinks explored in this review is hoped to offer key insights into the development and safer operation of the next generation Lithium-ion batteries. In the future, new battery technologies need to be utilized to further enhance the battery safety, see Fig. 8.

7. Future outlook

The current safety strategies for avoiding thermal runaway and their applications in areas such as electric vehicles have been explained in detail. The propagation events transmit thermic consequences to adjacent batteries and, finally, worsen the battery pack explosion. Despite this progress, there is still little knowledge on the thermal characteristics of Lithium-ion batteries in areas such as in the sky or cold countries (low pressure) [165], during their applications in sea areas (moist air), and mining and industrial areas (dust and variety of gases). For example, the knowledge concerning fire hazards of Lithium-ion battery such as ignition time, safety venting, mass loss rate, heat release rate due to chemical and flaming combustion, gas yields, lower flammability limit, and fire suppression at different state of charge, atmospheric pressure, moisture, gas concentration, etc. is scarce. In Ref. [209] a series of experiments were conducted to examine the fire hazards (ignition time, mass loss and heat release rate of flaming combustion) of Lithium-ion battery in sea-level city, Hefei city, (100.8 kPa, 24 m) and a high altitude city Lhasa (64.3 kPa, 3650 m), respectively. Notably, in elevated altitude, the cooling is lowered. So, the efficiency of fire suppressants should also be observed. These knowledge are beneficial to reduce the emerging risk after failure.

Thus, to reduce the thermal hazard of Lithium-ion battery, effective measures must be appropriately implemented. In the current work, measures under review are grouped as follow: (i) measures to prevent occurrence of thermal runaway, for example, usage of overcharge additives, improvement of electrodes, usage of thermally protective separators and safety devices, (ii) measures to reduce severity of thermal runaway, for example, usage of flame retardants and pressure-relieving devices, (iii) prevention of thermal runaway propagation by using passive devices such as metal plates (Aluminum) and phase change materials, (iv) firefighting by using freshwater, water coupled with additives and aqueous suppressing agents. However, challenges are not yet finished on the effectiveness of the countermeasures. The efficiencies of additives employed in flame retardants and overcharge suppressors are still unsatisfactory since battery performance is hampered during their applications. The lower volume of FR is also another hindrance that impede their efficacy. Moreover, the cost used for manufacturing

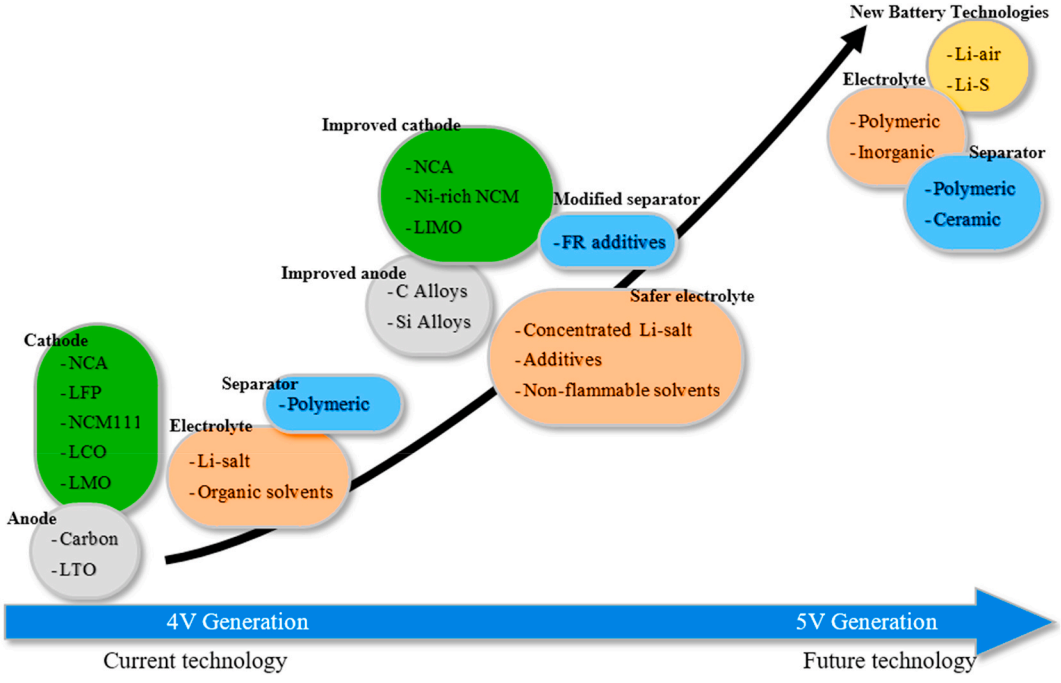

Fig. 8. The future development direction of safety of Lithium-ion battery.

additives, improving electrode materials and thermally protective separators is, however, an obstacle. Effective safety devices need to be developed to meet the requirements in practices that involve multi-battery configurations. The materials for mitigating thermal runaway propagation require higher thermal conductivity per volume in order to sufficiently dissipate generated heat energy from the battery and suppress propagation into the module. In extinguishing, the challenge of multi-class fire from the Li-ion battery should be addressed by proper knowledge and careful selection of the suppressant. In the future, an effective suppressant should be developed to simultaneously stop the multi-class fire and cool the Lithium-ion battery fire. Furthermore, the current firefighting guidelines need to add-in or match with the technologies of Lithium-ion battery and electric vehicles to efficiently extinguish the battery fire in the vehicle.

Author contributions

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