Review

A review of fire-extinguishing agent on suppressing lithium-ion batteries fire

Shuai Yuan [a], Chongye Chang [a], Shuaishuai Yan [b], Pan Zhou [b], Xinming Qian [a,*], Mengqi Yuan [a,*], Kai Liu [b,*]

[a] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100084, China
[b] Department of Chemical Engineering, Tsinghua University, Beijing 100081, China

ARTICLE INFO

ABSTRACT

Safety issue of lithium-ion batteries (LIBs) such as fires and explosions is a significant challenge for their large scale applications. Considering the continuously increased battery energy density and wider large-scale battery pack applications, the possibility of LIBs fire significantly increases. Because of the fast burning and the easy re-ignition characteristics of LIBs, achieving an efficient and prompt LIBs fire suppression is critical for minimizing the fire hazards. Different from conventional fire hazards, the LIBs fire shows complicated and comprehensive characteristics, and an effective and suitable fire-extinguishing agent particularly designed for LIBs is highly desirable. Considerable efforts have been devoted to this topic, to the best of our knowledge, a comprehensive review on this regard is still rare. Moreover, in practice, a guidance for the design and selections of a proper fire-extinguishing agent for LIBs is urgently needed. Herein, the special mechanisms and characteristics for LIBs fire and the corresponding design principles for LIBs fire-extinguishing agent were introduced. It is revealed that a fire-extinguishing agent developed for LIBs fire will most likely need a high heat capacity, high wetting, low viscosity and low electrical conductivity. After a comprehensive comparison of these agents in terms of these performances, water-based fire-extinguishing agents show best. Several typical fire-extinguishing agents such as gaseous agents, dry powders, water-based and aerosol fire-extinguishing agents were then introduced, and their fire extinguishment mechanisms were presented. Finally, their effectiveness in suppressing the fire were summarized. Water-based fire-extinguishing agents possess high cooling capacity and excellent anti-reflash performance for the fire. We believe this review could shed light on developing an efficient fire-extinguishing agent particularly designed for LIBs.

© 2021 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by ELSEVIER B.V. and Science Press. All rights reserved.
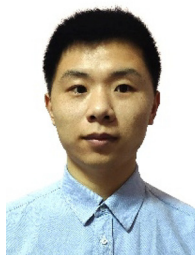
Shuai Yuan received his M.S. degree (2018) in Safety Science and Engineering from Northeast Petroleum University, China. He is currently pursuing a Ph.D. degree in safety science and engineering at the State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, China. His research interests mainly focus on the safety of lithium-ion batteries(such as fire prevention of lithium ion batteries).

Chongye Chang received her master's degree (2020) in Safety Science and Engineering from Nanjing University of Science and Technology, China. She is currently pursuing a Ph.D. degree in in safety science and engineering at the State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, China. Her research work mainly focus on thermal runaway of Li-ion battery.

* Corresponding authors.
  E-mail addresses: qsemon@bit.edu.cn (X. Qian), myuan@bit.edu.cn (M. Yuan), liukai2019@tsinghua.edu.cn (K. Liu).

Shuaishuai Yan obtained his bachelor's at China University of Petroleum (East China) in 2020. He is currently a Dr. candidate at the Department of Chemical Engineering, Tsinghua University with Assistant Prof. Kai Liu. His research interests focus on separator modification for lithium ion batteries and polymer electrolyte for all-solid-state lithium batteries.

Mengqi Yuan, Ph.D. graduated from the University of Texas at Austin, USA in 2013 (supervisor: Prof. Dave Bourell). She is now an associate professor and doctoral tutor at the School of Mechanical and Electrical Engineering, Beijing Institute of Technology. She focused on the research of safety mechanism and protection methods of explosions on facilities (such as lithium-ion batteries) and personnel.

pan Zhou received his bachelor's degree in the Department of Chemical Engineering from Tsinghua University and now is a doctor candidate in the Department of Chemical Engineering of Tsinghua University. His research interests focus on the design of novel electrolyte systems utilized in lithium metal batteries.

Kai Liu received his Ph.D. degree from Tsinghua University in 2014 (supervisor: Prof. Xi Zhang). After postdoc research in Prof Yi Cui's group in Stanford University (2014–2019), he was appointed as an assistant professor at Department of Chemical Engineering, Tsinghua University in 2019. His interests focus on safety of lithium-ion batteries and energy storage polymer materials.

Xinming Qian received his Ph.D. in Safety engineering from North Eastern University, China, 1996. He is now a professor at safety engineering at State Key Laboratory of Explosion Science and Technology Beijing Institute of Technology. His research has focused on the safety of hazardous chemical substance, such as Lithium-ion battery.

1. Introduction

LIBs technology is a successful energy revolution since the commercialization of the products in 1990s by Sony Inc. Compared with other traditional batteries, LIBs have many advantages such as higher energy, high power densities, longer cycle times, higher voltages, negligible memory effects, wider operating temperature ranges, easiness in integration, etc. [1–5]. Over the past decades, with the development of new materials science and technology, the energy density of LIBs has been increasing. For example, the theoretical energy density of conventional LIBs, with lithium transition metal oxide ($LiMO_2$, M=Ni, Co or Mn etc.) as cathode material and natural/artificial graphite as the anode material, is ~420 Wh/kg (1.51 MJ/Kg), whereas the value for Li-sulfur battery could be as high as 2567 Wh/kg (9.24 MJ/Kg). Nevertheless, polysulfide shuttling, the poor cycling, poor rate, low conductivity and volume changes of sulfur during the charge and discharge process are a result of the high sulfur adding in the electrode [6,7]. The increasing energy density of LIBs has facilitated their extensive usage in many fields including portable electronics, electric vehicles, electrical energy storage power stations, and even aerospace [8,9]. However, the high energy density is a "double-edge sword". At some extreme conditions (crushing, overcharge, high temperatures, seawater immersion, mechanical abuse, short-circuiting etc.), the large amount of chemical energy storing inside the limited space can be discharged abruptly, which transforms to heat [9–11]. This part of heat could lead to thermal runaway (TR) of the battery and eventually cause fire and explosion accidents. For instance, Samsung Galaxy Note 7 mobile phones have to be recalled due to explosion accidents in 2016 [8]. The safety issue is more critical in grid scale energy storage systems as the battery pack contains thousands of cells, which significantly increase the risk of fire and explosion events and the difficulty to extinguish it [12–14]. For instance, over 3500 LIBs occurred TR propagation due to TR occurring an single cell in energy storage system (ESS), Korea [15]. Table 1 lists several serious LIBs fire accidents and the corresponding fire-extinguishing agent people employed [16–22]. Currently, due to the lack of appropriate fire extinguishing system, it needs at least 200 gallons of water or foam to completely put out an electric vehicle fire accident [17–19], while the probability of re-ignition is still high.

To improve the safety of LIBs, researchers have performed considerable efforts in recent years. For instance, a thermal shutdown separator was designed, which could interrupt the Li-ion transportation between the anode and cathode and cut off the chemical reaction [23]. Inherent safe battery "internal" components including safer separators, non-flammable liquid electrolytes, lithium dendrite-free anodes, thermal stable cathodes etc. have been developed and reviewed [24]. However, they generally exhibit inferior electrochemical performances and thus are still immature. Based on heat dissipation and thermal insulation, many safer battery "external" materials and devices in battery modules have also been developed. For example, thermal management system [25], pulse current technology [26], phase change materials [13,27], aerogel felt coupled with flame-retarded phase change material [28,29] have been developed. Moreover, safety vent, positive tem-

perature coefficient (PTC) device, thermal fuses, and other circuit breakers have been designed for fire prevention of LIBs [30]. The disadvantage of these safe devices is that the "inert" and electrochemical inactive components are inevitable to increase the burden of battery modules and therefore decrease its overall energy density. More importantly, these devices are generally inefficient and could not completely eliminate the battery fire accidents, for which the number of LIBs fire accidents have not been reduced obviously in realistic circumstances.

Unfortunately, as the combustion characteristics of LIBs fire are not well understood, the effect of fire-extinguishing agent on LIBs fire is far from satisfactory. Although considerable efforts have been devoted to explore an efficient fire-extinguishing agent for LIBs, there still lacks a comprehensive review in this regard. Herein, a detailed TR process of LIBs and the characteristics of LIBs fire were discussed; the current progress on the fire-extinguishing agents to tackle with the LIBs fire was summarized, which could shed new light on the possible directions for the design of ideal fire-extinguishing agent.

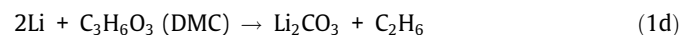## 2. Origin of LIBs fire and its combustion characteristics
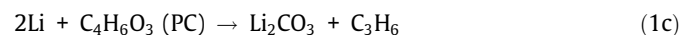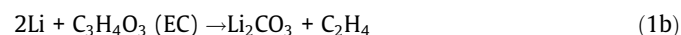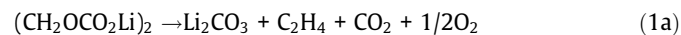
2.1. Origin of LIBs fire

An extensive understanding of the mechanism of lithium-ion battery (LIB) TR can guide us to explore an effective fire-extinguishing agent. Fig. 1 shows the process of TR of battery. The processes could be roughly summarized as follows.
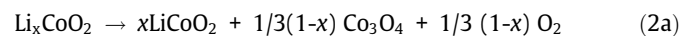
TR begins from lithium-ion battery short-circuiting, which could be categorized by internal and external short-circuiting. In most cases, the internal short-circuiting process starts from battery separator damage, which is caused by tearing separator though crash and penetration, lithium dendrite formed though overcharging, high charging current density or under low temperatures circumstance, and the collapse of separator by external high temperature [15,31]. The external short-circuiting may be caused by deformation of the battery structure, water immersion, aging conductor and faulty usage [11,32]. A high internal current might get through the battery, which caused by short-circuiting. Then, this abnormally large current causes the battery internal temperature to quickly climb up.

As the temperature increases, the components of solid electrolyte interphase (SEI) firstly decompose at ~100 °C, causing the

organic solvents such as $C_3H_4O_3$, $C_4H_6O_3$, $C_3H_6O_3$ inside the electrolyte to occur reaction with the lithium metal or lithiated carboneous anodes [33,34]. The equations are as follows:

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 + CO_2 + 1/2O_2 \tag{1a}$$

$$2Li + C_3H_4O_3 \text{ (EC)} \rightarrow Li_2CO_3 + C_2H_4 \tag{1b}$$

$$2Li + C_4H_6O_3 \text{ (PC)} \rightarrow Li_2CO_3 + C_3H_6 \tag{1c}$$

$$2Li + C_3H_6O_3 \text{ (DMC)} \rightarrow Li_2CO_3 + C_2H_6 \tag{1d}$$

These reactions belong to exothermal reaction, further rising temperature of the battery. Meanwhile, some gas products such as ethane, propane and ethylene will be generated in the limited space, which rises the pressure inside the battery (P_{In}). When P_{In} surpasses the sum of external environment pressure (P_{Out}) and the force that safety valve could sustain (P_{Crack}), the relief valve would crack with a sharp sound and these gas products and heat content will be vented [35]. The open moment of safety valve is illustrated in Fig. 2. Meanwhile, some electrolyte vapor and a small quantity of smoke releases from the safety valve. Although the surface temperature will slightly decrease because some heat contents are vented from the battery, separator would melt at around 130 °C, triggering further exothermal reactions between positive electrode and negative electrode [36]. Based on material, battery temperature stops to increase because separator occur a phase transition at around 130–137.4 °C, which belongs to endothermic reaction [37]. As the external system heats up, the battery begins to self-heat status. As the temperature climbs up, a large of heat accumulates inside battery result in the decomposition of cathode material and production of gaseous oxygen. For example, the decomposition reactions of $LiCoO_2$ at ~180 °C occur as follows [31,38]:

$$Li_xCoO_2 \rightarrow xLiCoO_2 + 1/3(1-x) Co_3O_4 + 1/3 (1-x) O_2 \tag{2a}$$

$$Co_3O_4 \rightarrow 3CoO + 1/2O_2 \tag{2b}$$

$$CoO \rightarrow Co + 1/2O_2 \tag{2c}$$

Then, toxic gases like hydrogen fluoride (HF) may be also generated from the decomposition of electrolyte salts [39]. Take electrolyte salt $LiPF_6$ (lithium hexafluorophosphate) as an example:

Table 1
Typical LIBs fire accidents and corresponding fighting strategies in recent years.

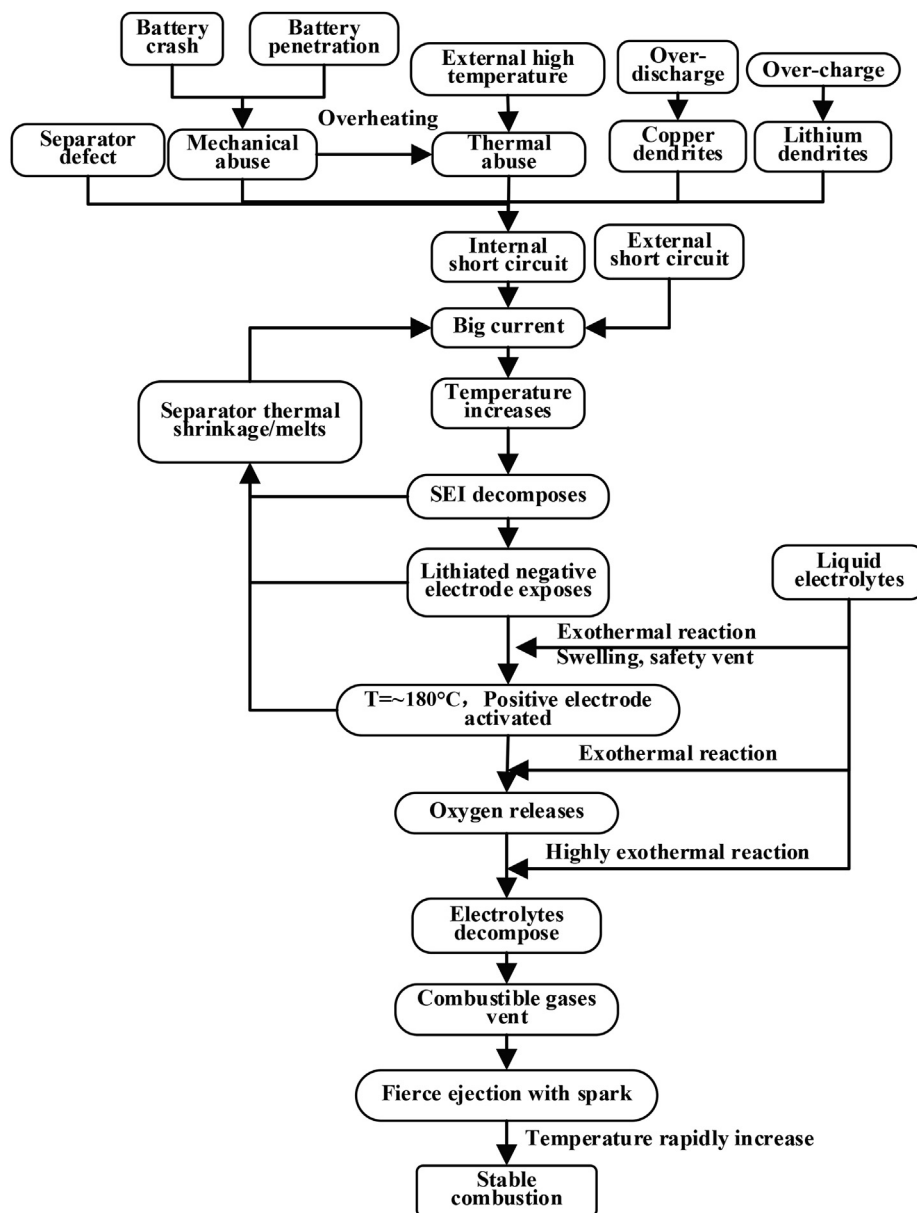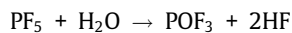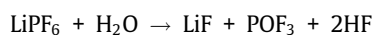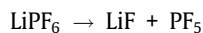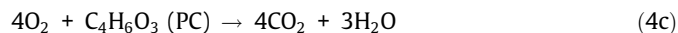| Date	Description of accident	Accidents cause	Agents	Extinguishment effectiveness	Ref.
1/7/13	Fire accident of Boeing 787 happened in Boston, USA	Short circuit	Dry chemical agent and Halon	Dry chemical agent was invalid; halon is valid but re-ignition happened; the fire was controlled within appropriately 1 hour 40 minutes	[16]
3/23/18	Tesla Model X caused fire in California, USA	Crash	200 gal water and foam	Re-ignition happened twice at impound lot	[17]
5/8/18	Tesla Model S caught fire in Florida, USA	Crash	200–300 gal water and foam	Re-ignition happened twice on a second tow truck and at the tow yard respectively	[18]
6/15/18	Fire accident of Tesla Model S happened in California, USA	Spontaneous combustion	<300 gal water and foam	/	[19]
3/7/17	ESS of a thermal power plant caught fire in China	High temperature	9% HFC-227ea	HFC-227ea is Ineffective because the container door was opened	[20]
3/8/18	A prefabricated cabin of lithium iron phosphate battery in an ESS caught fire, China	Overcharge	HFC-227ea and dry powder	HFC-227ea failed to trigger; dry powder is ineffective in this primary fire accident	[21]
2//8/17	Lithium-ion cells production plant caught in Tianjin city, China	Short circuit	Sprinkler system failed to trigger	/	[22]

Fig. 1. The Sequence of fire behavior of a single battery.

$$LiPF_6 \rightarrow LiF + PF_5 \tag{3a}$$

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF \tag{3b}$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \tag{3c}$$

The flammable organic electrolytes might decompose inside battery and large amounts of gas would be vented from the safety valve. At same time, the electrolyte solvents might take part in reaction with the oxygen released under a high temperature condition [34]. The reactions of the different electrolytes are as follows:

$$5/2O_2 + C_3H_4O_3 \ (EC) \rightarrow 3CO_2 + 2H_2O \tag{4a}$$

$$3O_2 + C_3H_6O_3 \ (DMC) \rightarrow 3CO_2 + 3H_2O \tag{4b}$$

$$4O_2 + C_4H_6O_3 \ (PC) \rightarrow 4CO_2 + 3H_2O \tag{4c}$$
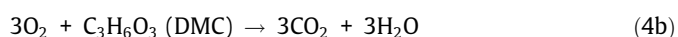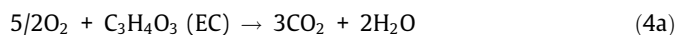
In addition, hydrogen gas might be released in reduction reactions between binder material and metallic lithium at ~350 °C [40]. The related reactions are as follows:

$$-CH_2\text{-}CF_2- + Li \rightarrow LiF + -CH = CF\text{-} + \,^1/_2H_2 \tag{5}$$
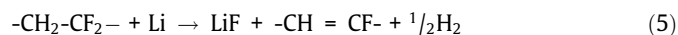
The ejection with sparks occurs when enough oxygen and heat are accumulated. These sparks might be the result of combustion of aluminum particles and electrode fragments [41]. Subsequently, the TR occurs from a location to the whole battery [42]. A jet fire subsequently happens above the battery safety valve due to the spray of flammable gases and volatile electrolytes [43]. Eventually, the battery undergoes a stable combustion stage, then the fire weaken to extinguishment.
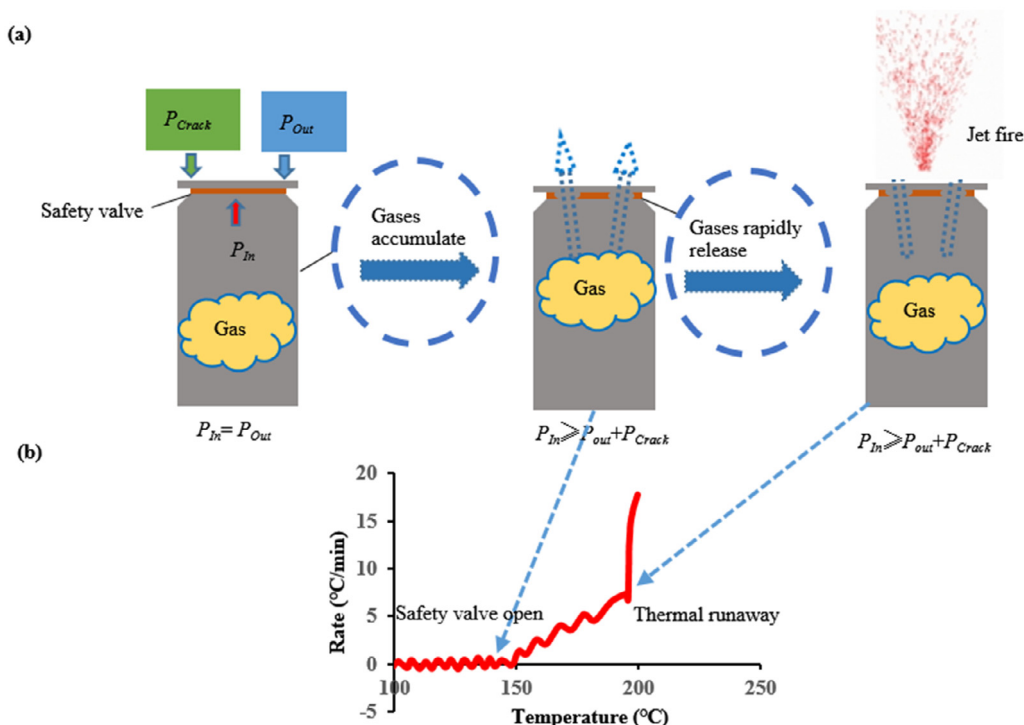
Fig. 2. TR process of LIBs: (a) the change of the battery pressure during TR. Adapted from Ref. [35] and (b) typical temperature rise rate in ARC test during TR of LIB. Adapted from Ref. [31].

2.2. Combustion characteristics LIBs fire

As mentioned about understanding of the mechanism of a lithium-ion batterLIBs TR, the key characteristics of LIBs fire can be summarized as follows:

The temperature rising rate is high, and it takes merely several seconds for the temperature to rise up to the maximum temperature of TR. Meanwhile, the maximum temperature of a LIB is very high, i.e. could be >800 °C, which may rapidly heat adjacent batteries and combustible materials, further resulting in a severer fire.

LIBs fire are complex fires (Fig. 3). As has been well categorized, generally, fire is divided into five classes, involving Class A (flammable solid materials such as paper, wood, cloth and graphite, etc., Class B (liquefiable solids or flammable liquids such as grease, oil, electrolytes and paraffin, etc.), Class C (flammable gases such as hydrogen, methane, ethane, ethylene, etc.), Class D (flammable metal, such as lithium, magnesium, aluminum, etc.) and Class F (cooking medias such as vegetable or animal oils and fats) [44]. The main components of LIBs include stainless or aluminum shell, plastic pouch, liquid electrolyte, anode material, cathode material, separator, binder and Cu foil [45], and most of these components are flammable. For example, anode materials of LIBs are combustible graphite or carbon fiber. As mentioned above, the organic electrolyte of LIB is combustible liquid. Meanwhile, gases released from the battery are flammable hydrogen (H_2), carbon monoxide (CO), ethylene (C_2H_4), methane (CH_4), ethane (C_2H_6) [46]. Lastly, aluminum shell and lithium metal/lithiated spices inside LIB are both combustible metal. Therefore, LIBs fire is complex fires, which involve Class A-D fire due to the complex components of LIBs.

Generally, the battery pack arrangement is tight to increase the system volumetric energy density, which makes the fire-extinguishing agents hard to access to the inner of the battery pack. Therefore, the deep-seated and inaccessible fire is difficult to be extinguished. In addition, plenty of water is required to cool down the battery pack after putting out the open fire [47]. Even so, re-ignition problem easily occurs due to cascading battery TR.

LIBs with different cathode material exhibit different combustion behavior. Compared with the LiFePO$_4$ battery, LiCoO$_2$ battery could spray higher energy and more violence fire in the jet-fire state. However, LiFePO$_4$ battery possessed bigger flame scale than LiCoO$_2$ battery in the subsequent combustion state [35]. This is possibly attributed to the larger release rate of combustible gases of LiFePO$_4$ battery. In addition, LiFePO$_4$ battery showed earlier TR contracted with the NCM battery under overcharge conditions, but the maximum temperature of LiFePO$_4$ battery was lower than the temperature of NCM battery [48]. Meanwhile, LiFePO$_4$ battery could not cause fire under overcharge behaviors, while higher ratio nickel in NCM cathode battery showed more violent fire and explosion.

According to the analysis of LIBs TR process, a lot of smoke and toxic gases would be released after opening of the safety valve. The smoke is the biggest obstacle for firefighters to try to locate the fire. Meanwhile, the toxic gases such as HF would be a huge threat to human health.

According to the characteristics of LIBs fire discussed above, an ideal fire-extinguishing agent for LIBs fire should exhibit the following properties: high heat capacity to cool the batteries and rapidly extinguish flame, electrically insulating to prevent the short circuit of the battery during fire extinguishment, a highly wettability and a low viscosity to facilitate fire-extinguishing agent penetration into a compact battery pack, which could prevent re-ignition and TR propagation of LIB module, be easily available and environment-friendly and rapid smoke reduction to eliminate the toxic smokes, which could also increase the visibility during the firefighting operations.

3. Typical fire-extinguishing agents for LIBs

In this part, fire-extinguishing agents are classified as gaseous fire-extinguishing agents, dry powders, water-based and aerosol fire-extinguishing agents according to their physical state. The

sorting method is to study the extinguishment mechanisms of different fire-extinguishing agents and find the appropriate extinguishing mechanism to track with LIBs fire. Firstly, their advantages and disadvantages were discussed and then the extinguishing mechanisms of these fire-extinguishing agents were introduced. The effectiveness of these agents on suppressing LIBs fire and some typical research work are then discussed accordingly. Moreover, a comparison of these fire-extinguishing agents was also discussed. Lastly, a perspective overlook about their future development directions were proposed.

3.1. Gaseous fire-extinguishing agents

Common gaseous fire-extinguishing agents such as carbon dioxide, HFC-227ea and Novec 1230 are widely used in precision equipment and general electrical fires due to free of corrosion and residues after extinguishment. We would cover each of these fire-extinguishing agents in the following sections.

3.1.1. Halon fire-extinguishing agents

Halon fire-extinguishing agents are fluorocarbons containing chlorine or bromine atoms. Typical halon fire-extinguishing agents include Halon 1301($CBrF_3$), Halon 1211($CBrClF_2$), and Halon 2402 ($C_2Br_2F_4$) [49]. Due to the recycling of existing halons is allowed, Halon 1211 is still currently used in military and aviation areas fields even though the production of Halons is banned in developed countries [50–51]. Therefore, Halon 1211 was mainly discussed in this section.

The extinguishment mechanisms of Halon 1211 is mainly ascribed to the superior chemical suppression, isolation and cooling. The active radicals such as Br. and Cl. may be released during decomposition of Halon 1211, which eliminates the radicals necessary to maintain combustion, and extinguishes fire by interrupting the chain reactions in the burning process. The chemical suppression of Halon 1211 can be represented by the reaction pathway of its pyrolysis in Fig. 4. Halon 1211 could put out LIBs fire, but re-ignition might occur once application of Halon 1211 interrupted. For example, based on the experimental data reported from Federal Aviation Administration (FAA), Halon 1211 could successfully extinguish the open fire of the three kinds of LIBs, but the re-ignition finally occurred after $LiCoO_2$ cells fire was extinguished [52]. Overall, the effectiveness of Halon 1301 and Halon 1211 on suppressing LIBs fire is attractive, as can be seen in Table 2. However, when entering the ozone layer, halons would be irradiated by ultraviolet light to decompose the Br or C1 atoms, which accelerates the depletion of the ozone layer [53]. The Montreal protocol has commanded a prohibition producing halons because of their high ozone

depletion potential (ODP) [55]. Therefore, seeking for Halon replacements is extensively explored in fire science research [56,57]. As a replacement of Halons, carbon dioxide (CO_2), HFC-227ea, Novec 1230 are less toxic, insulation, environmental friendly and chemically stable [58–61], as will be discussed respectively later.

3.1.2. Carbon dioxide

Carbon dioxide (CO_2) has been applied in preventing coal spontaneous combustion and inhibiting fire of International Space Station [61,65,66]. In addition, CO_2 is widely suitable for electrical fires due to its non-conductive properties. CO_2 inhibits the flame by a combination of smothering, isolation and cooling [61,65,66]. When the agent released, the oxygen around flammable materials is diluted to a point where the combustion cannot sustain. Therefore, the extinguishment efficiency of the agent highly depends on sealed enclosures. In addition, a part of heat in flame zone is absorbed by the evaporation and sublimation of solid or liquid
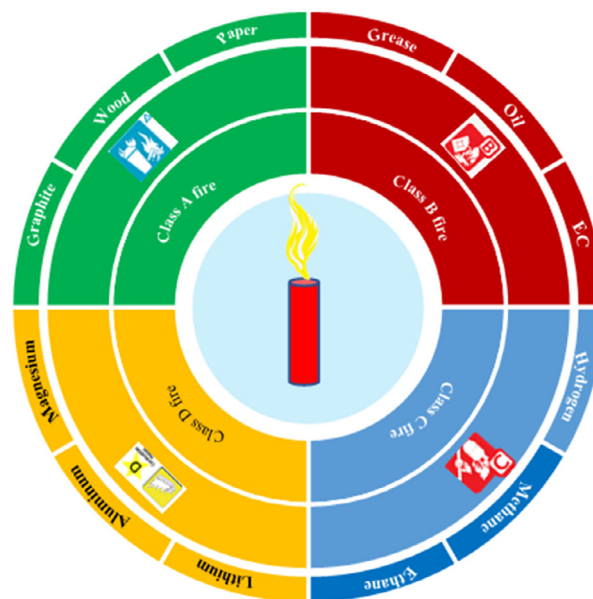

Fig. 3. The classification of LIBs fire.

CO_2, which could reduce the temperature and expedite the fire knockdown [61]. However, the contribution of endothermic reactions in lowering flame temperature seems slight [65].

Table 3 lists the extinguishment effectiveness of CO_2 on LIBs fire. Although CO_2 could put out LIBs fire by suffocation, it is hard to reduce the temperature of LIBs [60,67–69]. This is because heat capacity of carbon dioxide is such low that it cannot cool the battery down for a durable time. Meanwhile, re-ignition is also often observed when CO_2 is used as a fire-extinguishing agent to suppress LIBs fire [68,70,71]. As discussed above, CO_2 is not suitable fire-extinguishing agent for LIBs during the TR due to its low cooling capacity.

3.1.3. HFC-227ea

HFC-227ea (1,1,1,2,3,3,3-Heptafluoropropane, C_3HF_7) has many advantages of high extinguishment efficiency, less residue, less electrical conductivity and less toxicity, which is good for the fire protection of electrical equipment [73].

For HFC-227ea, its physical suppression makes more contributions to extinguishment efficiency than chemical suppression [74]. The physical suppression mainly depend on cooling and smothering. A lot of heat in flame reaction zone will be absorbed by its latent heat of evaporation and heat capacity. Meanwhile, the decomposition of the agent could absorb a part of heat, which could lower the flame temperature or slow down the radical chain reactions [73]. In addition, the oxygen concentration would decrease when gaseous HFC-227ea is released into the flame zone, which plays a part in isolation and suffocation of the fire to some extent. The chemical suppression of HFC-227ea is attribute to the removal of combustion chain-propagating species such as H., O. and OH. through fluorinated spices generated from the themolysis of HFC-227ea in the flame zone [75]. For instance, chemical suppression mechanisms of lean premixed hydrogen-C_2H_6-air by small amounts of HFC-227ea is that H, O and CH_3 radicals are absorbed by the fluorinated species such as CFO., CF_3. and CF_2. [76]. Nevertheless, the removal effectiveness of OH. radicals may be low because the OH. radicals could be produced by the reaction of F. with H_2O and the reaction of C_3F_7H with O. [77]. In conclusion, the chain-branching reactions rates would decrease due to the con-
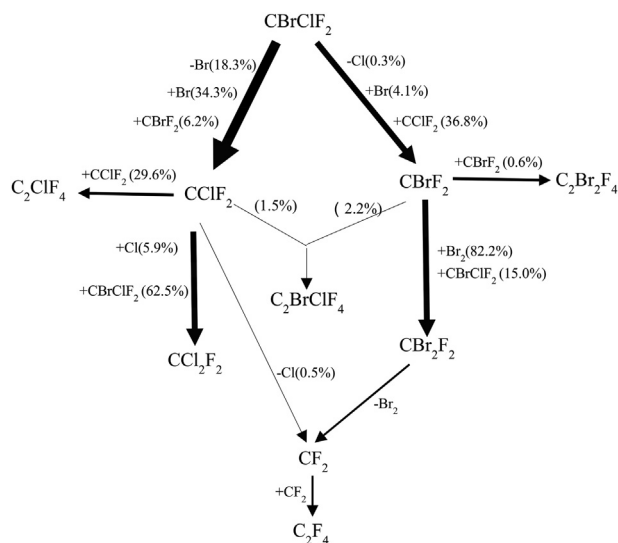
Fig. 4. Reaction fluxes for halon 1211 pyrolysis at the temperature of 923 K and a residence time of 1 s. Adapted from Ref. [54].

sistent removal of reactive radicals. Hynes et al. [77] conducted the experimental study on chemical extinguishment of premixed H_2-air with C_3HF_7 added, and the suppression mechanism of C_3HF_7 is shown in Fig. 5. At the higher inhibitor concentration, the more H. radicals will be absorbed by the fluorinated species, but the removal of OH. radicals is still not effective.

Some researches have been indicated that HFC-227ea could rapidly put out the open flame of LIBs within several seconds, but the extinguished fire burned again after the agent terminated [58,60]. The external temperature of theses batteries was still very high because chemical reactions inside battery would accelerate again once spray of the agent was interrupted. Similar to CO_2, HFC-227ea also could not effectively dilute the concentration of oxygen because cathode decomposition could generate oxygen. It was also found that reducing the spraying flow and prolonging spraying time of the agent could improve the extinguishment efficiency of HFC-227ea [60]. Table 4 summarizes extinguishment effectiveness of HFC-227ea on LIBs fire. As can be seen from Table 4, HFC-227ea are not remarkably valid in cooling capacity and suppression re-ignition. The environment pollution of the agent still not be neglect. For example, a large amount of halogen acid (HF) would generate in the decomposition process of HFC-227ea [78], which is harmful to the human healthy and electronic equipment.

3.1.4. $C_6F_{12}O$ (Novec 1230)

Perfluoro(2-Methyl-3-pentanone) (Novec 1230), is a new and clean fire protect product firstly commercialized by 3M in 2001

[79]. With nearly zero ODP, global warming potential (GWP) of 1 and atmospheric lifetime (ATL) of 0.014, the agent has already used in many fields and nearly completely replaced the Halon 1211 [80]. Novec 1230 puts out fire by a combination of its physical suppression and chemical suppression. The physical suppression depends on its cooling, which absorb heat content. Novec 1230 is liquid at room temperature and its boiling point is merely 49 °C. Therefore, vaporization could easily occur, which could carry a lot of heat away. Chemical suppression mainly depend on its thermal decomposition productions such as CF_3 and CF_2, which could lower radicals concentrations [81]. Surprisingly, Novec 1230 at a low concentration (by volume fraction, X_a < 2%) could promote the combustion of lean fuel (CH_4/air equivalence ratios is 0.63) because the agent takes part in burning reaction. What's more, the reaction might produce toxic by-products such as HF and CF_2:O gases, are shown in Fig. 6.

Table 5 lists the extinguishing effectiveness of Novec 1230 for LIBs fire. For instance, Wang's group [72] experimentally reported extinguishment efficiency of Novec 1230 on suppressing lithium titanate oxide battery fire. The experimental results indicated that the agent could control lithium-titanium battery fire within 30 s, but continuous spray of the agent on the battery surface is necessary to prevent the fire from re-ignition. By contrast, HFC-227ea could more rapidly extinguish the battery fire in similar discharge rate of agent [58]. This is because the release dose of Novec 1230 has a dramatically effect on the extinguishment efficiency for LIBs fire. For example, there exists a same peculiar phenomenon that lower dose of Novec 1230 enhanced the maximum temperature of LIBs. This maybe because the lower concentration of Novec 1230 could increase the flame velocity and adiabatic temperature in lean venting flammable mixed gas [82,83]. Fire detection technology is an effective method to detect LIBs fire and minimize the destroy. The individual ternary (Ni/Co/Mn) LIBs fire could be putted out within 5.6 s by using the fire detection technology [84]. Nevertheless, the effective radius of the fire detection pipe is merely within 18 mm, and the outer boundary battery combustion would destroy the suppression atmosphere or consume the agent. To improve the poor cooling performance of Novec 1230, Wang et al., [85] reported a novel safety strategy combining high cooling effect of water mist with Novec 1230 for LIBs fire, which have a positive effect on cooling ability and extinguishing speed for LIBs. The above results are received under the circumstance of releasing the agent after battery TR. Thermal behavior of $LiCoO_2$ battery pack immersed in liquid Novec 1230 would be remarkable suppressed [86]. Therefore, the release moment and optimum concentration of Novec 1230 for LIBs fire extinguishment is so vital.

3.2. Dry powders

According to the usage scenario, dry powders are mainly divided into ABC powder, D powder and BC powder [88]. The com-

Table 2
Summary of Halon fire-extinguishing agent on LIBs fire from literature survey.

Agent	The moment of release agent	Type	Suppression effectiveness	Ref.
Halon 1211	Failure of a single cell	8 lithium iron phosphate cylindrical 18650-style cells	No further ignition or venting event of other cells	[52]
Halon 1211	Failure of a single cell	8 lithium iron phosphate cylindrical 26650-style cells	No further ignition or venting event of other cells	[52]
Halon 1211	Failure of a single cell	8 lithium cobalt dioxide cells	Multiple re-ignition occur	[52]
Halon 1301	The first battery occurred TR	32 Sanyo CR2 batteries	All batteries occurred TR	[62]
Halon 1301	The first battery occurred TR	16 Duracell PL123A batteries	All batteries occurred TR	[62]
Halon 1301	Cells had begun to vent with burning jets	4 lithium ion prismatic battery pack	Individual cell occurred TR and venting	[63]
Halon 1301	Initial venting	8 recharged 18650-style batteries	Four cells reached first event; no fires occurred	[64]
Halon 1301	Release of electrolyte, producing a torch fire	8 recharged 18650-style batteries	Eight cells reached first event; six cells reached second event; no fires occurred	[64]

Table 3
Summary of extinguishment effectiveness of CO_2 on LIBs fire from literature survey.

| The moment of application and duration time of agent released/s	Type	Heating method	Suppression effectiveness	Ref.
Flame occur/450	Single NMC($LiNi_xCo_yMn_zO_2$) cell	External heating	Flame was not observed, but explosion occurred	[60]
Safety vent is activated/-	$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/graphite cell	500 w electric heater	Flame was extinguished within 30 s, but re-ignition occurred during the release	[68]
Electrolyte participates in the fire/-	Lithium iron phosphate power batteries with the type of CA100FI	External fire	Battery underwent TR and re-ignition	[70]
Flame occur/173	Single LTO($Li_4Ti_5O_{12}$)cell	5 kW electric heater	Flame was not putted out; re-ignition occurred	[72]
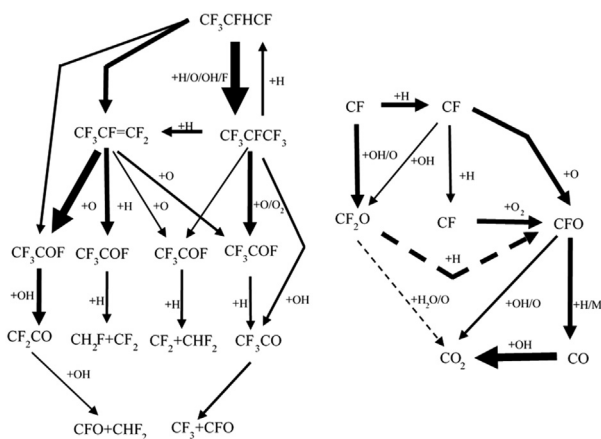
Fig. 5. Principle of 3.2 mol% C_3HF_7 inhibiting hydrogen-air flames. Adapted from Ref. [77].

ponents of ABC powder mainly consist of ammonium dihydrogen phosphate and ammonium sulfate [89]. The powder has the advantage of fighting Class A, Class B and Class C fire, thus it is called ABC powder. The main component of D powder is sodium chloride (NaCl) [90]. The powder could extinguish the metal fire, thus it is named as D powder. The main component of BC powder is sodium bicarbonate ($NaHCO_3$) [91,92]. BC powder could put out fire though the decomposition product (carbon dioxide) of sodium bicarbonate. Most materials of Class A contain carbonaceous materials, which could react with carbon dioxide to produce CO under high temperature condition. Thus, BC powder is in-appropriate for solid fire (Class A fire). Compared with BC powder, ABC powder is more widely used in fire and explosion protection. Fig. 7 shows the extinguishment mechanisms of ABC dry powder. The detail extinguishment mechanisms of ABC powder mainly can be summarized as followed.

3.2.1. Cooling and dilution action

The physical suppression of ABC powder depends on absorbing heat and dilute oxygen and flammable gases. The decomposition of ABC powder rapidly occurred when it entered the flames zone, which absorb heat from the flame [93]. The pyrolytic equations of ABC powders are expressed in Fig. 7(b) [94]. The released ammonia gas and water vapor in the decomposition equations could dilute the combustible gases and oxygen concentration in the flame zone.

3.2.2. Chemical suppression

Decomposition products of ABC powder at high temperature could generate many free radicals, which rapidly capture a great number of flame free radicals. For instance, these free radicals such as N., P. and PO. produced by decomposition of ABC powder could react with the high-energy free radicals such as H. and O. in the combustion chain, as shown in Fig. 7(b) [95].

3.2.3. Isolation and suffocation

The ABC powder could isolate oxygen and decrease the concentration of unburned fuels [93]. Ammonium phosphate powder would immediately melt and form glassy covering on the fuel, which blocks oxygen in the air. Meanwhile, ultra-fine ABC powder could stay for a long time and suffocate the fuel [93].

Table 6 lists the extinguishment effectiveness of ABC dry powder on LIBs fire. The extinguishment effectiveness of ABC powder is a comprehensive result of many factors. Based on experimental results conducted by Meng et al., [96], the extinguishment effectiveness of ABC powder become better with the increase of releasing pressure and releasing time, while the releasing angle has hardly no effect on fire-fighting and cooling capacity of ABC powder. In addition, inhibition re-ignition effectiveness of ABC powder exits differences for different types of LIBs. ABC powder could prevent re-ignition of LPF battery but not suppress re-ignition of $LiCoO_2$ cell packs [71,96]. The suppression of temperature rise is also an indicator to evaluate the effect of fire-extinguishing agent. Some experimental results found that surface temperature of the battery was still very high dur-

Table 4
Summary of HFC-227ea on LIBs fire from literature survey.

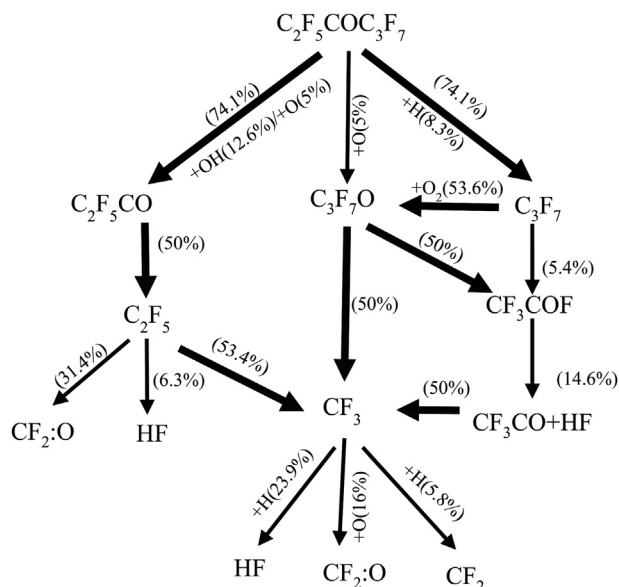| The moment of application and duration time of agent released/s	Type	Heating method	Suppression effectiveness	Ref.
Flame occur/33	LTO($Li_4Ti_5O_{12}$)cell	5 kW electric heater	Flame was putted out after 6 s; re-ignition occur	[58]
Flame occur/40	LTO($Li_4Ti_5O_{12}$)cell	5 kW electric heater	Flame was putted out after 25 s; no re-ignition occur	[58]
Flame occur/34	LTO($Li_4Ti_5O_{12}$)cell	5 kW electric heater	Flame was putted out after 17 s; no re-ignition occur	[58]
Flame occur/34	3 LTO($Li_4Ti_5O_{12}$)cells	5 kW electric heater	Flame was putted out after 10 s; no re-ignition occur	[58]
15 s after fired/28	LFP(LiFePO4) cell	Propane burner	Flame extinguished 2–74 s after operation; no re-ignition occur	[59]
Flame occur/80	NMC($LiNi_xCo_yMn_zO_2$) cell	External heating	Flame is immediately extinguished, but re-ignition occur after the spraying about 3 s	[60]
Flame occur/500	NMC($LiNi_xCo_yMn_zO_2$) cell	External heating	Flame is extinguished after the agent released for some time, and no re-ignition occurs	[60]

Fig. 6. The decompose reaction pathway of Novec 1230 for CH_4/air ϕ = 0.63 with added $C_6F_{12}O$ X_a = 0.01. Adapted from Ref. [81].

ing extinguishment process [69,97]. The high temperature could cause surround batteries TR. Therefore, ABC powder is appropriate for single battery, but is not suitable for battery module.

3.3. Water-based fire-extinguishing agents

Water is main component of water-based fire-extinguishing agents, which is widely applied in many fields. Currently, water-based fire-extinguishing agents divide into pure water, water mist additive, foams etc. Herein, we will discuss characteristics and extinguishment mechanisms of these water-based fire-extinguishing agents and their effectiveness on suppressing LIBs fire.

3.3.1. Water

Water is widely used in firefighting because of its environment-friendly, excellent cooling performance and cheap cost as well [98,99]. Therefore, it is valuable to explore water as fire-extinguishing agent on LIBs fire. Based on size of water droplets, water could divide into water injection, water sprinkler and water mist.

Generally, water injection is provided by a standardized hydrant, thus its water flow is very large [100]. Currently, injecting a large amount of water is the most effective way to extinguish electric vehicle (EV) fire. However, re-ignition and waste problem of water still exist during fighting LIBs fire process. For instance, the US Fire Protection Research Foundation (FPRF) [47,101] investigated the effect of water on extinguishing full-scale EV fire. The

experimental results indicated that water could successfully extinguish EV fire in all the six tests, while gas and smoke could still generate from the battery after the water terminated. To reduce the possibility of re-ignition, it needs additional water to cool down the battery pack. Obviously, the total volume of water used in fighting EV fire is larger than that applied in conventional vehicle fires. However, re-ignition still happened at 22 hours after the fire extinguished by water in one of six tests. Even so, Russoa et al., [69] has experimentally demonstrated that water and foam are the most effective fire-extinguishing agents among dry power, CO_2, water, water mist and foam on cooling effect on LIBs fire. Due to the run away and volatilization of water, the surface temperature of battery occurred rebound after water was discharged [69,102,103]. In conclusion, a large amount of water is the most effective way to solve LIBs fire, its disadvantages are also not neglect such as large amount of water and short circuit risk in battery system. Water sprinkler and water mist are commonly used techniques to improve contact efficiency of water, as will be discussed later.

Water sprinkler technology has been widely applied in protecting warehouses and factories [104]. Compared with bulk water, the droplets of water sprinkler could readily reach the flame region and absorb more heat due to its large diameter (above 1000 μm) [105]. The water sprinkler could extinguish Class A fire by cooling the heated gases and burning fuel surface [106]. Based on experimentally conducted by Ditch [107,108], water sprinkler system could extinguish a developed LIBs fire. However, the duration time of water sprinkler operation is as long as 20 minutes. Meanwhile, the application scenarios of water sprinkler will affect the inhibitory effect on fighting LIBs fire. For example, Research Institutes of Sweden (RISE) conducted a series of total compartment system tests and direct agent injection into LFP cell modules tests [109]. The results indicated that water sprinkler system could extinguish LIBs fire in direct injection fire tests, while it is ineffective in total compartment system tests because it is difficult to penetrate inside the battery.

Water mist (WM) refers to fine water spray, and diameters of 99% of volume in drops ($D_v0.99$) is smaller than 1000 microns within the nozzle working pressure [110]. Compared to water sprinkler and water injection, WM is characterized by less water consumption, low cost, no toxic and asphyxiation problems, low electric conduction and environment-friendly [69,111], thus it is widely used in many special scenarios such as library, transformer substation and archive. Actually, WM could extinguish fires by a combination of oxygen dilution by steam, cooling and wetting the fuel surface, cooling fire plume, radiant heat attenuation to fuel surface, the kinetic effect on flames and vapor dilution [111,112], among which the cooling and oxygen dilution play a dominant role among these suppression actions [113]. The extinguishment mechanisms of WM are shown in Fig. 8. The National Aeronautics and Space Administration (NASA) [114] developed a portable WM extinguisher, called EDU, for stored energy battery fires in the International Space Station (ISS). The EDU is highly efficient for extinguishing the fire, where merely 1 out of 16 tests were failed

Table 5
Summary of the extinguishment effectiveness of Novec 1230 on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/graphite battery fire from literature survey.

| Mass (kg)	Working pressure (MPa)	The moment of application and duration time of agent released/s	Heating method	Suppression effectiveness	Ref.
3.666	1.5	4 s after ignition/50	5000 W electric heater	Flame was extinguished at 15 s after agent released later	[72]
3.974	1.0	3 s after ignition/40	5000 W electric heater	Flame was extinguished at 23 s after agentreleased later	[72]
5.076	1.0	3 s after ignition/45	5000 W electric heater	Flame was extinguished at 21 s after agent released later	[72]
1.6	2.5	3 s after the jet flame formed/19	400 W electric heater	Flame was extinguished at 19 s after the agent release later	[85]
0.5	2.5	3 s after TR/9	400 W electric heater	Flame was extinguished within 2 to 3 s; no re-ignition occur	[87]
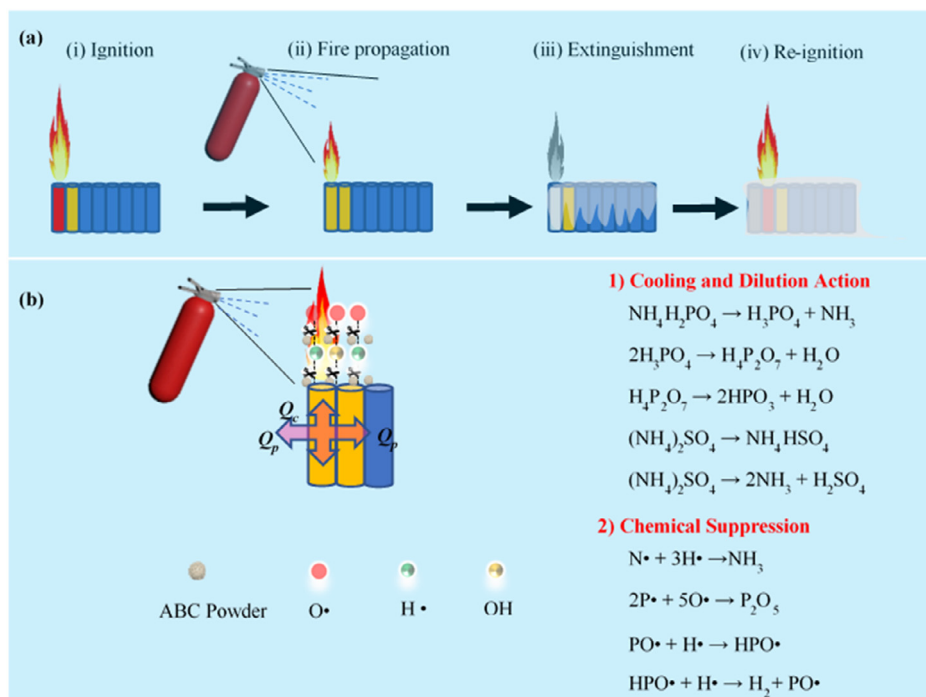
Fig. 7. Schematic illustration of ABC powder for LIBs fire. (a) An outline of the ABC powder used for extinguishing battery module fire. The path connects the whole extinguishment process. Firstly, the battery on the far left of the module is ignited. ABC powder is released, but the second battery also happened fire due to rapid heat propagation. Then the second battery fire is rapidly putted out. However, the temperature of second battery is still high, which bring the heat to the third battery. Lastly, the third battery causes fire. The black arrows represent the direction of heat transfer and (b) LIB fire-extinguishing mechanism for ABC powder. The red spheres represent O.. The green spheres denote H.. The yellow spheres denote OH.. The black dotted lines donate reaction chain. The black scissors denote the interruption pathway of the upper materials of reaction chain. The heat from battery includes Q_c and Q_p. Q_c denotes the heat used for decomposing ABC powder and air. In other word, the heat is absorbed by ABC powder. Q_p denotes the quantity of heat used for heat surrounding battery. The transparent layer on the surface of the battery represents the layer of glass formed by ABC powder.

Table 6
Summary of extinguishment effectiveness of ABC dry powder on LFP battery fire from literature survey [96].

Mass (kg)	Spraying distance (cm)	Spraying angle (°C)	The moment of application and spraying time/s	Heating method	Suppression effectiveness
2267.7	40	90	Jet fire appeared for 5 s and/9	A 500 W electric heater	Flame was extinguished at 1 s after the agent was applied; TDR is 0.8 °C/s
2384.5	60	90	Jet fire occurred/9	A 500 W electric heater	Flame was extinguished; TDR is 0.5 °C/s
2148.4	80	90	Jet fire occurred/9	A 500 W electric heater	Flame was not extinguished
2246.4	40	60	Jet fire occurred/9	A 500 W electric heater	Flame was extinguished; TDR is 1.6 °C/s
2212.5	40	30	Jet fire occurred/9	A 500 W electric heater	Flame was extinguished; TDR is 1.2 °C/s
1728.2	40	90	Jet fire occurred/6	A 500 W electric heater	Flame was extinguished; TDR is 0.2 °C/s
1047.6	40	90	Jet fire occurred/3	A 500 W electric heater	Flame was extinguished; TDR is 1.2 °C/s

to put out the fire. Based on experimentally conducted by Liu et al. [99], WM could prevent TR of single 18,650-type LIB when the surface temperature of LIB is less than the threshold temperature. However, the critical temperature should be more than 20 °C below the TR onset temperature. Suppression efficiency of WM on preventing TR propagation is subjected to spray moment, spray time and water volume. According to the experimental results conducted by Zhang et al. [115], enough spraying time and sufficient water volume could effectively prevent TR propagation in multi-batteries, but TR propagation still happened under the condition of a limited water volume. Based on experimental results conducted by Liu et al. [116], the longer duration and the earlier moment of WM release, the more effective TR propagation prevention effect in LIBs module of WM showed. In addition, spray intensity is also a significant factor affecting the extinguishment effectiveness. For example, WM cannot effectively extinguish or suppress the battery pack fire when the spray intensity is less than

2.0 L/min·m² [71]. Therefore, the effect of atomization intensity on the LIBs fire is worth further study. It should be noted that some researchers have found that there was a flame intensification due to the introduction of water mist [117–119]. Moreover, WM has many other problems: the uniformity of WM, hardly reach the surface of LIBs, and easily affected by the ventilation condition and obstacles [69,115,120,121]. The maximum concentrations of toxic gases productions such as CO, HF and H_2 are also higher using water as agent than without [9,115,122]. Therefore, it is necessary for firefighters to take good personal protection during the firefighting process. The extinguishment effectiveness of water mist on LIBs fire is summarized in Table 7.

3.3.2. Water mist containing additives

To improve the extinguishment efficiency of water mist, researchers have studied the influence of additives on water mist [124–127]. Based on action mechanisms and components, water

mist additives include chemical additives and physical additives. Chemical additives such as water-soluble inorganic salts could suppress fire by the radical sacrificing to block the combustion chain reaction [128–133]. Physical additives such as surfactants mainly relies on reducing the surface tension of water [134–136]. For similar surfactants, the length of hydrophobic hydrocarbon chain have a great influence on the extinguishing effect of surfactant solution [137]. In recent years, complex components that combine multiple surfactants have been reported as they can combine the relative advantages of different surfactants [138].

In recent years, the use of water mist additives in extinguishing LIBs fire and explosion suppression have been reported. Table 8 summarizes the extinguishment effectiveness of water mist containing additives on LIBs fire. One of the outstanding example is F-500. The extinguishment mechanisms of F-500 and its application effectiveness for firefighting LIBs fire are emphatically discussed in here. According to Material Safety Data Sheet (MSDS), F-500 produced by Hazard Control Technologies, Inc. is an aqueous mixture containing fatty alkyl ethers reaction products with aliphatic acids (40–50%), alcohols, C_{6-12} (5–8%) and 2,2,22-Nirilotrisethanol aliphatic acid soap (2–4%) [139]. The main composition is a kind of amphiphilic surfactant, whose polar head could dissolve in water, and the nonpolar tail repel water molecules to seek other types of molecules such as hydrocarbons [140]. F-500 could rapidly extinguish fire by a combination of reducing surface tension of water, formation and maintenance of encapsulator and interruption of free radicals participating in chain reaction [140–143]. The extinguishment mechanism of F-500 is shown in Fig. 9. When F-500 is mixed with water in a certain proportion, F-500 could improve the wettability of water, which enhance the penetration possibility of water into the pores and gaps between LIBs. A group of F-500 molecules can arrange around the hydrocarbon molecules to form a microcellular called "Chemical Cocooning", which causes the hydrocarbon molecules to lose their flammability. At the same time, the formation and the maintenance of microcells make the released flammable gases inert to reduce the probability of re-ignition. In addition, F-500 could absorb the energy of free radicals during the collision process, which further inhibits the combustion chain reactions.

German motor vehicle inspection association (DEKRA) [100] reported several kinds of water-based fire-extinguishing agents such as water, F-500 and a gelling agent used in extinguishing lithium-ion traction batteries fires. The flame of power LIBs was rapidly extinguished by 1% F-500 within merely 7 s. Luo et al. [96] studied the efficiencies of 5% self-developed anionic-nonionic surfactants and 5% F-500 solution on LIBs fire. Compared with water mist, the spherical micro-capsule technology has more excellent extinguishing performance in putting out flame, prevention of re-ignition and rapid reduction of harmful products. In addition, 5% F-500 and 5% anionic-nonionic surfactants show a precipitous drop in surface temperatures of the battery than pure water. Meanwhile, water mist containing surfactant has the positive action on weaken TR gases explosion. In another work, DNV·GL [144] conducted a series of experiments on assessing the suppression effect of water-based agents including F-500, FireIce, PyroCool and plain water on LIBs fire. F-500 possesses an excellent performance in delaying induction time of ignition and reducing maximum flame temperature. Similar to the extinguishment mechanisms of F-500, adding potassium monoalkyl ether phosphate and fatty acid ester polyoxyethylene ether to water could absorb flammable gases such as CO and CH_4, which enhance the extinguishment effectiveness of water mist for LIBs fire [137,138]. Therefore, a kind of fire extinguishing material that absorbs TR gases has a good prospect. From the experimental date conducted by Zhu et al., [145] water mist containing anionic/nonionic surfactants could effectively reduce both maximum explosion temperature and flame propagation speed of CO regarded as the main component of TR gases. Meanwhile, polyoxyethylene castor oil ester or FC-4 belonging to a kind of fluorocarbon surfactants also help water to reduce the surface tension, which enhance the extinguishment performance of water mist [146,147]. In another aspect, chemical additive extinguish LIBs fire by capturing radicals such as H• and OH•, which break off the combustion reaction [148]. In this study, water mist containing chemical additives possess higher cooling ability than containing surfactant during TR of LIBs [85]. However, water mist adding chemical materials might enhance the electric conductivity of water, which should be paid attention to. A compound additive containing surfactants and chemical additives could reduce surface tension and combine with free radicals to improve the suppression capacity of water mist for LIBs [147,149].

3.3.3. Foam extinguishing agents

Foam extinguishing agents have been widely used in fighting Class A and Class B fires due to their high extinguishment effectiveness, low cost and low pollution. Based on foaming mechanisms, foams can be divided into chemical foams and mechanical foams. Chemical foams are produced by the reaction of aluminum sulphate ($Al_2(SO_4)_3$) and sodium bicarbonate ($NaHCO_3$) in aqueous solution [150]. The usage of chemical foams are very limited because of their corrosion. Mechanical foams are obtained by the mixture of an aqueous solution with pressure gases or other mechanical method [151,152]. Mechanical foams are paid attention to many researchers due to their low pollutions to environment. Although different foams are suitable for different fires, extinguishment mechanisms of foams fire-extinguishing agents on LIBs fire are similar, as shown in Fig. 10. Based on base stock, mechanical foams could be approximately divided into three kinds of foams.

In the early stage, people used plain water to extinguish Class A fire. However, it was found that most of woods were not capable of absorbing water, which led to the loss of water resource. Commonly, it takes a lot of time and a great quantity of water to wet the fuel by plain water. In the mid-1970s, Texas department of forest fire prevention developed a kind of foam extinguishing agent named "Texas Snow Job", which is the earliest Class A foam [153]. Then, Class A foam was used for suppression of structural fires [154]. The components of Class A foam mainly include hydrocarbon surfactants and water [155]. These surfactants make more water penetrate into solid fuels due to reduction of surface tension of water. In fact, the primary extinguishment mechanisms of Class A foam still relies on the cooling capacity of water because proportion of water is very high. Class A foam may make liquid water rapidly turn into steam due to its larger surface area of water, and it also provides a vapor barrier between solid fuel and oxygen [154]. Class A foam concentrate contains several hazardous chemicals, which could irritate to the skin and eyes, corrode metals, and pollute environment [156]. There are a few researches on the effectiveness of Class A foam on extinguishing LIBs fire. For instance, the results of Research Institutes of Sweden (RISE) indicated that Class A foam possess faster fire control than water, but the cooling effect of Class A foam is less effective than plain water [157]. In addition, the test verified that the quality of foam is significant for fighting internal pressure generated from battery. Compared with Class A foam, compressed Air Foam System (CAFS) is a high-quality foam. The foam is formed by a solution of water and a kind of foam concentrate through compressed air. Based on the proportion between foam and water, CAFS foam includes dry CAFS foam and wet CAFS foam. A wet CAFS foam exhibits more excellent cooling effectiveness than dry CAFS foam because wet CAFS includes more water [157].
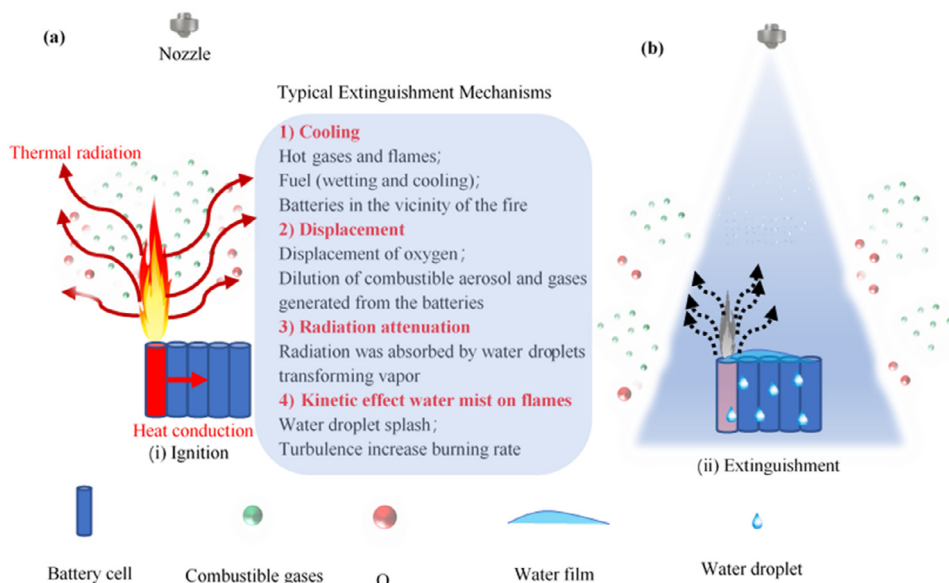
Fig. 8. Extinguishment mechanisms of WM on LIBs fire. (a) Typical LIBs ignition and propagation and (b) extinguishment of LIBs fire in circumstance of water mist.

Table 7
Summary of extinguishment effectiveness of water mist on LIBs fire from literature survey.

Water pressure (MPa)	Battery type	Release time and duration/s	Suppression effectiveness	Ref.
0.5	5 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/Carbon cells	After battery #1 TR/60	Suppressed	[116]
0.5	5 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/Carbon cells	After battery #3 TR/80	Battery #4 TR; Battery #5 TR after WM terminated	[116]
0.5	5 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/Carbon cells	After battery #3 TR/120	Battery #4 TR; Battery #5 suppressed	[116]
0.5	5 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/Carbon cells	After battery #4 TR/120	Suppressed	[116]
0.2	$Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$/Graphite	TR/10	TR propagation happened at 7 s after water sprayed	[123]
0.1	$Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$/Graphite	TR/35	TR propagation issuppressed	[123]
0.2	$Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$/Graphite	TR/20	TR propagation happened at 230 s after water sprayed	[123]
0.3	$Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$/Graphite	TR/15	TR propagation happened at 81 s after water sprayed	[123]
0.2	$Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$/Graphite	TR/30	TR propagation is suppressed	[123]

AFFFs are the most commonly used agents for extinguishment of liquid fuel fires such as oil tank fire, airports and military sites [158–162]. The typical formulations of AFFFs include fluorinated surfactants, hydrocarbon surfactants, cosolvents and solvents [160]. The fluorinated surfactants and hydrocarbon solutions are important components, which are helpful to form aqueous duplex film on the surface of hydrocarbon fuels [160,161,163]. Actually, the films consist of two kinds of monolayers due to the immiscibility of two surfactants, which contains the air–water surface formed by fluorocarbon surfactant and the oil–water surface absorbed by hydrocarbon surfactant [164]. Meanwhile, the fluorocarbon surfactant could effectively reduce the surface tension of water and hydrocarbon surfactant could decrease the interfacial tension between hydrocarbon and water, which improves the fluidity of AFFFs. The aqueous films are vital to extinguish Class B fire by forming a vapor barrier between fuels and air, which could cool down the burning liquid fuel and prevent the re-ignition [160,163]. Meanwhile, the barrier dilutes the oxygen in the air, and it also isolates the flammability liquid [165]. AFFFs could extinguish the open flames of 18650-type of $LiCoO_2$ battery [71]. However, extinguished fire burned again 47 s after the open fire was extinguished. It should be noted that as the main components of AFFFs, fluorocarbon surfactants are harmful to human beings and the environment [166–168]. PFOS and its precursors have been listed as persistent organic pollutants (POPs) in the international Stockholm convention [160].

Protein foam (PF) is one of the most popular foam extinguishing agent and composed of protein hydrolyzed by animal or plant source, suitable stabilizers, antiseptic and antifreeze [169,170]. PF possesses low cost, biodegradability, stable structure and good fire resistance, which is widely employed in liquid fire, especially petrochemical tank fire [171]. As the main component of protein foam, hydrolyzed protein is a kind of amphoteric surfactant, which can reduce the surface tension of water and increase the surface viscosity and elasticity of liquid film. In addition, the component is helpful to obtain a thick and stable foam [172,173]. Compared with Class A foam, PF is more stable, and it can form a barrier between flame and oxygen to extinguish fire [174]. FP foam can suppress the fire though isolation, cooling and smothering [175]. However, to the best of our knowledge, we have not found related reports about suppressing LIBs fire by PF.

3.4. Aerosol fire-extinguishing agent

Aerosol fire extinguishing technology was developed in the 1960s on the basis of pyrotechnics [176]. Aerosol is a gas dispersion system with the largest particle size less than 5 μm in the sol medium [177]. The agent has many advantages of low environmental impact, low toxicity, non-conductive and low residue [178,179]. And the generation of aerosols does not require pipelines and pressure vessels, which makes it widely used in equipment, aircraft cargo containers, fuel storage tanks, UPS/battery cells and armored vehicle engine compartments [180–182]. Currently, aerosol extinguishing agents have been developed from K-type generation-I (potassium nitrate as oxidizers) to S-type generation-III (strontium nitrate as oxidizers agents) [179]. The

Table 8
Summary of extinguishment effectiveness of water mist containing additives on LIBs fire from literature survey.

| Agent	Battery type	Release moment/duration (s)	Suppression effectiveness	Ref.
Water	Pouch cell	Release at 9 min after Initializing fire burned/447	Water consumption is 400 L; extinguishing time is 40 s and re-ignition happened	[100]
F-500	Pouch cell	Release at 9 min after Initializing fire burned/100	Water consumption is 80 L; extinguishing time is 70 s and re-ignition was not observed	[100]
Firesorb	Pouch cell	Release at 9 min after Initializing fire burned/91	Water consumption is 120 L; extinguishing time is 6 s and re-ignition was not observed	[100]
3% SDS	30 Ah LFP cell	–	Water consumption is 7.2 L; suppression time is 28 s	[138]
3% EL-20	30 Ah LFP cell	–	Water consumption is 7.9 L; suppression time is 46 s	[138]
SDS + EL-20	30 Ah LFP cell	–	Water consumption is 4 L; suppression time is 15 s	[138]
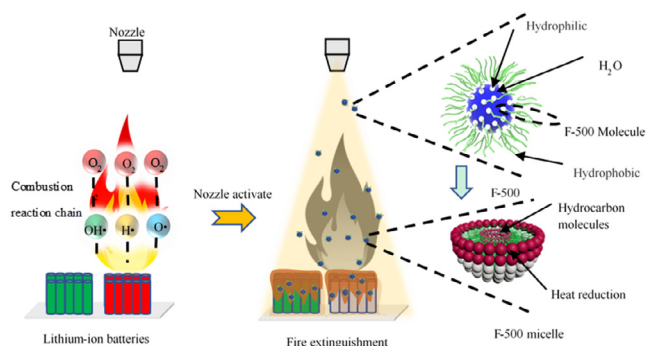
Fig. 9. The extinguishment mechanisms of F-500 for LIBs fire.

extinguishment mechanisms of K-type aerosol is mainly attributed to K collision with flame propagation radicals (H., O., OH.) in the flame, and reducing the oxygen concentration though CO_2 and water vapor, as illustrated in Fig. 11. The extinguishment mechanisms of S-type aerosol is similar to K-type aerosol, which mainly relies on Sr collision with the flame propagation radicals during extinguishment process. Some researchers have demonstrated each substance exits a size limit, which shows an obvious improvement in flame extinguishment effectiveness once below the particle size [183,184]. According to the experimental results of particle size distribution of aerosol forming compositions (AFCs), the large number of particles sizes of K-type and S-type aerosol are less than 0.5 µm [177]. Therefore, aerosol could extinguish the fire depending on its high diffusion ability and low deposition performance. AFCs comprises of oxidizing agents (such as nitrate, chlorate or perchlorate), reducing agents (such as carbohydrate, carbon black), binders (such as epoxy and phenolic resins) and functional additives (such as stearate and sodium azide) [185]. Oxidizer is one of the most important composition of AFCs, where potassium nitrate is considered as the most appropriate oxidizers in the AFCs due to its low cost and less hygroscopic [179]. However, potassium oxide produced from the K-type aerosol generator would contact with water, which further form potassium hydroxide. If not cleaned in time, the protected equipment would be corrode by the alkali [186]. Hence, AFCs based on potassium nitrate are not suitable for electronic or electrical equipment. S-type aerosol possesses less corrosion because the strontium oxide (SrO) and strontium carbonate ($SrCO_3$) produced are stable and insoluble in water [187]. However, the application of S-type aerosol is limited because of its high decomposition temperature and slow reaction speed [188].

Aerosol could rapidly extinguish LIBs fire in a relatively closed places, while re-ignition problem is still the biggest challenge. DNV-GL reported aerosol could extinguish the LIBs fire [189,190]. Compared with water, aerosol could remain low oxygen levels for a long time. However, the extinguished fire

occurred flashover once open the door. Thus, similar to gaseous fire-extinguishing agents, aerosol play its efficient extinguishment ability merely in a closed site. In addition, K-type aerosol would produce by-products with high temperature due to its exothermic reaction, which might increase the risk of battery re-ignition.

3.5. Comparison of different fire-extinguishing agents

In order to screen out existing fire extinguishing agents that can effectively deal with lithium-ion battery fire, considerable of comparative experimental studies have been conducted [68–70,103,190]. The extinguishment effectiveness of different fire-extinguishing agents for LIBs fire have been summarized in Table 9. Aqueous agents showed more excellent cooling capacity and prevent re-ignition than gaseous fire-extinguishing agents.

Through analysis above, the performances of eleven common fire-extinguishing agents are shown in radar plots in Fig. 12. The main properties required for fire-extinguishing agents are: viscosity, insulativity, heat capacity, wettability, biodegradable capability, smoke absorption and cost. In the following subsections, we will discuss the performances of common fire-extinguishing agents.

The insulation property of gaseous fire-extinguishing agents, aerosol fire-extinguishing agents, and dry powders are better, followed by water mist, foams, water sprinkler, water and F-500. This means that gaseous fire-extinguishing agents would not cause short circuit and rarely damage the integrity of the battery module during the fire extinguishment process. However, dry powders might damage the integrity of the battery module because of its a mass of residues.

Viscosity is also significant index to evaluation delivery capacity of fire-extinguishing agents. Among water-based fire-extinguishing agents, viscosity of water is the lowest, followed by F-500 and foams.

A high heat capacity is most essential characterization parameter for reducing the temperature of battery. Obviously, water-based fire-extinguishing agents possess excellent cooling capacity. Among water-based fire-extinguishing agents, the durable heat capacity of F-500 is highest, followed by water and foams. In addition, gaseous fire-extinguishing agents, dry powder and aerosol possess poor cooling capacity. Among other fire-extinguishing agents, the cooling ability of aerosol is worst, followed by dry powders, HFC-227ea, CO_2 and Novec 1230.

The wettability is the index of the fire-extinguishing agent to moisten the surface of battery pack. Among these fire-extinguishing agents, the wettability of F-500 is best, followed by foams and water.

Biodegradable capability is essential index to protection environment, where pure water is best, followed by F-500, foams. Table 10 summarizes environmental index (Toxicity, ODP, GWP, ALT9) of typical fire-extinguishing agents. Gaseous fire-
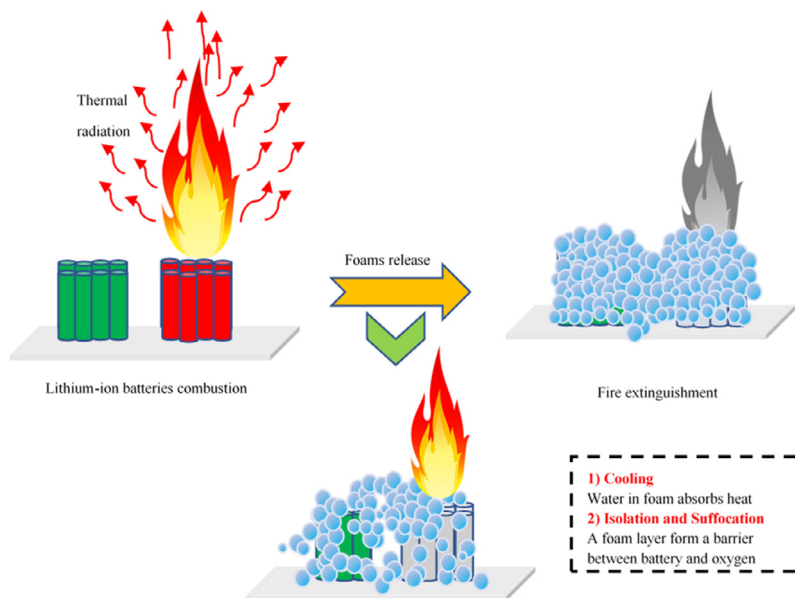
Fig. 10. The extinguishment mechanisms of foam on LIBs fire.

extinguishing agents would generally cause air pollution. The degree of pollution from serious to moderate is CO_2, HFC-227ea, Novec 1230, dry powders and aerosol in turn. Among these fire-extinguishing agents, halons are the most serious.

The cost of fire-extinguishing agent is an important index to assess its range of application. Clearly, water-based fire-extinguishing agents are the cheapest, followed by dry powders and CO_2. The cost of aerosol and other fire-extinguishing agents such as Halons, HFC-227ea and Novec 1230 are all very high.

Smoke absorption of fire-extinguishing agent is vital index to improve the visibility of fire scenario. Among these fire-extinguishing agents, the smoke reduction capacity of F-500 is the best, followed by foams, water mist, water sprinkler and water. Gaseous fire-extinguishing agents are very poor in absorbing smoke, followed by dry powder and aerosol.

Considered from comprehensive comparison, water-based extinguishers have better performance in extinguishing LIBs fire, particularly in reducing the temperature of battery and low cost. However, the electric conductive is the biggest challenge for water-based fire-extinguishing agents used for LIBs fire. Gaseous fire-extinguishing agents and aerosol show poor performances except insulation performance. Dry powders show excellent performance in preventing short circuits and low cost. However, other performances of dry powders are all fair. In a word, water-based fire-extinguishing agents are probably a suitable fire-extinguishing agents for LIBs.

4. Summary and outlook

With the further development of LIBs towards higher energy and power density, more serious fire or explosion accidents related to LIBs would possibly occur. Although many methods have been developed to decrease the possibility and severity of thermal runway of LIBs, the issue of battery fire and explosion has not been completely solved. Therefore, study on the TR process and combustion characteristics of LIBs fire, and developing a novel fire-extinguishing agent particularly designed for LIBs are of significance for battery safety.

Commonly, TR of LIB can be induced by separator defect, mechanical abuse, thermal abuse, over-charge and over-discharge. These factors can result in short circuit of the battery, which builds up the internal temperature of the battery and further induce TR. During the TR process of battery, the materials of LIBs such as SEI, negative electrodes, positive electrodes and electrolytes would be decomposed which produces a lots of gaseous products. The gaseous products are generally flammable and toxic, which can be easily ignited by heat or external fire to induce jet fire and even explosion. Moreover, combustion characteristics of LIBs fire are summarized here. LIBs fire possesses several special features: (1) high temperature rising rate; (2) complex fire types; (3) different fire behaviors for different LIBs; (4) TR happened in deep-inside the battery pack; (5) production of toxic gases and smoke.

In this paper, several fire-extinguishing agents including gaseous fire-extinguishing agents, dry powders, water-based fire-extinguishing agents and aerosol are discussed. However, these fire-extinguishing agents have many defections for fighting LIBs fire such as large amount of dosage, long time and easy to reignite. With the aim to rapidly extinguish the LIBs fire, an effective LIBs fire suppressant is require to be developed. Gas fire-extinguishing agents such as Halons, HFC-227ea, CO_2 and Novec 1230 are beneficial to integrity protection of battery system during the fire extinguishing process. However, gas fire-extinguishing agents could not effectively reduce the temperature of battery. Similar to gaseous fire-extinguishing agents mentioned above, dry powders and aerosol are not conductive, while these agents would contaminate battery system. In addition, their heat capacity is not optimistic. Water-based fire-extinguishing agents exert comprehensive performance in high wettability, low viscosity, high heat capacity, environmental friendliness and superior smoke absorption. The suppressant with high heat capacity could cool battery to reduce the possibility of re-ignition. However, their suitability is subject to further verification, as it may cause a short circuit in the battery system.

Thus, a novel kind of fire-extinguishing agent with high wettability, low viscosity, excellent insulation property, high heat capacity, environmental friendliness and good smoke absorption is
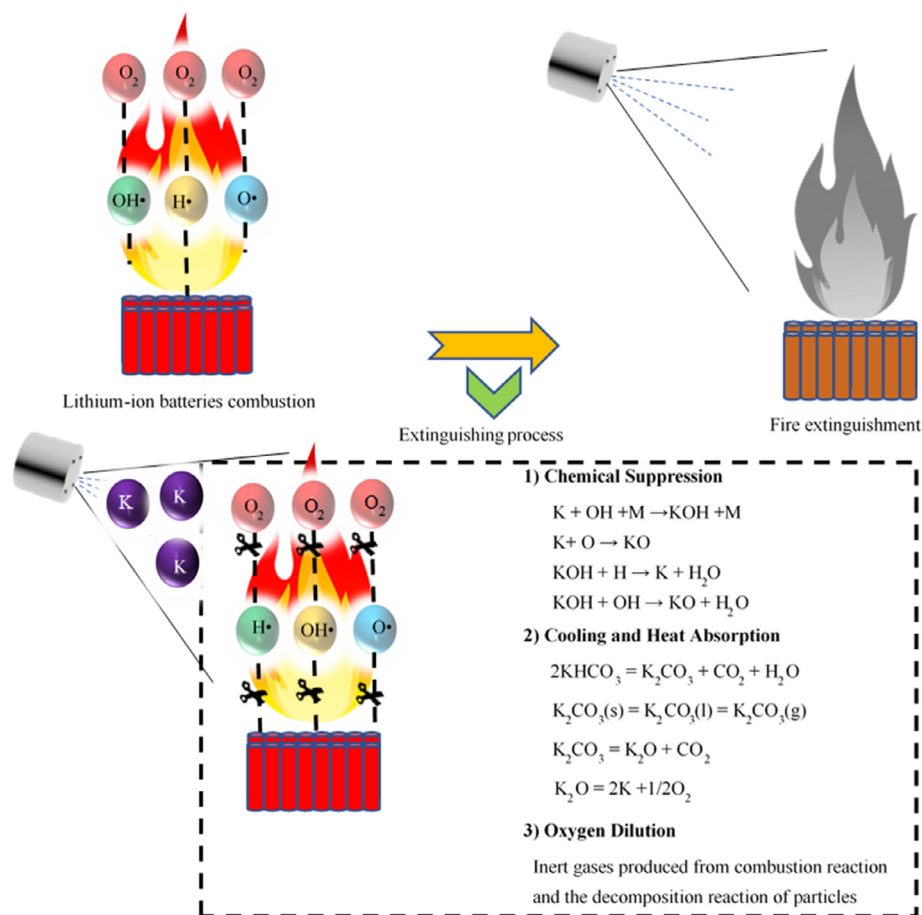
Fig. 11. The extinguishment mechanisms of K-type Aerosol on LIBs Fire.

Table 9
Summary of extinguishment effectiveness of different fire-extinguishing agents on LIBs fire.

| Agent	Battery type	Release moment	Suppression effectiveness	Ref.
CO_2	$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Graphite	Safety valve is opened	It took 30 s to suppress the fire, but re-ignition was observed during the releasing	[68]
HFC-227ea	$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Graphite	Safety valve is opened	It took 22 s to suppress the fire, but re-ignition was observed during the releasing	[68]
Water mist	$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$/Graphite	Safety valve is opened	No flame appeared	[68]
Water	Ni oxides/Graphite	Temperature of battery up to 650 °C	Extinguished fire within 20 s	[69]
CO_2	Ni oxides/Graphite	Temperature of battery up to 650 °C	Having no effect on reduced the temperature	[69]
Foam	Ni oxides/Graphite	Temperature of battery up to 650 °C	Extinguished fire within 20 s	[69]
Water mist	Ni oxides/Graphite	Temperature of battery up to 650 °C	No effect on reducing the temperature	[69]
Dry powder	Ni oxides/Graphite	Temperature of battery up to 650 °C	No effect on reducing the temperature	[69]
CO_2	LFP	Battery occurs fire	Re-ignition happened	[70]
HFC-227ea	LFP	Battery occurs fire	Suppressed the fire	[70]
Superfine powder	LFP	Battery occurs fire	Explosion and thermal runaway occurred	[70]
CO_2	13S5P 18650-type $LiCoO_2$ cells	15 s after fire occurred	Re-ignition occurred at 10 s after the suppression of open fire	[71]
Dry powder	13S5P 18650-type $LiCoO_2$ cells	15 s after fire occurred	Re-ignition occurred at 8 s after the suppression of open fire	[71]
3% AFFF	13S5P 18650-type $LiCoO_2$ cells	15 s after fire occurred	Re-ignition occurred at 45 s after the suppression of open fire	[71]
Aqueous agents	5 18650-type LIBs	First battery occur TR	None of the cells propagated	[103]
Gaseous agents	5 18650-type LIBs	First battery occurred TR	All of the cells propagated	[103]
Aerosol	75 Ah NCM Li-ion pouch cells.	Within 5 s of the thermal spiking event	Flames are fully suppressed by 10 s, but flashover happened	[190]
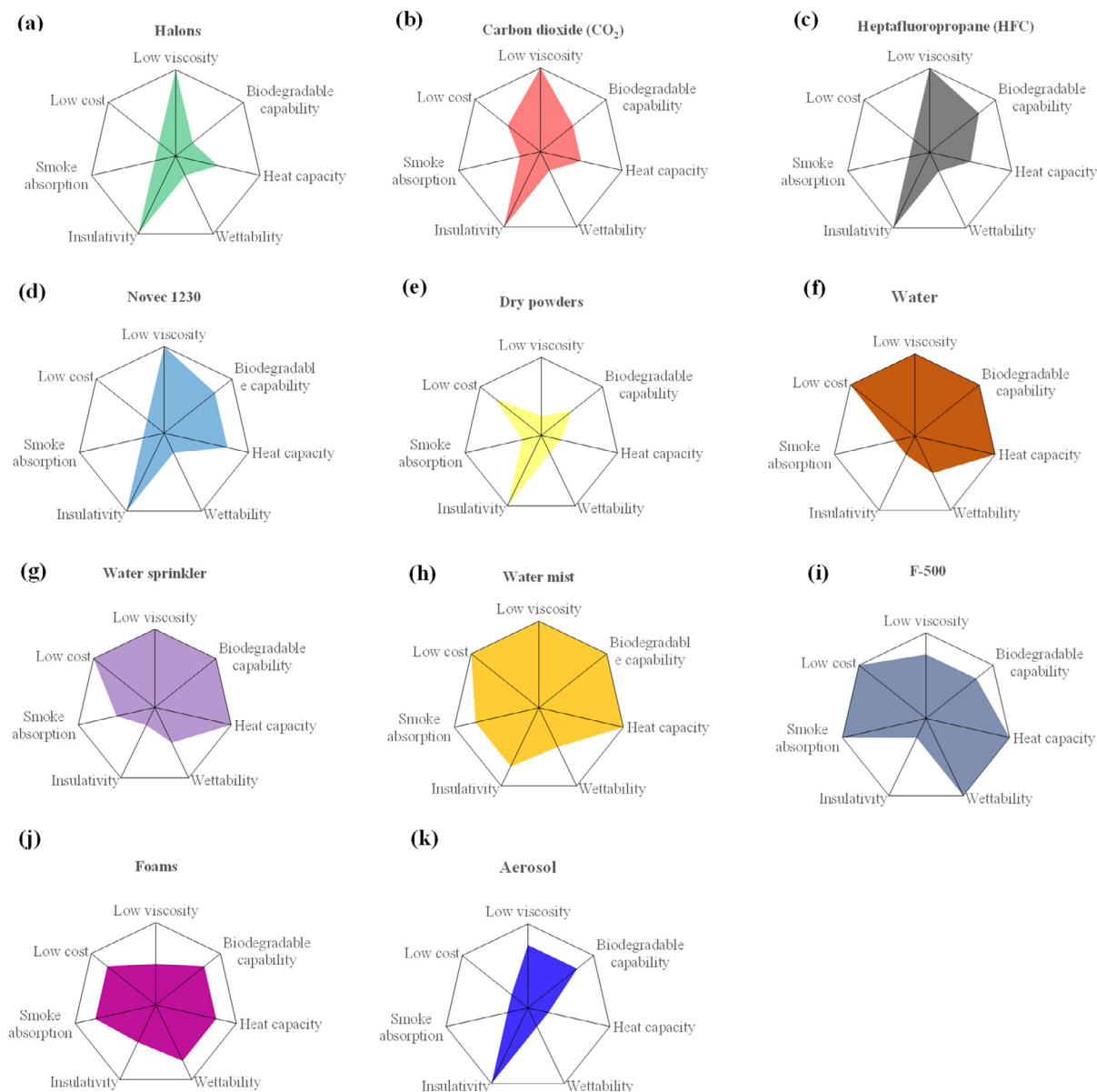
Fig. 12. Radar plots of the performances of (a) halons, (b) carbon dioxide, (c) heptafluoropropane, (d) Novec 1230, (e) dry powders, (f) water, (g) water sprinkler, (h) water mist, (i) F-500, (j) foams and (k) aerosol.

Table 10
Extinguishing characteristics and environmental impact of typical fire extinguishing agents [179].

No.	Fire extinguishing agent	Extinguishing mechanism	Toxicity	ODP	GWP	ALT9 (Years)
1	Halon 1301 (CF3Br)	Cooling, dilution; chemical reaction	Low	16	4900	77
2	Carbon dioxide (CO_2)	Dilution, suffocation	High	0	–	–
3	Heptafluoropropane	Chemical reaction, dilution	Low	0	2050	31
4	Novec 1230 [(CF3)2CFCOC2F5]	Chemical reaction	Low	0	1	0.014
5	Chemical powders	Chemical reaction inhibition, cooling	Low	0	0	0
6	Water mist	Cooling, dilution	Low	0	0	0
7	Aerosol	Cooling, dilution, chemical reaction	Low	0	0	0

worth developing and is highly desirable both for the academic and industrial community. It should be noted that to evaluate the effectiveness of the fire-extinguishing agents, previous studies are mostly focus on single battery or battery module. However, the

suppression tests of TR propagation in a large-scale battery pack also need to be paid more attentions. Thus, an intimate cooperation between the academic and industrial community should be paid enough attention. Moreover, an efficient fire-extinguishing equip-

ment should not just rely on a suitable fire-extinguishing agents but a multi-disciplined system, which also contains effective and proper smoke/fire/temperature monitor/detector and feed-back system. Currently, a reasonable combination and design of existing fire-extinguishing agent, devices and opportunities is the most possible way to achieve efficient fire extinguishing. It calls for a good collaboration between professional people with different background such as chemistry, materials science, electronic engineering etc. With this, we believe the scarcity of battery fire is not a major hindrance for its wider applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

References

[1] C.H. Lee, S.J. Bae, M.Y. Jang, J. Power Sources 293 (2015) 498–510.
[2] Z.H. Liao, S. Zhang, K. Li, G.Q. Zhang, T.G. Habetler, J. Power Sources 436 (2019) 226879.
[3] Y. Nishi, J. Power Sources 100 (2001) 101–106.
[4] S.Y. Ni, S.S. Tan, Q.Y. An, L.Q. Mai, J. Energy Chem. 44 (2020) 73–89.
[5] X.Q. Zhang, X.B. Cheng, Q. Zhang, J. Energy Chem. 25 (2016) 967–984.
[6] L. Kong, Q. Jin, X.T. Zhang, B.Q. Li, J.X. Chen, W.C. Zhu, J.Q. Huang, Q. Zhang, J. Energy Chem. 39 (2019) 17–22.
[7] X. Liu, Q. He, H. Yuan, C. Yan, Y. Zhao, X. Xu, J.Q. Huang, Y.L. Chueh, Q. Zhang, L. Q. Mai, J. Energy Chem. 48 (2020) 109–115.
[8] T.Q. Wu, H.D. Chen, Q.S. Wang, J.H. Sun, J. Hazard Mater. 344 (2018) 733–741.
[9] F. Larsson, P. Andersson, P. Blomqvist, B.E. Mellander, Sci. Rep. 7 (2017) 1–13.
[10] F. Larsson, B.E. Mellander, J. Electrochem. Soc. 161 (2014) 1611–1617.
[11] C.F. Tao, Q.P. Ye, C.M. Wang, Y.J. Qian, C.F. Wang, T.T. Zhou, Z.G. Tang, J. Clean. Prod. 242 (2020) 118539.
[12] C.F. Lopez, J.A. Jeevarajan, P.P. Mukherjee, J. Electrochem. Soc. 162 (2015) A1905–A1915.
[13] S. Wilke, B. Schweitzer, S. Khateeb, S. Al-Hallaj, J. Power Sources 340 (2017) 51–59.
[14] X.N. Feng, X.M. He, M.G. Ouyang, L.G. Lu, P. Wu, C. Kulp, S. Prasser, Appl. Energy. 154 (2015) 74–91.
[15] Q.S. Wang, B.B. Mao, S.I. Stoliarov, J. Sun, Prog. Energy Combust. Sci. 73 (2019) 95–131.
[16] NTSB Office of aviation safety, Interim Factual Report, Boston, 2013.
[17] National Transportation Safety Board, Preliminary Report Highway HWY18FH011, California, 2018.
[18] NTSB, Highway Accident Brief Single-Vehicle Run-off-Road Crash and Fire, Florida, 2018.
[19] NTSB, Preliminary Report Highway HWY18FH014, California, 2018.
[20] H.D. Zhang, H.L. Zhang, Fire Sci. Technol. 36 (2017) 1473–1476.
[21] P.Y. Guo, Z.R. Wang, L. Qian, Electr. Saf. Technol. 21 (2019) 26–30.
[22] T. Zhou, H. Zhao, Fire Sci. Technol. 36 (2017) 716–720.
[23] C.R. Zhang, H. Li, S.X. Wang, Y.L. Cao, H.X. Yang, X.P. Ai, F.P. Zhong, J. Energy Chem. 44 (2020) 33–40.
[24] M.Q. Yuan, K. Liu, J. Energy Chem. 43 (2020) 58–70.
[25] S.Q. Wang, L.G. Lu, D.S. Ren, X.N. Feng, S. Gao, M.G. Ouyang, J. Electrochem. Energy Convers. Storage 16 (2019) 1–10.
[26] S.Q. Zhu, C. Hu, Y. Xu, Y. Jin, J.L. Shui, J. Energy Chem. 46 (2020) 208–214.
[27] D.X. Ouyang, J.W. Weng, J.Y. Hu, M.Y. Chen, Q. Huang, J. Wang, Thermochim. Acta. 676 (2019) 205–213.
[28] J. Weng, D.X. Ouyang, X.Q. Yang, M.Y. Chen, G.Q. Zhang, J. Wang, Energy Convers. Manag. 200 (2019) 112071.
[29] C.C. Yuan, Q.S. Wang, Y. Wang, Y. Zhao, Appl. Therm. Eng. 153 (2019) 39–50.
[30] P.G. Balakrishnan, R. Ramesh, T. Prem Kumar, J. Power Sources 155 (2006) 401–414.
[31] K. Liu, Y.Y. Liu, D.C. Lin, A. Pei, Y. Cui, Sci. Adv. 4 (2018), eaas9820.
[32] D.X. Ouyang, M.Y. Chen, Q. Huang, J.W. Weng, Z. Wang, J. Wang, Appl. Sci. 9 (2019) 2483.
[33] M.N. Richard, J.R. Dahn, J. Power Sources 83 (1999) 71–74.
[34] R. Spotnitz, J. Franklin, J. Power Sources 113 (2003) 81–100.
[35] M.Y. Chen, D.X. Ouyang, J.W. Weng, J.H. Liu, J. Wang, Process Saf. Environ. Prot. 130 (2019) 250–256.
[36] G. Venugopal, J. Power Sources 101 (2001) 231–237.
[37] S.Q. Liu, T.Y. Ma, Z. Wei, G.L. Bai, H.T. Liu, D.P. Xu, Z.Q. Shan, F. Wang, J. Energy Chem. 52 (2021) 20–27.
[38] D.D. MacNeil, J.R. Dahn, J. Electrochem. Soc. 148 (2001) A1205.
[39] H. Yang, G.V. Zhuang, P.N. Ross, J. Power Sources 161 (2006) 573–579.
[40] A. Du Pasquier, F. Disma, T. Bowmer, A.S. Gozdz, G. Amatucci, A. Du Pasquier, F. Disma, S.A.S. Gozdz, J.M. Tarascon, J. Electrochem. Soc. 145 (1998) 472–477.
[41] G.B. Zhong, B.B. Mao, C. Wang, L. Jiang, K.Q. Xu, J.H. Sun, Q.S. Wang, J. Therm. Anal. Calorim. 135 (2018) 2879–2889.
[42] H. Li, Q.L. Duan, C.P. Zhao, Z.H. Huang, Q.S. Wang, J. Hazard. Mater. 375 (2019) 241–254.
[43] X.N. Feng, M. Fang, X.M. He, M.G. Ouyang, L.G. Lu, H. Wang, M.X. Zhang, J. Power Sources. 255 (2014) 294–301.
[44] ISO, 2007, Classification of fires. ISO copyright office, Switzerland, No. ISO 3941:2007(E).
[45] Y.P. Wang, N. An, L. Wen, L. Wang, X.T. Jiang, F. Hou, Y.X. Yin, J. Liang, J. Energy Chem. 55 (2020) 391–419.
[46] D.H. Doughty, E.P. Roth, C.C. Crafts, G. Nagasubramanian, G. Henriksen, K. Amine, J. Power Sources 146 (2005) 116–120.
[47] A. Blum, R.T. Long, SAE Int. J. Passeng. Cars – Mech. Syst. 8 (2015) 565–572.
[48] K. Ando, T. Matsuda, D. Imamura, J. Energy Chem. 53 (2020) 285–289.
[49] K. Li, E.M. Kennedy, B.Z. Dlugogorski, Ind. Eng. Chem. Res. 38 (1999) 3345–3352.
[50] O. Mathieu, C. Keesee, C. Gregoire, E.L. Petersen, J. Phys. Chem. A. 119 (2015) 7611–7626.
[51] R.G. Hill, W.I.T. Trans, Built Environ. 110 (2009) 171–179.
[52] S.M. Summer, Flammability Assessment of Lithium-Ion and Lithium-Ion Polymer Battery Cells Designed for Aircraft Power Usage, FAA, 2010.
[53] P.S. Liss, P.G. Slater, Nat. Commun. 249 (1974) 810–912.
[54] H. Yu, E.M. Kennedy, M.A. Uddin, S.P. Sullivan, B.Z. Dlugogorski, Int. J. Chem. Kinet. 37 (2005) 134–146.
[55] J.L. Pagliaro, N. Bouvet, G.T. Linteris, Combust. Flame. 169 (2016) 272–286.
[56] E. Braun, C.A. Womeldorf, W.L. Grosshandler, Fire Saf. J. 33 (1999) 141–152.
[57] A. McCulloch, J. Fluor. Chem. 100 (1999) 163–173.
[58] Q.S. Wang, G.Z. Shao, Q.L. Duan, M. Chen, Y.Q. Li, K. Wu, B.J. Liu, P. Peng, J.H. Sun, Fire Technol. 52 (2016) 387–396.
[59] D.X. Yu, Y. Li, S.Y. Zhang, Y.L. Du, H.B. Dong, Chinese J. Power Sources 43 (2019) 60–63.
[60] R.J. Si, D.Q. Liu, S.Q. Xue, Procedia Eng. 211 (2018) 629–634.
[61] Z.G. Jiang, H.R. Wu, R.Q. Song, X. Chen, Phys. Numer. Simul. Geotech. Eng. 21 (2015) 36–42, https://doi.org/10.5503/J.PNSGE.2015.21.006.
[62] H. Webster, Flammability Assessment of Bulk- Packed, Nonrechargeable Lithium Primary Batteries in Transport Category Aircraft, FAA, 2004.
[63] W.-J.A. Olajczak CJ, US FAA-Style Flammability Assessment of Lithium Ion Cells and Battery Packs in Aircraft Cargo Holds Addendum — Prismatic Battery Packs and Pressure Measurements US FAA-Style Flammability Assessment of Lithium Ion Cells and Battery Packs in Aircraft Cargo, FAA, 2005.
[64] H. Webster, Flammability Assessment of Bulk- Packed, Rechargeable Lithium-Ion Cells in Transport Category Aircraft, FAA, 2006.
[65] S.S. Environments, J. Fire Sci. 20 (2002) 391–399.
[66] N. Saito, Y. Ogawa, Y. Saso, C. Liao, R. Sakei, Fire Saf. J. 27 (1996) 185–200.
[67] L.X. Kong, C. Li, J.C. Jiang, M.G. Pecht, Energies 11 (2018) 1–11.
[68] J.J. Xu, P.Y. Guo, Q.L. Duan, X.C. Yu, L. Zhang, Y. Liu, Q.S. Wang, Appl.Therm. Eng. 171 (2020) 115057.
[69] P. Russo, C. Di Bari, M. Mazzaro, A. De Rosa, I. Morriello, Chem. Eng. Trans. 67 (2018) 727–732.
[70] H. Rao, Z. Huang, H. Zhang, S. Xiao, in: ICTIS 2015 – 3rd Int. Conf. Transp. Inf. Safety, Proc., 2015, pp. 865–870.
[71] Y. Li, D.X. Yu, S.Y. Zhang, Q.M. Hu, X. Liu, J.Q. Wang, J. Saf. Environ. 15 (2015) 120–125.
[72] Q.S. Wang, K. Li, Y. Wang, H.D. Chen, Q.L. Duan, J. Electrochem. Energy Convers. Strorage 15 (2019) 1–10.
[73] M.L. Robin, Process Saf. Prog. 17 (1998) 209–212.
[74] R.W.M. Choy, Int. J. Eng. Performance-Based Fire Codes 6 (2004) 46–51.
[75] W.M. Choy, N.K. Fong, Int. J. Eng. Performance-Based Fire Codes 5 (2003) 181–184.
[76] R.G. Hynes, J.C. Mackie, Energy & Fuels 13 (1999) 485–492.
[77] R.G. Hynes, J.C. MacKie, A.R. Masri, Combust. Flame 113 (1998) 554–565.
[78] M.L. Robin, in: ACs Symp. Ser., Washington, 1997, pp. 85–98.
[79] P.E Rivers, in: Halon Options Tech. Work. Conf., 2001, pp. 341–348.
[80] J.L. Pagliaro, G.T. Linteris, Fire Saf. J. 87 (2017) 10–17.
[81] W. Xu, Y. Jiang, X.Y. Ren, J. Fire Sci. 34 (2016) 289–304.
[82] T.W. Zhang, H. Liu, Z.D. Guo, Y. Wang, J. Eng. Thermophys. 40 (2019) 2919–12917.

[83] L. Liu, Z.M. Du, T.W. Zhang, Z.D. Guo, M.Q. He, Z.Q. Liu, Int. J. Hydrogen Energy 44 (2019) 22282–22300.
[84] K. Li, Q.S. Wang, J.H. Sun, Fire Saf. Sci. 27 (2018) 124–132.
[85] Y.J. Liu, Q.L. Duan, J.J. Xu, H. Li, J.H. Sun, Q.S. Wang, J. Energy Storage 28 (2020) 101–185.
[86] X. Mi, Z.H. Lu, J. Zhang, X.W. Wang, K. Fang, Chinese J. Power Sources 40 (2016) 2483–2485.
[87] Y.J. Liu, Q.L. Duan, J.J. Xu, H.D. Chen, W. Lu, Q.S. Wang, RSC Adv. 8 (2018) 42223–42232.
[88] H.M. Liu, Z.M. Du, Z.Y. Han, X. Du, J. Saf. Environ. 14 (2014) 70–75.
[89] Y.M. Zhang, G.W. Zou, Y. Gao, H. Dong, Y. Huo, J. Harbin Eng. Univ. 33 (2012) 449–453.
[90] L.J. Zhang, Q.Q. Han, J.H. Zhao, Ind. Saf. Environ. Protction. 40 (2014) 38–39.
[91] H. A, Symp. Combust. 27 (1998) 2857–2864.
[92] J.C. Zhao, Y.Y. Fu, Z.T. Yin, H.R. Xing, S. Lu, H.P. Zhang, Mater. Des. 186 (2020) 108331.
[93] M.H. Li, J.C. Xu, Q. Li, C.J. Wang, B.Z. Wang, J.C. Jiang, Process Saf. Prog. (2019) 1–10.
[94] C.H. Su, C.C. Chen, H.J. Liaw, S.C. Wang, Procedia Eng. 84 (2014) 485–490.
[95] Z.M. Luo, T. Wang, Z.H. Tian, F.M. Cheng, J. Deng, Y.T. Zhang, J. Loss Prev. Process Ind. 30 (2014) 17–23.
[96] X.D. Meng, K. Yang, M.J. Zhang, F. Gao, Y.J. Liu, Q.L. Duan, Q.S. Wang, J. Energy Storage 30 (2020) 101532.
[97] Y.J. Liu, Q.L. Duan, K. Li, H.D. Chen, Q.S. Wang, Energy Storage Sci. Technol. 7 (2018) 1105–1112.
[98] T.W. Zhang, Z.Y. Han, Z.M. Du, K. Liu, Z.L. Zhang, Appl. Therm. Eng. 107 (2016) 863–869.
[99] T. Liu, Y. Liu, X. Wang, X.X. Kong, G.C. Li, Energy Convers. Manag. 199 (2019) 111969.
[100] M. Egelhaaaf, D. Kress, D. Wolpert, SAE Int. J. Alt. Power. 2 (2013) 37–48.
[101] R. Long, A. Blum, T. Bress, B. Cotts, Best Pratices for Emergency Response to Incidents Involving Electric Vehicles Battery Hazards: A Repot on Full-Scale Testing Results, National Fire Protection Research Foundation. https://www.energy.gov/sites/prod/files/2014/02/f8/final_report_nfpa.pdf/, 2013.
[102] W.T. Luo, S.B. Zhu, J.H. Gong, Z. Zhou, Procedia Eng. 211 (2018) 531–537.
[103] T. Maloney, Administration, Extinguishment of Lithium-Ion and Lithium-Metal Battery Fires, US Department of Transportation, 2017.
[104] A. Cablé, K. Chetehouna, N. Gascoin, A. Settar, K. Van Herpe, M. Kadoche, J. Loss Prev. Process Ind. 60 (2019) 76–86.
[105] H.R. Liu, C. Wang, I.M. De Cachinho Cordeiro, A.C.Y. Yuen, Q. Chen, Q.N. Chan, S. Kook, G.H. Yeoh, J. Build. Eng. 28 (2020) 1–14.
[106] B. Craig, J. Fire Prot. Eng. 4 (1991) 5–16.
[107] B. Ditch, J. De Vries, Flammability Characterization of Li-Ion Batteries in Bulk Storage, FM Glob. https://www.fmglobal.com/~/media/Files/FMGlobal/Research%20Technical%20Reports/p13037.pdf?la=en&isGated=true&itemId=%7BE40FF1B5-4893-41AB-92DA-8DFD818EF663%7D/, 2013.
[108] B. Ditch, Fire Technol. 54 (2018) 359–377.
[109] P. Andersson, M. Arvidson, F. Evegren, M. Jandali, F. Larsson, M. Rosengren, Lion Fire: Extinguishment and Mitigation of Fires in Li-Ion Batteries at Sea, 2018.
[110] NFPA, 2019, Standard on Water Mist Fire Protection Systems, National Fire Protection Association, Quincy, MA, Standard No. NFFPA 750.
[111] Z.G. Liu, K.A.K. Kim, J. Fire Prot. Eng. 10 (2000) 32–50.
[112] J. Mawhinney, B. Dlugogorski, A. Kim, Fire Saf. Sci. 4 (1994) 47–60.
[113] K. Andrew K, D. Z, Bogdan, M. Jack R, in: Proc. Halon Options Tech. Work. Conf., Albuqerque, New Mexico, 1994.
[114] B. Rodriguez, G. Young, in: 43rd Int. Conf. Environ. Syst., 2013, pp. 1–8.
[115] L. Zhang, Q.L. Duan, Y.j. Liu, J.J. Xu, J.H. Sun, H.H. Xiao, Fire Saf. J. (2020) 103117.
[116] T. Liu, C.F. Tao, X.S. Wang, Appl. Energy. 267 (2020) 115087.
[117] H.D. Tang, J. Qian, Q.W. Li, J.D. Li, S. Li, Fire Saf. Sci. 19 (2010) 68–73.
[118] R.X. Ma, X.M. Ma, Fire Sci. Technol. 36 (2017) 61–66.
[119] Q.W. Li, J. Qin, H.D. Tang, J.D. Ni, X.Y. Zhang, B. Lei, G.X. Liao, J. Combust. Sci. Technol. 16 (2010) 274–280.
[120] C.Z. Xin, L.G. Zhi, Fire Saf. Sci. 10 (2001) 174–177.
[121] X.M. Ni, W.K. Chow, Appl. Therm. Eng. 31 (2011) 3864–3870.
[122] F. Larsson, P. Andersson, P. Blomqvist, A. Lorén, B.E. Mellander, J. Power Sources 271 (2014) 414–420.
[123] L. Zhang, Q.L. Duan, Y.j. Liu, J.J. Xu, J.H. Sun, H.H. Xiao, Fire Saf. J. (2020) 103117.
[124] B.B. Wu, G.X. Liao, Procedia Eng. 62 (2013) 317–323.
[125] X.J. Huang, P.P. Chen, M.J. Lan, X.S. Wang, G.X. Liao, Procedia Eng. 62 (2013) 852–858.
[126] X.M. Zhou, G.X. Liao, B. Cai, Fire Saf. J. 41 (2006) 39–45.
[127] D. Lv, W. Tan, G.R. Zhu, L.Y. Liu, Process Saf. Environ. Prot. 129 (2019) 168–175.
[128] T.W. Zhang, H. Liu, Z.Y. Han, Z.M. Du, Y. Wang, Appl. Therm. Eng. 122 (2017) 429–438.
[129] T.W. Zhang, Z.Y. Han, Z.M. Du, Z.W. Zhang, K. Liu, Int. J. Hydrogen Energy 41 (2016) 15078–15088.
[130] Y. Koshiba, S. Okazaki, H. Ohtani, Fire Saf. J. 83 (2016) 90–98.
[131] X.Y. Cao, J.J. Ren, Y.H. Zhou, Q.J. Wang, X.L. Gao, M.S. Bi, J. Hazard. Mater. 285 (2015) 311–318.
[132] T.W. Zhang, Z.M. Du, Z.Y. Han, K. Liu, Appl. Therm. Eng. 102 (2016) 1069–1074.
[133] P. Joseph, E. Nichols, V. Novozhilov, Fire Saf. J. 58 (2013) 221–225.
[134] H.L. Jia, H.D. Shen, H.J. Xiang, D.H. Li, R.P. Zhai, Combust. Sci. Technol. 192 (2020) 902–914.
[135] M. Chao, S.B. Zhu, L.T. Jia, X.L. Wu, Procedia Eng. 84 (2014) 558–564.
[136] Y.S. Huang, W.C. Zhang, X.Y. Dai, Y. Zhao, Procedia Eng. 45 (2012) 649–654.
[137] M. Zhu, S.B. Zhu, W.T. Luo, Fire Sci. Technol. 37 (2018) 799–803.
[138] X. Li, S.B. Zhu, W.Y. Zhuang, X.T. Hao, in: 2018 IEEE Int. Conf. Saf. Prod. Informatiz., IEEE, 2018, pp. 53–56.
[139] Hazard Control Technologies Inc., Material Safety Data Sheet F-500 Multi-Purpose Encapsulator Agent, 2018.
[140] D.L. Zhao, T.Y. Fang, F. Lian, J. Saf. Scince Technol. 6 (2010) 9–14.
[141] F. Wu, J.C. Jiang, Q. Chen, L.J. Shi, D. Zhao, Fire Sci. Technol. 35 (2016) 657–659.
[142] D.L. Zhao, F. Lian, Y.X. Liu, Saf. Sci. Technol. 5 (2009) 62–66.
[143] H.B. Luo, Mar. Fire (2005) 44–45.
[144] N. Warner, Overview of a Year of Battery Fire Testing by DNV GL for Con Ed, NYSERDA and FDNY, DNVGL, 2017.
[145] M.X. Zhu, S.B. Zhu, J.H. Gong, Z. Zhou, Procedia Eng. 211 (2018) 1083–1090.
[146] Z. Zhou, J.H. Yang, P. Zhu, Q. Zhang, S.B. Zhang, Fire Sci. Technol. 38 (2019) 512–516.
[147] Q.S. Zhang, X.J. Cheng, W. Bai, J. Saf. Sci. Technol. 14 (2018) 43–50.
[148] Q.S. Zhang, X.N. Luo, X.J. Cheng, W. Bai, J. Beijing Univ. Aeronaut. Astronaut. 46 (2019) 1073–1079.
[149] Q.S. Zhang, X.J. Cheng, W. Bai, Fire Sci. Technol. 37 (2018) 1211–1214.
[150] L.R. Summerlin, Chemical Demonstrations: A Sourcebook for Teachers, second ed., American Chemical Society, Washington, 1985.
[151] A.K. Kim, G.P. Crampton, Fire Technol. 48 (2012) 549–564.
[152] L. Su, L. Wang, Z.H. Wang, J. Zhang, Y.X. Tian, Y.G. Yan, Procedia Eng. 45 (2012) 663–668.
[153] X.C. Fu, H.L. Ye, Z.M. Bao, T. Chen, G. Xue, Y.N. Hu, Fire Sci. Technol. 27 (2008) 590–592.
[154] J. Stern, J. Gordon Routley, Class A Foam for Structural Firefighting, US Fire Administration, 1996.
[155] P. Schlobohm, in: Biswell Symp. Fire Issues Solut. Urban Interface Wildl. Ecosyst., 1995, pp. 81–84.
[156] US Forest Service, Foam vs Fire Class A Foam for Wildland Fires, 1993.
[157] P. Andersson, M. Arvidson, F. Evegren, M. Jandali, F. Larsson, M. Rosengren, Lion Fire: Extinguishment and Mitigation of Fires in Li-Ion Batteries at Sea, RISE Research Institutes of Sweden, 2018.
[158] C.D. Vecitis, Y. Wang, J. Cheng, H. Park, B.T. Mader, M.R. Hoffmann, Environ. Sci. Technol. 44 (2010) 432–438.
[159] C.A. Moody, J.A. Field, Environ. Sci. Technol. 34 (2000) 3864–3870.
[160] B. Weiner, L.W.Y. Yeung, E.B. Marchington, L.A. D'Agostino, S.A. Mabury, Environ. Chem. 10 (2013) 486–493.
[161] Y.J. Sheng, N. Jiang, X.X. Sun, S.X. Lu, C.H. Li, Fire Technol. 54 (2018) 211–228.
[162] W.J. Pan, M.G. Zhang, X.Y. Gao, S.F. Mo, J. Loss Prev. Process Ind. 63 (2020) 103997.
[163] A.J. Laundess, M.S. Rayson, B.Z. Dlugogorski, E.M. Kennedy, Fire Technol. 48 (2012) 625–640.
[164] K. Shinoda, T. Nomura, J. Phys. Chem. 84 (1980) 365–369.
[165] Z.S. Xu, X. Guo, L. Yan, W.D. Kang, Case StudTherm. Eng. 17 (2020) 100578.
[166] X.H. Jia, H.D. Bo, Y.H. He, Chem. Pap. 73 (2019) 1777–1784.
[167] Y.H. He, Q. Sun, H. Xing, Y. Wu, J.X. Xiao, J. Dispers. Sci. Technol. 40 (2019) 319–331.
[168] A.R. Sontake, S.M. Wagh, Chem. Eng. Sci. 2 (2014) 11–14.
[169] B. Bo, Fire Sci. Technol. 33 (2014) 92–95.
[170] W.D. Kang, L. Yan, F.X. Ding, X.S. Guo, Z. Xu, Case Stud. Therm. Eng. 16 (2019) 100557.
[171] A. Bourgeois, J. Bergendahl, A. Rangwala, Chemosphere 131 (2015) 104–109.
[172] G.J. Zhu, Spec. Petrochemicals (1993) 47–49.
[173] A. Zaggia, L. Conte, G. Padoan, R. Bertani, J. Surfactants Deterg. 13 (2010) 33–40.
[174] H.A. Alsaati, D. Ditzler, V. Burapatana, R.D. Tanner, Brazilian Arch.Biol. Technol. 46 (2003) 735–740.
[175] I. Tureková, B. Karol, Res. Pap. Fac. Mater. Sci. Technol. Slovak Univ. Technol. 18 (2012) 111–120.
[176] X.T. Zhang, M.H.S. Ismail, F.R.B. Ahmadun, N.B.H. Abdullah, C. Hee, Brazilian J. Chem. Eng. 32 (2015) 707–724.
[177] H.M. Liu, in: 2015 2nd Int. Conf. Simul. Model. Methodol. Appl. (SMTA 2015), 2015, pp. 556–558.
[178] Y. Spector, in: Halon Options Tech. Work. Conf., New Mexico, 1994, pp. 391–403.
[179] M. Rohilla, A. Saxena, P.K. Dixit, G.K. Mishra, R. Narang, Fire Technol. 55 (2019) 2515–2545.
[180] K. Kwon, Y. Kim, Korean J. Chem. Eng. 30 (2013) 2254–2258.
[181] W. Polytechnic, in: Halon Options Tech. Work. Conf., Albuquerque, NM, USA, 1994, pp. 379–390.
[182] C.J. Kibert, D. Dierdorf, Fire Technol. 30 (1994) 387–399.
[183] C.T. Ewing, F.R. Faith, J.T. Hughes, H.W. Carhart, Fire Technol. 4 (1992) 35–51.
[184] C.T. Ewing, F.R. Faith, J.T. Hughes, H.W. Carhart, Fire Technol. 25 (1989) 134–149.

[185] Y. Ye, Z.M. Du, Z.Y. Han, Fire Mater. 43 (2019) 84–91.

[186] X.D. Li, R.J. Yang, J.M. Li, X.M. Li, Fire Saf. Sci. 11 (2011) 142–146.

[187] J. Ma, X.R. Liu, H.J. Jin, J. Deng, Y.P. Wu, Adv. Mater. Res. 239–242 (2011) 2479–2483.

[188] C. Zhu, J. Wang, W. Xie, T. Zheng, C. Lv, Fire Technol. 51 (2014) 97–107.

[189] H. Davion, Considerations for ESS Fire Safety, DNVGL, 2017.

[190] H. Davion, Testing of Aerosol Fire Extinguishing Agent for Li-Ion Battery Fires, New York, 2017.