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SUPPRESSION OF LI-ION BATTERY FIRES

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Suppression of Li-ion Battery Fires

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Abstract

This thesis presents a systematic literature review of fixed fire suppression systems and extinguishing agents for lithium-ion battery (LIB) fires. The review identifies 85 relevant sources published between 2013 and March 2023, and categorises different research experiments into cell-level, module-level, electric vehicle (EV) pack-level, battery energy storage system (BESS) rack-level and warehouse storage experiments, according to LIB configurations. It was found that about 67% of the publications focused on small-scale cell-level and 9% on module-level experiments. However, large-scale EV pack-level and BESS rack-level experiments are lacking. More than twenty (20) different extinguishing agents (water-based, gas-based, powder-based and novel combinations of agents) and two (2) dispersion modes (total flooding and direct internal injection) are evaluated systematically. The advantages and drawbacks of each type of extinguishing agent are compared and discussed based on dispersion modes and LIB configurations. Lastly, suggestions on how to apply the findings from the small-scale experiments onto large-scale experiments and key findings of potential applications of extinguishing agents in EV and BESS are presented.

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摘要

本文系统地对锂电池相关火灾固定抑制系统和灭火剂的文献进行了综述。该综述包含了2013年至2023年3月间发表的85个相关文献，并根据锂电池的不同配置将收集到的研究实验分为单体级、模块级、电动汽车包级、电池储能系统机架级和仓储实验。发现约67%的文献集中在小尺度单体级实验上，而仅有9%的文献集中在模块级实验上。然而，大规模的电动汽车包级和电池储能系统机架级实验还明显不足。本文系统地评估了20多种灭火剂（水基、气体、粉末和新型组合灭火剂）和2种应用方式（全面覆盖和直接内部喷射）。根据应用方式和电池配置的不同，比较和讨论了每种灭火剂的优缺点。最后，提出了如何将小尺度实验的研究成果应用于大规模实验的一些建议以及总结了灭火剂在电动汽车和电池储能系统中潜在应用的关键发现。

List of Abbreviations

Abbreviation (In alphabetical order)	**Description**
2-BTP	2-Bromo-3,3,3-trifluoroprop-1-ene ($C_3H_2F_3Br$)
AASD	Aluminium ammonium sulfate dodecahydrate
AEC	Sodium fatty alcohol polyoxyethylene ester carboxylate
AEO	Fatty alcohol polyoxy- ethylene ether
AFT	Adiabatic flame temperature
APG	Alkyl glycoside
AVD	Aqueous vermiculite dispersion
BESS	Battery energy storage system
BMS	Battery management system
CAFS	Compressed air foaming system
CEA	European Insurance and Reinsurance Federation
DMMP	Dimethyl methylphosphonate
EL20	Polyoxyethylene ricinoleate
EL90	Castor oil polyoxyethylene ether
EN	European Norm
ESS	Energy storage system
EV	Electric vehicle
DNV	Det Norske Veritas (Norway, U.S.) (Formerly DNV-GL)
DOT	Department of Transportation (U.S.)
FC4330	Fluorocarbon surfactant (3M)
FFS	Fixed firefighting system
FM	Factory Mutual (U.S.)
FMEE	Fatty methyl ester ethoxylate
HMR	Hazardous Materials Regulations (U.S.)
HPWM	High-pressure water mist
IEC	International Electrotechnical Commission
IG	Inert gas
IMO	International Maritime Organization
ISO	International Organization for Standardization
LCO	Lithium cobalt oxide
LFP	Lithium iron phosphate
LI	Lithium
LIB	Lithium-ion battery
LMO	Lithium manganese oxide
LPWM	Low-pressure water mist
LTO	Lithium titanate oxide
MAEPK	Potassium monoalkyl ester phosphate
MIIT	Ministry of Industry and Information Technology (China)
$N_2(g)$	Gaseous nitrogen
$N_2(l)$	Liquid nitrogen
NASA	The National Aeronautics and Space Administration (U.S.)
NCA	Lithium nickel cobalt aluminium oxide
NFPA	National Fire Protection Association (U.S.)
NMC (or NCM)	Lithium nickel manganese cobalt oxide

PFAB	Polyfluoroalkyl betaine
PRISMA-ScR	Preferred reporting items for systematic reviews and meta-analysis extension for scoping reviews
RISE	Research Institute of Sweden
RTI	Response time index
SDBS	Sodium dodecylbenzene sulfonate
SDS	Sodium dodecyl sulfate
SOC	State-of-charge
TC	Thermocouple
TEOA	Triethanolamine
TR	Thermal runaway
UL	Underwriters Laboratories (U.S. and Canada)
UN	United Nation
WM	Water mist
ZSW	Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (Research Institute in Germany)

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1 Introduction and Objectives

1.1 General

Driven by the ‘net zero’ CO_2 emissions target 2050 set by the International Energy Agency [1], government agencies and industrial sectors have invested and researched heavily to reduce carbon emissions using greener energy over the last decade. The paradigm has been shifted in end-users such as industry, transportation and building sectors to use alternative green energies (e.g., converting solar, wind or hydro energy into electric energy) compared with the conventional burning of coals or fossil fuels. To achieve this goal, lithium-ion battery (LIB) is adopted as an energy carrier to store the converted green electric energy and deliver them to the end-users. LIBs were developed in the 1970s and first commercialised by Sony in 1991 for the handheld video recorder. In the last decade, LIB technology has been developing rapidly and becoming more mature. Nowadays, the use of LIBs is growing across many applications, from consumer electronics, electric vehicles to many other industrial applications, because of their lightweight, high energy density, long battery life, fast charging capability and high efficiency [2].

In 2020, the worldwide market size for LIBs was valued at USD 36.90 billion, and it is expected to exhibit a consistent growth trajectory, reaching USD 193.13 billion by 2028. Though COVID-19 has slowed down the global supply chain of raw materials of LIBs and the overall growth of LIBs, it is expected that the demand and growth will recover to the pre-pandemic’s prediction because most restrictions due to the pandemic are already lifted [3].

In the land transportation sector, electric vehicles using LIBs have a positive impact on climate change compared with conventional internal combustion engines. Governments from many countries promote and support the development of greener and pollution-free mobility in public transportation systems. According to an independent advisory firm, Accuracy [4], the growth of the UK’s electric bus fleet is anticipated to be the largest in Europe by 2024. Throughout Europe, there is a prediction of a rise in the quantity of electric buses by 198% by 2024, with substantial expansion expected in France and the Nordic countries, followed by Poland, The Netherlands and Italy. In November 2022, the Netherlands and Sweden joined the cohort of seven countries, consisting of the U.S., Canada, Israel, Australia, Germany and New Zealand, to transition their government-operated fleets to zero-emission vehicles [5]. Promoting more electric buses is also envisaged to reduce the number of passenger vehicles on the roads. This helps in achieving the ultimate goal of ‘net-zero’ emissions.

In the industrial sectors, having the same ‘net zero’ emission goal, the market for battery energy storage systems (BESS) utilising LIBs is growing rapidly with increasing demand mainly due to its high energy density, reduction in cost and considerable stability compared with other types of batteries. Energy Storage Systems (ESS) is a broad term that refers to the capability of a system to store energy through thermal, electro-mechanical or electrical-chemical methods. A BESS is a subset of ESS using the electrochemical solution [6]. LIBs in ESS offer sizable energy storage capacity for a reliable application and can be repeatedly charged and discharged over their long lifespan. The battery energy storage used by power grid operators helps decrease the peak demand for electricity in a grid system, as well as receives compensation and incentives from local regulators [7]. Some ship or aircraft operators use the containerised BESS as an alternative fuel for propulsion or uninterruptible power supply. Some factories or business operators use the BESS as a backup emergency power supply to sustain their critical operations.

1.2 Categorisation of Lithium-ion Batteries

It is important to differentiate between primary and secondary lithium batteries. The primary lithium battery refers to the non-chargeable lithium metal battery, and the secondary lithium battery refers to the chargeable lithium-ion batteries. In this thesis, the study only focuses on chargeable secondary lithium-ion batteries – LIBs. Broadly, the chargeable LIBs can be categorised in the following ways, as shown in Table 1.

Table 1 Various categorisations of lithium-ion batteries [8].

By Battery Electrode Materials		By Battery Chemistry Type	By Product Type	By Capacity and Voltage
Cathode	Anode			
• Lithium nickel manganese cobalt • Lithium iron phosphate • Lithium cobalt oxide • Lithium titanate oxide • Lithium manganese oxide • Lithium nickel cobalt aluminium oxide	• Natural graphite • Artificial graphite • Titanate • Any other anode materials	• Lithium Nickel Manganese Cobalt Oxide (NMC or NCM) • Lithium Iron Phosphate (LFP) • Lithium Cobalt Oxide (LCO) • Lithium Titanate Oxide (LTO) • Lithium Manganese Oxide (LMO) • Lithium Nickel Cobalt Aluminium Oxide (NCA)	• Cell ○ Cylindrical ○ Pouch ○ Prismatic • Module • Battery Pack • Stationary Rack	Capacity: • 0 to 3,000mAh • 3,000 to 10,000mAh • 10,000 to 60,000mAh • 60,000mAh and above Voltage: • Low (Below 12V) • Medium (12-36V) • High (Above 36V)

Global Market Insights provides an analysis of the latest market segmentation of different types of LIBs, as shown in Figure 1. The two most frequently utilised LIBs in the market are NMC and LFP, such as in consumer electronics, electric vehicles and energy storage [5].

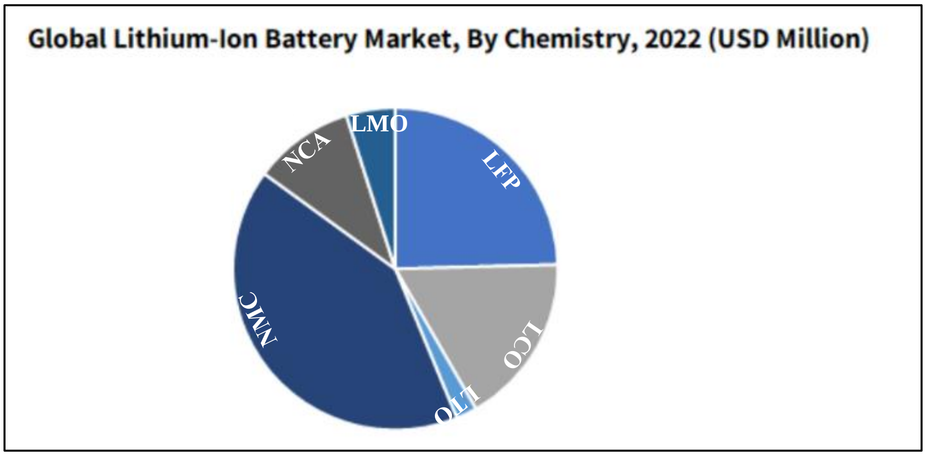


Figure 1 Market segmentation of different types of lithium-ion batteries [5].

1.3 Fire and Societal Problems Associated with the Usage of Lithium-ion Batteries

Despite the rapid growth in LIBs globally, the development of fire protection measures for LIB applications is lagging. For instance, the first edition of NFPA855:2020, *"Standard for the installation of stationary energy storage systems"*, was only published in late 2019 after a series of LIB fire incidents. The fire risks associated with high-energy LIBs have posed a severe issue and safety concern to life and property. When a LIB's temperature increases to approximately 130-150°C, the reaction of the high-energy anode and the flammable electrolyte takes place. The deterioration of the battery separator due to high temperature leads to an internal short circuit between the anode and cathode. The battery's exothermic reaction is prone to generating more heat [9]. If the heat is generated greater than being dissipated, the temperature of the LIB will continue to accumulate and increase rapidly. The process of the rapid temperature increase is understood as a thermal runaway (TR) that produces a significant amount of heat and releases flammable and toxic gases, which will result in hazardous fire, smoke and even explosion. LIBs can fail in both non-energetic and energetic modes, as shown in Figure 2. The thermal runaway belongs to the energetic failure, which is a consequence of (i) thermal abuse (e.g., high external temperature or heating), (ii) mechanical abuse (e.g., mechanical damages such as external impact forces, puncturing and collision), (iii) electrical abuse (e.g., external short-circuiting, overcharge or over-discharge) or (iv) internal short-circuiting due to deformation and dendrites [10].

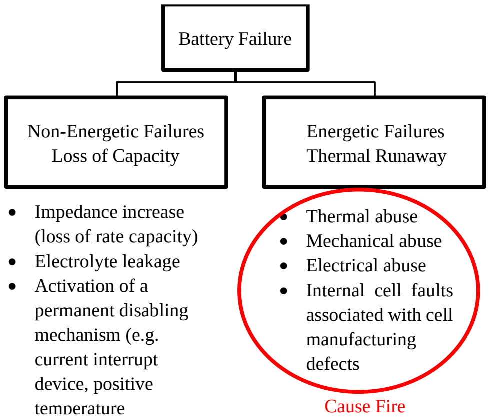


Figure 2 Non-energetic and energetic failure of Lithium-ion batteries [10].

Since the rapid development and proliferation of LIBs from 2010, news on fire incidents related to LIBs used in smartphones and electric bikes/scooters/cars/buses can be frequently seen on television, the internet and in newspapers. News on LIB-related fire incidents for BESS are not as frequently seen as others, probably due to limited systems on the market and less exposure to human beings' daily life. However, such fire incidents did occur in real life and often followed with more severe consequences in terms of operational and economic losses but a less direct impact on human beings' daily life.

Therefore, the fire safety of LIBs has drawn the increasing attention of researchers, fire specialists, LIB manufacturers/integrators and authorities in recent years. They conducted LIB fire experiments, trialled different fire suppression methods and extinguishing agents, set test requirements and published fire protection guidelines. Since this thesis will discuss fire suppression for LIBs, the focus will be on the potential field applications where fixed fire suppression systems could be installed, such as the fire suppression systems provided for electric buses and battery energy storage systems.

As shown in Table 2, in 2021 and 2022 alone, there were numerous bus fire incidents related to electric buses using LIBs globally, not to mention many more electric bus-related fire incidents before 2021. Though the causes of some fire incidents have not been concluded, most evidence pointed to LIBs-initiated fires. Figure 3 shows the fire scenes of some electric bus fire incidents captured by surveillance cameras.

Table 2 List of electric bus fire incidents in 2021 and 2022.

Date	Location	Remark
11 Nov 2022	South Philadelphia, U.S.	Batteries in an electric bus caught fire in a depot [11]
23 Jul 2022	Connecticut, U.S.	An electric bus catches fire at a transit bus depot [12]
22 May 2022	London, UK	A number of buses catch fire at the town centre transport depot [13]
29 Apr 2022	Paris, France	A fire broke out on an electric bus while it was in transit [14]
4 Apr 2022	Paris, France	A fire broke out on an electric bus while it was in transit [14]
11 Oct 2021	Stuttgart, Germany	25 buses were destroyed in a massive fire, likely caused by a charging electric bus at a bus depot [15]
5 Oct 2021	Rome, Italy	30 buses were destroyed in a massive fire at a bus depot [16]
20 Aug 2021	Rome, Italy	Three buses were gutted in a fire at a bus depot [16]
19 Jun 2021	Rome, Italy	A fire broke out in the back of the vehicle on the road [16]
5 Jun 2021	Hanover, Germany	Electric buses caught fire at a bus park [17]
16 May 2021	Guangxi, China	Electric buses caught fire at a bus park [18]
15 Feb 2021	South Korea	An electric bus caught fire at the manufacturer’s garage [19]

Figure 3 (a) Electric bus fire at a bus depot in Stuttgart, Germany [15]; and (b) Electric bus fire at a campus bus park in Guangxi, China [18].

As reported by the U.S. Consumer Product Safety Commission, there were more than 25,000 instances of fires or overheating caused by LIBs from 2018-2022. Three of the most impactful fires related to battery storage were (i) in 2021, an abandoned paper mill in Morris, Illinois, stored more than 200,000 lithium batteries, created a chain reaction of battery explosions after an initial ignition of batteries; (ii) the 300-megawatt battery storage facility owned by Vistra Energy in Moss Landing, California, was forced to shut down in September 2021 after several battery packs overheated and melted, causing the fire suppression system to activate. This facility is the largest battery storage facility globally for solar and wind energy; (iii) in April 2019, a 2MW battery storage facility in Arizona caught fire due to an internal failure of a battery cell and the fire extinguishment system could not stop the thermal runaway. This was one of the most significant battery ESS fires in U.S. history [20,21]. Also, according to the statistic collated by Electric Power Research Institute's StorageWiki [22], from 2011 to January 2023, there were a total of 58 fire incidents related to the stationary battery energy storage system globally. Among these, South Korea alone has reported more than 30 energy storage fires related to LIBs [23]. One example of the BESS fire incidents is shown in Figure 4.

Source: Haenam Fire Station

Figure 4 A fire broke out at a solar power BESS in South Jeollo, South Korea [23].

Though LIBs play a vital role in a green transition, the fire problem is a critical side effect that has already caused the loss of life, property, operation and economy. Fire specialists, research centres and fire product companies are working tirelessly to tackle the problem. However, the expansion and development of LIBs are much ahead and quicker than the development of effective fire suppression systems. Even so, the catch-up of fire suppression systems is imperative because only a safe system can maximise the benefits of LIBs moving forward.

1.4 Development of Solutions and Test Methods

Commercial buyers of LIBs-related products are often not energy or power specialists and with limited understanding of the inherent fire hazards. These buyers also often lack of mindset to provide extra investment to enhance fire safety in a LIB-operated environment. They simply follow and trust the safety claims from the Original Equipment Manufacturers, who may or may not conduct thorough fire tests of their LIB products in appropriate environments or with appropriate methods.

LIB fires are often intense, rapid and uncontrollable, with no single fire extinguishment measure due to their complex chemistries and different field applications. In extreme cases, complete extinguishment of LIB fires can take days or weeks. Still, there is a risk of reignition even after they seem to be completely extinguished.

LIB fires are challenging to extinguish due to their intrinsic nature of self-sustained heating. There are many different commercially driven and claimed solutions against LIB fires. There are different extinguishing agents and dispersion modes available. The extinguishing agents generally include (i) water-based agents such as water, foam and water mist with and without additives; (ii) gas-based agents such as $C_6F_{12}O$ (Novec1230), inert gases (IG100, IG541, IG55, etc.), FM200 and Halon-based; and (iii) powder-based agents such as dry chemical powders and aerosols. The dispersion modes include total flooding, localised spray (i.e. semi total flooding) and direct internal injection of agents. Only from 2017, increasing independent evaluations of different extinguishing agents and dispersion modes started to be published and recognised scientifically after increasing LIB-related fire incidents occurred. Several studies also show that different types of LIB and the construction and configuration of battery modules/packs/racks require their tailor-made dispersion systems of extinguishing agents. Therefore, there is no single solution to fight against all LIB fires in their specific field applications. A thorough review of different extinguishing agents based on battery configurations and dispersion modes and key findings of LIB fire suppression are presented in Chapter 4, Chapter 5 and Appendix B.

1.5 Objectives

The thesis applies a systematic methodology to conduct a thorough literature review of published data and analyse different extinguishing agents and fixed fire suppression systems against LIB fires in their potential field applications, such as battery energy storage systems (stationary application) and electric buses (mobile application).

The final goal of the thesis is to gain a deeper insight and better understanding of the definition of the effectiveness of fixed fire suppression systems / extinguishing agents based on different levels of battery configurations in cells, modules, packs and racks in order to achieve appropriate fire protection of lithium-ion batteries in a field application.

1.6 Limitation

Since the thesis is entirely theoretical-based, no actual experiments will be conducted. The results and findings are wholly based on the literature data obtained. However, it is anticipated that a large volume of literature data is required for perusal. Therefore, a set of inclusion and exclusion criteria is established to form a realistic boundary of literature review in Chapter 3.

2 Background

2.1 Regulations and Safety Standards of Lithium-ion Batteries

In the European Union (EU), the Battery Directive [24] regulates lithium batteries, including lithium-ion batteries, lithium-ion polymer batteries and lithium metal batteries manufactured, sold, disposed and recycled in the EU countries. The Directive covers restricted substances and requirements for the labelling and registration of lithium batteries. There are a series of IEC/EN standards detailing the requirements and test requirements of LIBs, which are generally not mandatory but highly recommended.

Lithium batteries are subject to regulation as a hazardous material in the U.S.. These regulations fall under the U.S. Department of Transportation's (DOT) Hazardous Materials Regulations (HMR; 49 C.F.R., Parts 171-180). The HMR are applicable to materials that are considered by the DOT to have the potential to pose an unreasonable threat to health, safety and property when transported commercially. Underwriters Laboratories (UL), as an independent organisation, develops standards for safety aspects, test methods, substance restrictions and other requirements of LIBs [25].

In China, the regulatory body for lithium batteries is the Ministry of Industry and Information Technology (MIIT). The requirements shall comply with the Electronic Industry Standard - SJ/T 11798 "Safety Requirements for the Production of Lithium-ion Batteries and Battery Packs" [26].

The safety concerns of LIBs are associated with voltage and temperature, as shown in Figure 5 using NMC cells as an example. Overcharging and temperature increment exceeding certain thresholds will lead to direct battery damage, exothermic reaction and potentially start a fire. Mechanical damage and internal short-circuiting will also result in an exothermic reaction within a LIB leading to the temperature increment. Overcharging is usually associated with LIBs' operating condition; temperature is related to the environment and ambient conditions where the battery is installed; mechanical damage could be due to external predictable or unpredictable factors; and internal short-circuiting could be due to manufacturing defects, inferior materials used, poor maintenance or consequence of electrical/mechanical/thermal abuses.

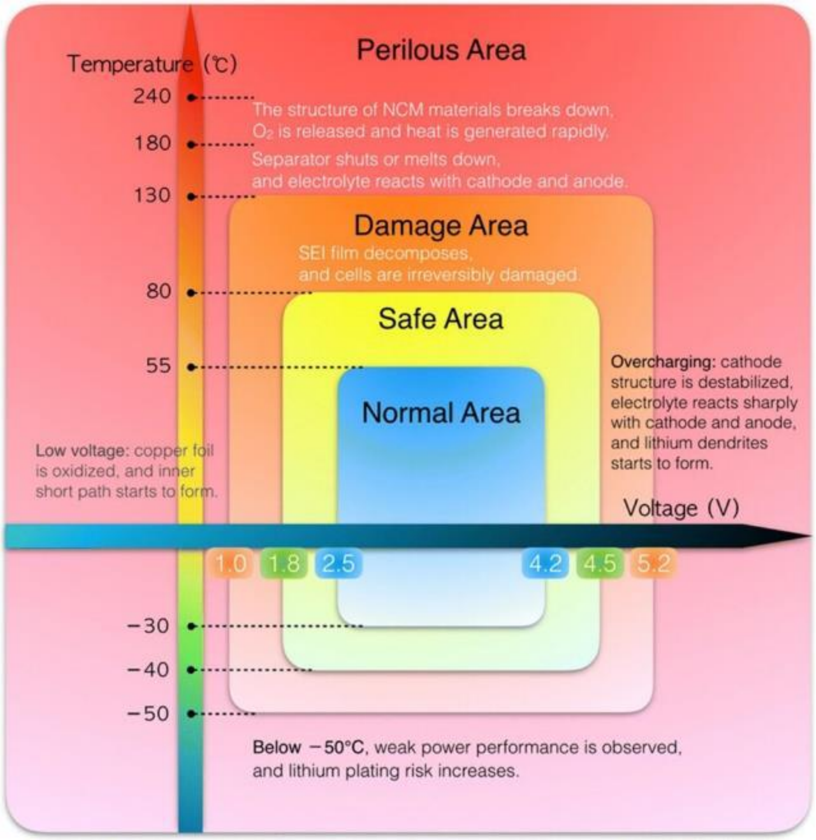


Figure 5 How operating voltage and temperature influence LIB safety [27].

With these safety concerns, a variety of safety standards have been established to ensure the safe use of LIBs. Table 3 outlines some of the most frequently used safety standards.

Table 3 Five most common safety standards for LIBs.

Standard Number	Standard Title	Coverage
IEC/EN 62133-2 [28]	*"Secondary cells and batteries containing alkaline or other non-acid electrolytes – Safety requirements for portable sealed secondary cells, and for batteries made from them, for use in portable applications – Part 2: Lithium systems"*	The standard outlines criteria and examinations to ensure that portable sealed secondary lithium cells and batteries containing non-acid electrolytes operate safely during intended usage and potential misuse. In addition, the standard takes into account chemical and electrical dangers, as well as mechanical considerations such as shock and vibration.
IEC/EN 62619 [29]	*"Secondary cells and batteries containing alkaline or other non-acid electrolytes – Safety requirements for secondary lithium cells and batteries, for use in industrial applications"*	The standard pertains to both stationary and motive applications. Stationary applications include telecom, uninterruptible power supplies, electrical energy storage systems, utility switching, emergency power, and other comparable applications. Motive applications refer to forklift trucks, golf carts, automated guided vehicles, railway vehicles, and marine vehicles, with the exception of road vehicles.
IEC/EN 62660-2 [30]	*"Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing."*	The standard outlines a set of testing procedures to assess the reliability and abuse behaviour of secondary lithium-ion cells and cell blocks utilised in electric

		vehicle propulsion, encompassing both battery electric vehicles and hybrid electric vehicles.
UN/DOT 38.3 [31]	*"The United Nations Manual of Tests and Criteria - Recommendation on the Transport of Dangerous Goods - Section 38.3 – Lithium metal and lithium-ion batteries"*	The section of the document covers transportation safety tests for LIBs. It specifies eight (8) test requirements and procedures of LIBs which include altitude simulation test, thermal test, vibration test, shock test, external short circuit test, impact test, overcharge test and forced discharge test.
UL 1642 [32]	*"Lithium batteries"*	The standard applies to both primary (non-rechargeable) and secondary (rechargeable) lithium batteries that serve as power sources in various products. Its purpose is to minimise the potential of fire or explosion in cases where lithium batteries are used.
UL 2580 [33]	*"Batteries for use in electric vehicles"*	The standard applies to electrical energy storage assemblies that include battery packs and combination battery pack-electrochemical capacitor assemblies, as well as the subassemblies/modules that comprise these assemblies, for use in electric vehicles. Its purpose is to assess the electrical energy storage assembly's capacity to withstand simulated abuse conditions safely and prevent any potential hazards to individuals resulting from such abuse.

2.2 Root Causes of Fire Relating to The Usage of Lithium-ion Batteries

The basic unit of a lithium-ion battery is called battery cell, which primarily comprises four components: anode, cathode, separator and electrolyte, as shown in Figure 6. The electrolyte is an organic solvent containing lithium salts (i.e. lithium ions) [34]. The function of the electrolyte allows the movement of lithium ions between two electrodes (anode and cathode). The separator physically prevents the two electrodes from contacting each other while allowing the lithium ions to pass through. During the charging process, the lithium ions move from the cathode toward the anode and deposit onto the anode. The process reverses during the discharging reaction (i.e. when LIB is in use) [35].

The battery cell is the smallest energy storage unit and is commonly available in three shapes: cylindrical, prismatic and pouch, as shown in Figure 7. To achieve the required level of capacity and voltage, the battery cells can be connected in series to increase the voltage or in parallel to increase the capacity. The connection of multiple battery cells forms a battery module. Subsequently, a series connection of multiple modules forms a battery string to determine the voltage level of a battery system; and a parallel connection of multiple strings to raise the capacity of a battery system forms a battery pack or rack. To form a complete installation-level LIB system, multiple packs or racks will be connected and integrated into a battery array to obtain the required capacity for the system [36]. A simple illustration is shown in Figure 8.

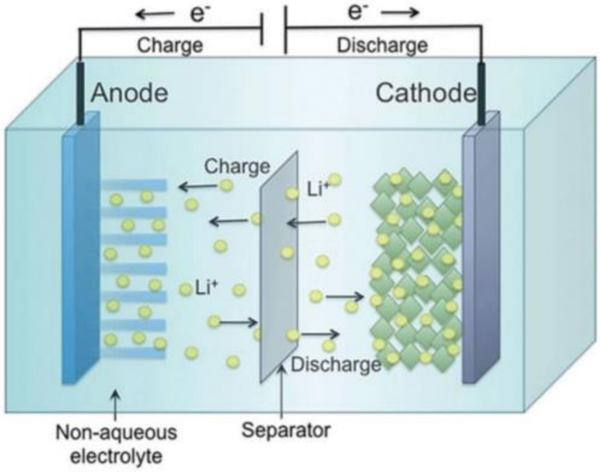


Figure 6 Illustration of lithium-ion cell and its main components [37].

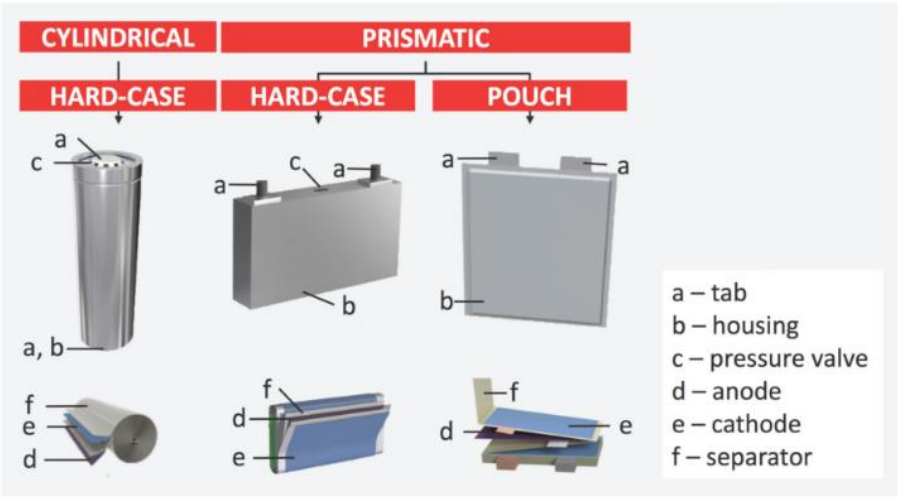


Figure 7 Different shapes of lithium-ion battery cells: cylindrical, prismatic and pouch [38,39].

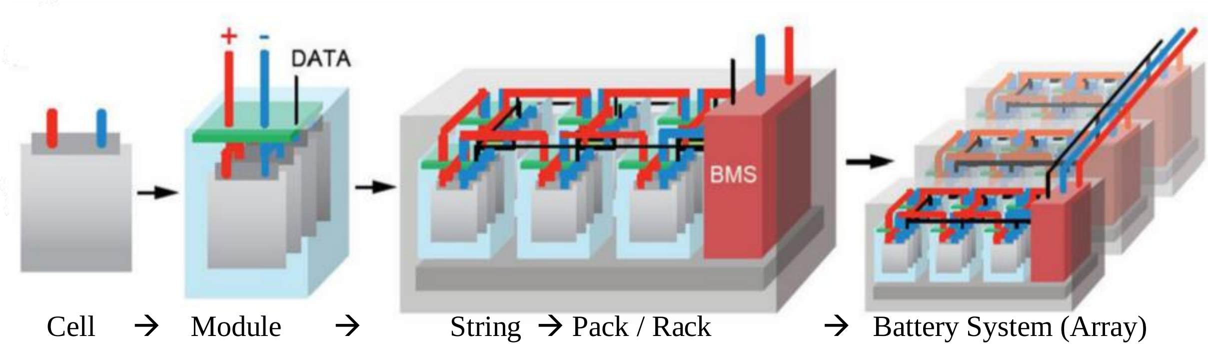


Figure 8 Illustration of connection of battery cells into a LIB battery system [40].

One must first understand how LIBs could initiate a fire before one can suggest appropriate fire extinguishment methods. The common causes of a battery fire include battery-induced fires (which the thesis will focus on) and other associated electrical and electronic induced fires, such as overheated electrical cables and electrical faults in electronic components.

For battery-induced fires, thermal runaway initiated by the battery's exothermic reaction is a primary safety concern of LIBs. There are various factors contributing to thermal runaway (i.e. rapid internal temperature increment in LIB cells) and leading to the release of flammable/toxic gases, fires or explosions [10]. If the thermal runaway propagates, adjacent battery cells and modules will experience the same phenomena and worsen a fire situation. The common factors contributing to thermal runaway are as follows and shown in Figure 9:

(i) Mechanical abuse – Due to external forces causing damage to the batteries, such as penetration, crash, etc.;

(ii) Electrical abuse – Due to overcharging, over-discharging, over-current and external short circuits;

(iii) Thermal abuse – Due to high external temperature or heat; and

(iv) Internal short circuit – The above abuses could lead to the damage of the separator or manufacturing defects leading to early deterioration of the separator. These will result in an internal short circuit when the cathode and anode are touching.

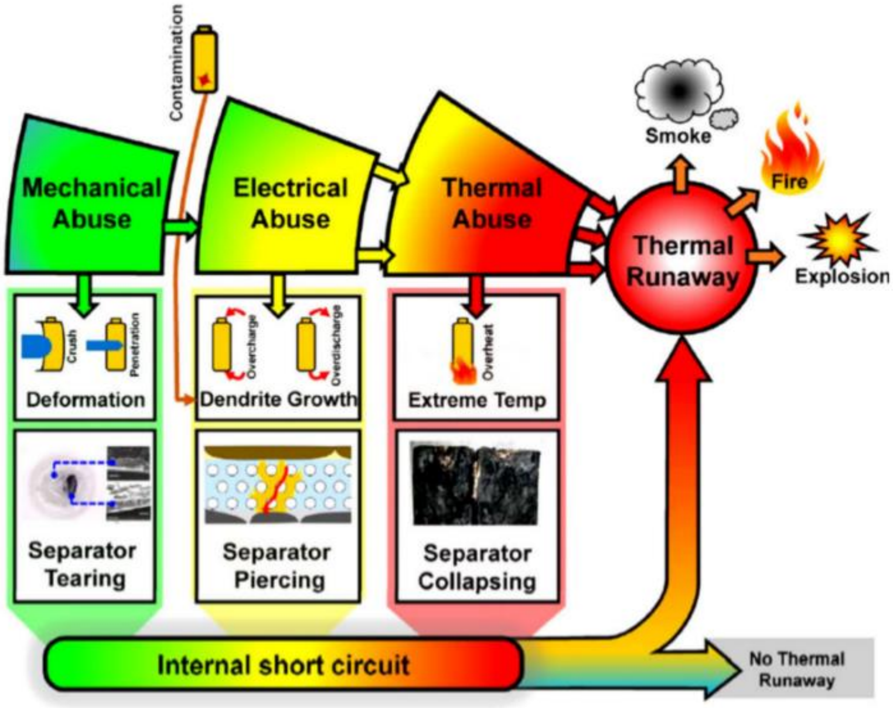


Figure 9 Various factors leading to thermal runaway [41].

Fundamentally, three essential elements are needed for a fire to happen, called the “Fire Triangle”, which consists of energy(heat), fuel and oxygen, or the “Fire Tetrahedron” with the addition of the fire chemical reaction on top of the three fire elements. When such a rapid increment of internal temperature (i.e. exothermic reaction releases energy) occurs within LIBs, the high temperature decomposes the LIB’s materials and releases oxygen, coupled with the active electrolyte of LIBs turning into flammable gases as fuel sources, the three fire elements meet and initiate a self-sustained fire. Suppose there are no proper means of fire extinguishment or no proper separation/insulation among batteries. In that case, the fire will continue propagating between cells and further cascading to modules, racks and so on, resulting in quicker and more massive combustion. Even if a fire extinguishment is provided, insufficient or improper fire extinguishment will lead to re-ignition if the damaged batteries are not completely cooled down. If any of the three elements can be eliminated completely or the combustion chemical reaction chain can be isolated or stopped, a fire can be prevented, controlled or extinguished effectively.

Though this thesis focuses on the analysis of fire suppression of LIB fires, there are two other essential systems also closely related to the fire safety of LIBs in BESS and electric buses: battery management system (BMS) and fire detection system, which serve as a watchdog for any early signs of LIB fires, detecting any anomalies (e.g. battery defect, overcharge, over-current, over-voltage, over-discharge, external/internal short-circuit and external force/factor leading to sudden temperature increment within battery cells and modules) and activating the fire suppression timely to prevent catastrophic damages. Three systems form a complete suite for an effective fire safety system to tackle LIB fires. However, due to time and resource constraints, only the fixed fire suppression system will be analysed in the thesis.

2.3 Field Applications of Lithium-ion Batteries

2.3.1 General

Since the first commercial LIB by Sony in 1991 for their handheld recorders [2], the uses of LIB have expanded rapidly and become an inseparable part of mundane life. The majority of LIBs are commercialised for consumer electronics (e.g. smartphone, laptop, tablet, digital camera, camcorder, torchlight, etc.), power tools (e.g. cordless drill, garden equipment, mining equipment, medical equipment, etc.) and electric vehicles (e.g. electric car, hybrid car, bus, forklift, motorbike, bike, scooter, wheelchair, etc.). Other much larger scale commercialised applications of LIBs include energy storage systems for aircraft, ship, grid power supply, emergency power backup, hydro-power, fire-power, wind-power, solar-power, etc.. As mentioned in Chapter 1, the thesis will mainly focus on analysing LIBs in electric buses and battery energy storage systems (i.e. installed within rooms/containers for grid-scale application) where fire suppression systems can be provided onboard for electric buses and within or in the vicinity of the energy storage system room/container, respectively.

2.3.2 Field Application in Electric Buses

Owing to the advancement of LIB technology from around 2010, mass production of LIB-driven buses started emerging and booming globally to gradually replace diesel-driven buses. China was the first country to roll out modern battery-powered electric buses on a large scale since 2011 [42]. To date, China still dominates the electric bus market, followed by European countries and the United States. India is also catching up to become one of the world's largest markets for electric buses. The global growth trend of electric buses from 2010 to 2021 is presented in Figure 10.

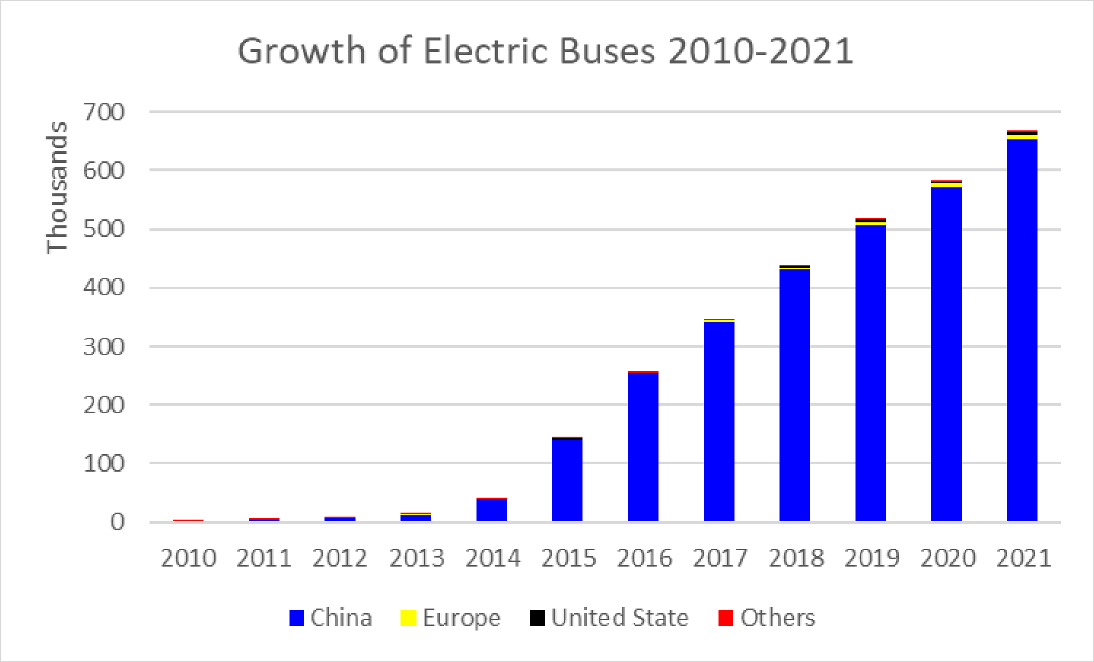
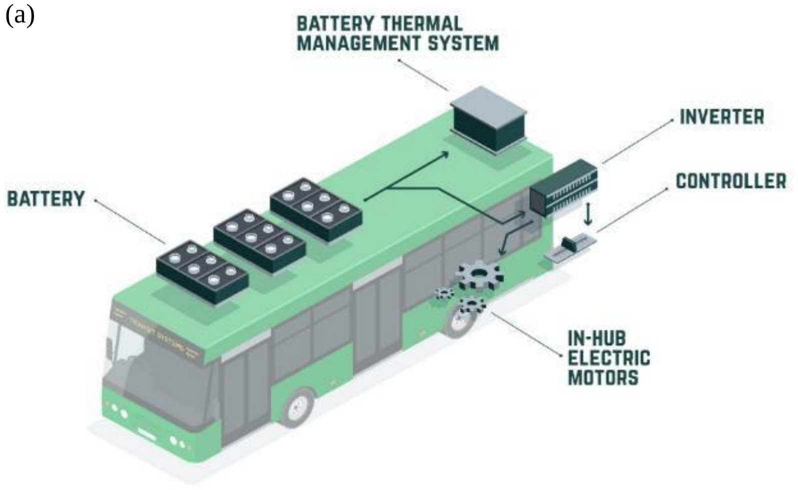


Figure 10 Growth trend of electric buses (Others include Korea, Japan, New Zealand and Canada) [43].

Electric buses use onboard LIBs to power the drive motor and all other onboard devices and equipment. The commonly used LIBs are NMC, LFP and LTO. The charging of LIBs usually takes place in the bus terminal or depot via the manual plug or pantograph while stationary, and some are charged while driving under the rigid overhead cable. The field applications of LIBs on typical urban buses are 12m single-deck bus, 18m articulated bus, 24m bi-articulate bus and double-deck bus [44]. These LIBs can be located on the bus roof or in the rear compartment, as shown in Figure 11, extracted from manufacturers' websites.

(a)



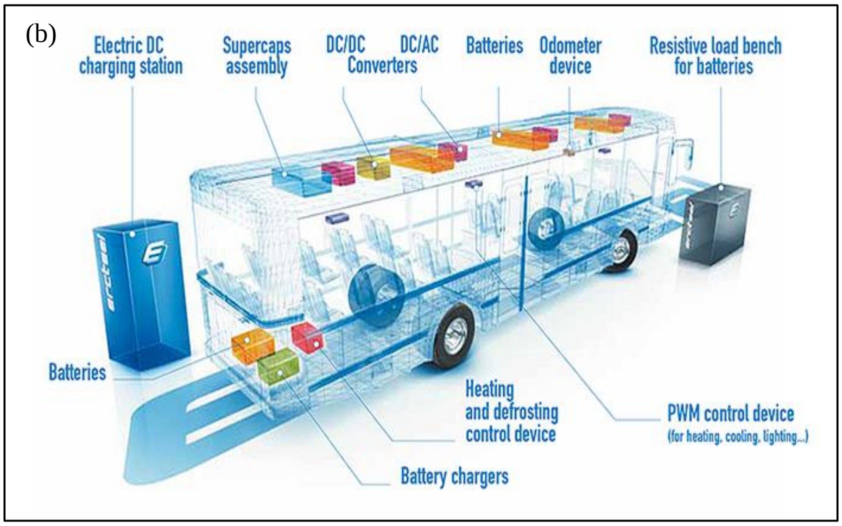


Figure 11 Examples of various mounting positions of lithium-ion batteries on an electric bus (a) on the bus roof; and (b) at the bus rear compartment [45,46].

2.3.3 Field Application in Battery Energy Storage Systems

In 2015, the United Nations Climate Change Conference in Paris set the framework for a rapid worldwide shift to a sustainable energy system to avoid the risk of disastrous climate change. Among all approaches to using more sustainable and renewable energy, energy storage plays a crucial role in enabling such a significant transition from the conventional burning of coal and fossil fuels into the era of greener energy. Within energy storage approaches, BESS is one of the approaches with a higher potential [47]. BESS can be utilised to store renewable energy from hydro-power, wind-power, solar-power, etc. and release the stored energy for the primary/grid power supply or be used as an emergency/uninterruptible backup power supply.

Hannan et al. [48] provided an overview of different battery energy storage technologies considering life cycle, advantages, limitations and applications. Table 4 below extracts part of their overview of LIBs relating to BESS in industry applications.

Table 4 Overview of LIBs relating to BESS in the industrial application [48].

Type of LIBs	Lift cycle at 80% depth of discharge	Specific energy (Wh/L)	Advantage	Limitation	Application
NMC	1000-2000	150-220	High capacity and high power; leading system.	Highly expensive; complex monitoring and control	E-bikes; medical instruments; electric vehicles; industry application
LFP	>2000	90-120	Safe; stable voltage discharge	Low capacity; used for preliminary energy storage	Portable and stationary applications where the high load current is needed
NCA	500	200-260	High specific energy and stability; works as energy cell	Expensive; limited power capacity	Medical application; industry application; power train

LTO	3000-7000	50-80	High life cycle; fast charging and safer technology; wide thermal range	Expensive; lower specific energy	Uninterruptible power supply; solar-powered street lighting

Some examples of commercialised LIB energy storage systems are shown in Figure 12.

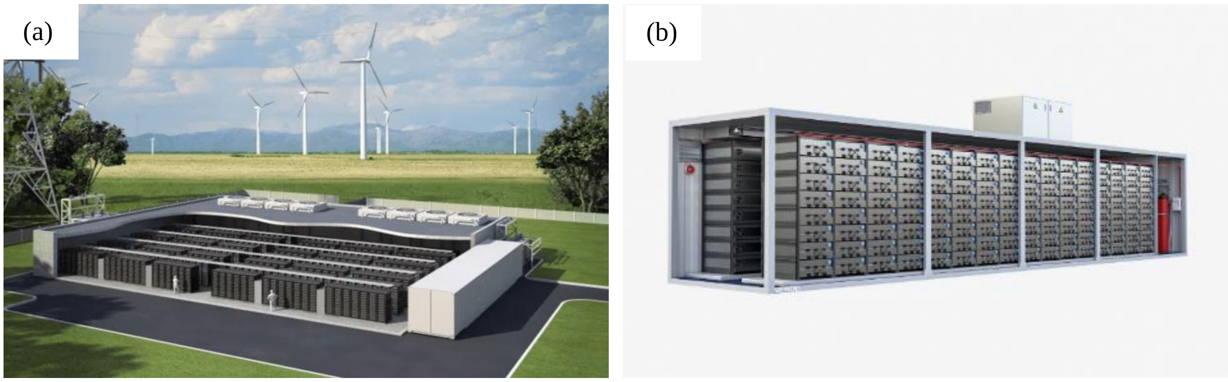


Figure 12 Examples of LIB energy storage systems. (a) grid-scale BESS [49]; and (b) Simens BESS [50].

2.4 Fire Suppression Systems

The following subsections give a general overview and basic working principles of common fire suppression systems, including water-based, gas-based, powder-based, etc. It is worth noting that halon and FM200 (HFC-227ea) gases are not discussed in the thesis due to their environmentally unfriendly nature, which have been phased out for halon and started phasing down for FM200 since January 2022, respectively. The designs of the following systems are governed by relevant international standards and local regulations, such as IEC, ISO, EN, CEA, NFPA, etc.

2.4.1 Water-Based Suppression System – Sprinkler System

A conventional sprinkler system is a water-based fire control and suppression system. It uses closed glass-bulb sprinkler heads, which will break to discharge water when the activation temperature is reached. The breakage of the blub requires hot gases or smoke from the fire source raised by the buoyance to the roof or ceiling where the sprinkler heads are usually installed. Depending on the different hazard groups and applications, the sprinkler heads can also be installed in-rack or sideways. There are also open sprinkler heads available, which form a deluge system. Permanent installation space, water supply and power supply are required to enable sprinkler pumps and water tanks to deliver water to the fire incident areas.

Sprinkler water has a high heat capacity of 4.187 kJ/kgK, which is effective in absorbing heat and reducing temperature. Water droplets from sprinkler heads land on the hot burning surface to start surface cooling and hinder the radiation from the flames back to the burning surface, which continually reduces the pyrolysis or gasification until the surface temperature reduces below the pyrolysis temperature, and the fires can be controlled or stopped with a sufficient amount of water [51]. Concurrently, wetting of the non-fire neighbouring objects also slows down the fire propagation. If a large amount of sprinkler water fully covers and wets a burning object, it also isolates the fuel from the oxygen.

2.4.2 Water-Based Suppression System – Water Mist System

Similar to the sprinkler system, a water mist (WM) system is also a water-based fire control and suppression system, which requires fixed installation space, power supply and water supply for pumps and water tanks. Alternatively, the system can be more flexible that be equipped with pressurised gas cylinders and water bottles for discharging. Generally, there are two types of water mist systems: low-pressure system (<16 bar) and high-pressure system (16 to 200 bar). The main difference between the sprinkler and water mist systems is the diameter/size of the water droplets. The sprinkler system produces a diameter of water droplets of >1000μm. Compared with the water mist systems, Class 3 low-pressure water mist (LPWM) system produces a diameter of 400-1000μm; Class 2 LPWM system produces a diameter of 200-400μm; and Class 1 high-pressure water mist (HPWM) system produces a diameter of 1-200μm [51]. The smaller the droplet sizes, the longer the floating duration in the air and the larger the contact areas with the heat source. Furthermore, WM can be blended with additives to improve its performance, such as isolating the fuel surface from oxygen and/or inhibiting chemical reaction.

The activation modes come with either closed-head with glass bulbs or open nozzles, depending on the design intents. The working principle for the closed-head with glass bulbs is similar to the sprinkler for localised discharge where the glass bulbs break. Open nozzles used in the WM system are for total flooding of a room. Open nozzles work with a control valve which receives a triggering signal from a fire detection system or other signals according to the users' requirements (e.g. a signal from the battery management system or gas sensors) or a combination of both.

The pressurised system produces large amounts of fine water droplets through the specially designed discharge nozzles. These fine water droplets have long floating times in the air and large total contact surfaces with flames and hot gases, providing fast and effective cooling capacity. The water mists will also evaporate quickly and turn into vapours, acting like an inerting gas which leads to oxygen depletion and adds thermal bulk to reduce the flame temperature. Concurrently, fine water droplets aggregated and landed on the non-fire surfaces slow down the flame or thermal propagation to the neighbouring objects.

2.4.3 Water-Based Suppression System – Foam System

A foam system is identical to the sprinkler system except for the extra foam tank, foam pump, air compressor, nozzle type and proportioner to mix water and foam with a pre-determined ratio. The system can be activated via closed-bulb heads or open heads linked to a fire detection system. After discharging, water foam covers the burning fuel surface, preventing the flammable gaseous fuels from being released, limiting the surface contact with the oxygen and separating the fuel from the external heat. Concurrently, the water-based foam also cools a hot burning surface [51].

2.4.4 Gas-Based Suppression System – Novec 1230 ($C_6F_{12}O$) System

Novec1230 is a fire suppression trademark product from 3M Company [52]. It is an environmental-friendly alternative for Halon and FM200 agents because of its properties of zero ozone depletion potential, global warming potential of less than one and atmospheric lifetime of only five days. Its chemical formula is $CF_3CF_2C(O)CF(CF_3)_2$, and its ASHRAE nomenclature is FK-5-1-12 complying with NFPA and ISO 14520 clean agent standards. Novec1230 is stored as a liquid in pressurised cylinders at room temperature and discharged as a gas due to its high vapour pressure (0.404 bar) at ambient conditions and low heat of vaporisation (88kJ/kg) at its boiling point of 49.2^oC. Hence, it evaporates much easier than the water of

2260 kJ/kg heat of vaporisation at the water's boiling point of 100°C. These properties enable Novec1230 molecules to rapidly turn into the gas phase at room temperature.

Novec1230 agent is applied via a total flooding fire suppression system for an enclosed room or space. The discharge of Novec1230 gases is through specially designed nozzles with activation signals from the fire detection system, battery management system or manual activation. With Novec1230's high heat capacity (280J/mol), the gaseous Novec1230 extinguishes fires primarily by absorbing energy, removing heat from the flame front, cooling the flame and inhibiting fire chemical reactions until the flaming combustion stops. The oxygen concentration in the enclosure remains unchanged [51].

2.4.5 Gas-Based Suppression System – Inert Gas System

The inert gas fire suppression system, by its name, uses inert gases to extinguish Class A, B and C fire hazards. The commonly used gases are nitrogen (N_2), argon (Ar) and carbon dioxide (CO_2), where nitrogen and argon are applied in a total flooding system, and carbon dioxide can be applied in either a total flooding system or a local application. The gases are stored in pressurised cylinders and discharged via specially designed nozzles upon automatic or manual activation signals similar to the water mist system and Novec1230 system. The design of the system is governed by either NFPA or CEA standards. The commercially available inert gas suppressants are designated as IG01 (100% Ar), IG100 (100% N_2), IG541 (52% N_2, 40% Ar, 8% CO_2 – tradename Inergen) and IG55 (50% N_2, 50% Ar – tradename Argonite) according to the standards.

With appropriate extinguishing or design concentration of the required inert gases, the inert gases deplete the oxygen level to approximately 12.5% in the environment where the protected objects are located and reduce the adiabatic flame temperatures to limit the flaming combustion [51].

2.4.6 Powder-Based Suppression System – Aerosol System

The aerosol fire suppression system uses specially designed aerosol generator heads with a built-in combustion process of solid aerosol-forming compounds to generate finely divided alkaline metal salt solid particles (e.g. less than 10µm potassium-based salt) and by-products of gaseous matters (e.g. N_2, CO_2 and water vapours). The design of the system is governed by EN 15276 and NFPA 2010 for total flooding applications and is applicable to Class A, B and C fire hazards similar to Novec1230 and inert gas systems. The installation of the aerosol systems can be standalone without pipeworks which offers flexibility compared with water-based and gas-based systems.

The discharged aerosols interfere with and inhibit the chemical reaction in the flame and reduce adiabatic flame temperature to extinguish the flames. Some aerosols could also deplete the oxygen concentration in an air-tight environment [51].

2.4.7 Powder-Based Suppression System – Dry Powder System

The dry powder system is similar to the aerosol system but with larger alkaline-based metal salt particles to inhibit the chemical reaction of combustion. Compared with other agents, dry powder might be the most challenging agent to reach a deep-seated fire [51].

2.4.8 Other Suppression System – Aqueous Vermiculite Dispersion (AVD)

Aqueous Vermiculite Dispersion (AVD) [53] is a patented product manufactured by a UK-based Company - Dupré Minerals Limited. This is similar to the water mist system with additives. According to the manufacturer, original vermiculite is from a group of hydrated aluminium-iron-magnesium silicates in the form of thin and flat flakes containing microscopic layers of water. Chemical exfoliation of vermiculites turns them into microscopic platelets that are freely suspended in water. Therefore, the chemical exfoliation technology turns the vermiculite into an aqueous form and applies it to a fire in a mist form that expands when heated, instantly dries, encapsulates the burning surface with a film and creates a non-flammable oxygen barrier to extinguish the fire and prevent the propagation. Water content in AVD also provides a cooling effect on the fuel source.

2.4.9 Summary of Various Fire Suppression Systems

As described in Section 2.2, an effective fire suppression system shall always tackle a fire by eliminating one or more of the four elements in the "fire tetrahedron". Table 5 provides an overview of the working mechanism of each suppression system. Definitions of each working mechanism are as follows and illustrated in Figure 13:

(i) Surface cooling refers to reducing the surface temperature of a burning object.
(ii) Gas cooling refers to reducing the temperature of hot gases produced from combustion.
(iii) Smothering refers to separating the fuel surface from contact with air.
(iv) Reducing adiabatic flame temperature (AFT) refers to adding thermal bulks to quench flaming combustion.
(v) Suffocating refers to depleting or diluting oxygen concentration in an air-tight environment.
(vi) Chemically inhibiting refers to taking away the radicals to break the chemical reaction from combustion and reduce the flame temperature.

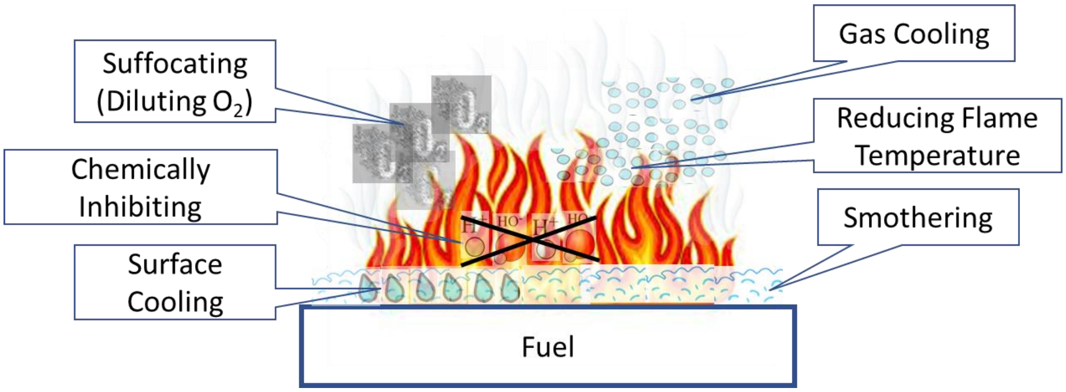


Figure 13 Illustration of extinguishment working mechanism (Sources: Fire[54]; O_2[55]; Radicals[56] & Author).

Table 5 Extinguishing mechanism of fire suppression System / extinguishing agent.

Suppression System - Extinguishing Agent	Working Mechanism	
	Primary	Secondary
Sprinkler System - Water Droplets	Surface Cooling	Smothering
Water Mist System - Water Fog	Gas Cooling; Reducing AFT	Surface Cooling; Suffocating
Water Mist System - Water Fog with Additives	Gas Cooling; Reducing AFT; Chemically Inhibiting and/or Smothering	Surface Cooling; Suffocating
Foam System - Water mixed with Foam	Smothering	Surface Cooling
Novec1230 System - $C_6F_{12}O$	Chemically Inhibiting	Gas Cooing
Inert Gas System - Single or Mix of Inertising Gases	Reducing AFT	Suffocating

Aerosol System - Fine Alkaline Metal Salt Particles and Gaseous Matters	Chemically Inhibiting; Reducing AFT	Suffocating
Dry Powder System - ABC Dry Powders	Chemically Inhibiting	Smothering
AVD System	Smothering	Surface Cooling

2.5 Commercially Claimed Fire Products for LIB Fires

From the internet search, several fire product companies claimed that their extinguishing agents or suppression systems were effective in handling LIB fires, such as aerosol, Hi-Fog, N_2, AVD and compressed air foaming systems, as listed in Table 6. The effectiveness of such systems/extinguishing agents will be further discussed in Chapter 5.

Table 6 Commercialised fire suppression system for LIBs.

Extinguishment System	**Area of Application**	**Claims by the Manufacturers**	**Working Principle stated by the Manufacturers**
Aerosol system, as shown in Figure 14 and Figure 15, using potassium hydrogen carbonate from RSL Fire [57,58]	• Storage areas of electric bicycles, e-scooters and electric golf trolleys • Battery transport boxes • Battery storage cabinets • Electricity storage • Laboratories • Test benches • Assembly lines • Buses and coaches	• Claimed to be the most effective fire protection system for LIB fires • Certified by VdS/TÜV • UNECE R107 certified by TÜV/Nord	The aerosol generator produces the aerosol form of potassium hydrogen carbonate. A chemical reaction that absorbs heat transforms potassium hydrogen carbonate into potassium carbonate, thereby chemically eliminating oxidising substances from the combustion process and putting out the fire. Additionally, the process extracts extra heat from the combustion.
Aerosol system using patented FPC solid compound (i.e. potassium-based salt) from FirePro [59]	• All major industries, not limited to LIB fires.	• Compliance with ISO15779, NFPA2010, IMO/MSC1270, UL2775, EN15267	Upon activation, the FPC solid compound undergoes a rapid transformation and produces a condensed aerosol to efficiently and effectively extinguish the fire. Rather than relying on oxygen depletion and cooling as in the traditional fire triangle, the extinguishing process is achieved by interrupting the chemical chain reactions taking place in the flame.
HI-FOG® high-pressure water mist fire protection system from Marioff [60]	• LIB energy storage system-related applications • Transformer and substation • Power generation plant • Industrial premises	• Claimed the effectiveness of the system in line with DNV-GL's Technical Reference for Li-Ion Battery Explosion Risk and Fire Suppression.	Rapidly extinguishes the external fire; cools batteries and prevents thermal runaway in the neighbouring cells/modules/racks; cools combusting materials and ambient gases; Reduces gas concentration.
Sinorix N_2® inert gas fire suppression and extinguishing system from Siemens [50]	• Stationary LIB energy storage system-related applications	• In-house test to prove its effectiveness against LIB thermal runaway and fire. • VdS approval was also obtained when the system was combined with early	The system works concurrently with FDA241 air sampling detectors by detecting early battery off-gassing and total-flood the room/space with N_2 inert gas by overly depleting the oxygen concentration of a room/space.

		detection using air sampling sensors.	
Aqueous vermiculite dispersion (AVD) fire extinguishing agent (shown in Figure 16) from AVD Fire [53]	• LIB energy storage systems and LIB cells in general	• Patented product • Third-party performance test by ZSW Germany • Handheld bottles and trolleys available similar to conventional handheld fire extinguishers • Can be integrated with a fixed firefighting equipment	AVD, in the form of mist, covers over the fuel surface and creates a barrier over the LIB cells preventing them from contacting with air and further thermal runaway and limiting the fire spread. The water content within the AVD product also cools down the surface temperature.
Compressed air foaming system (CAFS) (shown in Figure 17) from FIFI4Marine [61]	• Major industries where lithium batteries are used include shipping, oil-rig helicopter platform, solar system, wind turbine, data centres and mining.	• The fire suppression system is claimed to be the most efficient and safe system for lithium batteries globally. • Tested and approved by DNV-GL.	The system uses compressed air to transform the Bio4C premix into a fire extinguisher foam and applied to the affected batteries creating a direct cooling effect. The foam dramatically reduces the battery temperature and prevents module-to-module propagation.

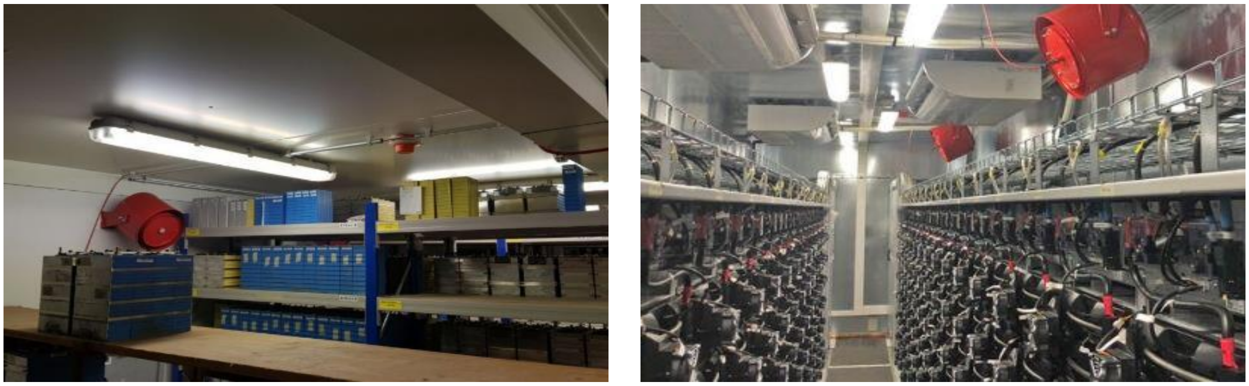


Figure 14 Aerosol system for battery room from RSL Fire [57].

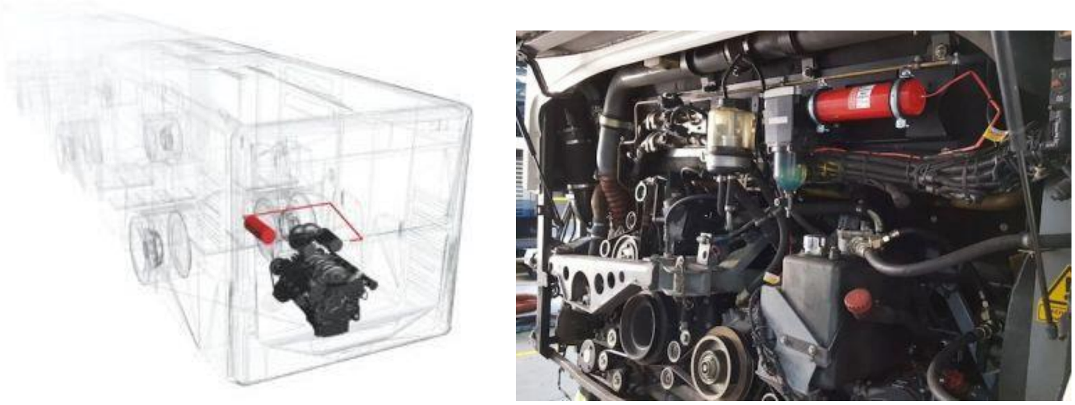


Figure 15 Aerosol system for LIB used in bus/coach engine compartment from RSL Fire [58].

Figure 16 Demonstration of AVD encapsulates LIB cells to extinguish the fire and stop propagation [53].

Figure 17 FIFI4Marine CAFS Compact C-SKID with the integration of detection and suppression systems [61].

3 Methodology

As mentioned in the limitations of Chapter 1, the thesis is entirely based on a theoretical review of published papers and reports. Therefore, it is vital to ensure that the literature review is conducted thoroughly and systematically to better present the past research on the topic, identify the strengths and gaps and propose areas of improvement for future works.

The systematic literature search for the thesis topic adapts the PRISMA-ScR (Preferred Reporting Items for Systematic reviews and Meta-Analysis extension for Scoping Reviews) framework [62]. The framework provides guidance for a systematic review of relevant research in a topic or area of interest.

Two of the largest scientific literature databases: Scopus and Web of Science, are chosen for the data sourcing, which cover journal and conference papers from major publishers, including the fire science community [63]. Google Scholar and Google search engine are used to supplement and locate the full text of journal/conference papers and technical reports or white papers that were not published on journal platforms.

The literature sourcing of relevant research on the fixed fire suppression techniques for LIB fires was cut off on 26 March 2023 without a start date because it is envisaged that the relevant LIB fire suppression research was relatively new and emerged less than 15 years ago after LIB technology became popular.

Step 1 – Gathering of Relevant Journal Articles

Before the commencement of the first attempt of literature data sourcing, the following keywords are identified: “lithium-ion” or “li-ion”, “batter*” (covers the singular and plural forms of battery), “fire” and “suppression”. The search of the identified keywords in Scopus and Web of Science database applies to the fields of title, abstract and keyword indexing. In the second attempt, the search is expanded to include synonyms and variants, such as “LIB”, “fire*”, “flame*”, “suppress*”, “extinguish*” and “mitigate*”. In the third attempt, by looking at the keyword indexing from the second attempt, the “lithium metal battery” which is not part of the analysis in this thesis, is excluded. The literature search results are shown in Table 7 below, and the search strings of three attempts are recorded in Appendix A.

The third attempt is deemed to fit better to the thesis topic and therefore is used for further analysis. The duplication is then removed using the “Remove Duplicate” function in Microsoft Excel, based on the search results from the third attempt, followed by manual removal of duplications not identified by Microsoft Excel due to special symbols, e.g. semi-column, dash or double spacing.

Table 7 Literature search results as of 26 Mar 2023.

	1st attempt	2nd attempt	3rd attempt	Final Count
Scopus	$n_{1a}=78$	$n_{2a}=381$	$n_{3a}=328$	$n_{Step1}=n_{3a}+n_{3b}-$duplications =328+325-227=426
Web of Science	$n_{1b}=67$	$n_{2b}=403$	$n_{3b}=325$	

Therefore, Step 1 gathers $n_{Step1}=426$ search results of literature data from Scopus and Web of Science to be further screened in the next step.

Step 2 – Title Screening

In Step 2, the titles of 426 articles gathered in Step 1 are screened to identify the most relevant articles following the exclusion and inclusion criteria below.

Exclusion criteria for non-relevant article titles in Step 2: (i) the titles apparently focus only on studies of battery characteristics and researches, such as electrolyte, separator, anode or cathode, to improve the stability or flame-retardant capability of LIBs; (ii) the titles apparently are not related to fire suppression of LIBs, e.g. focus on battery's thermal management, electrical protection management, battery management system, numerical model simulation, risk assessment, smart/IoT system, mitigation of LIB's failure, safety in LIB's manufacturing process/laboratory testing; (iii) the titles only analyse the LIB's safety based on the design, passive protection, performance or operating condition of LIBs, e.g. state-of-charge (SOC), explosion-proof materials; (iv) the titles focus on smart firefighting's technology by fire services, e.g. robot; and (v) the titles are just generic conference titles or book chapters.

Inclusion criteria of relevant article titles in Step 2: (i) the titles are relevant to fire suppression of LIBs; (ii) the titles are relevant to thermal runaway mitigation of LIBs; and (iii) the titles are too general or not detailed enough to determine their relevancy, which are included for next screening for the benefit of doubts.

After the title screening in Step 2, the search results are refined from n_{Step1}=426 to n_{Step2}=167.

Step 3 – Abstract Screening & Skimming of Main Text

In Step 3, the abstracts of 167 articles from Step 2 are assessed, and the main texts are skimmed through to determine their relevancy, following the inclusion and exclusion criteria below.

Inclusion criteria in Step 3: (i) the whole article or some sections in the article are relevant to fire suppression of LIBs; (ii) the articles discuss the thermal runaway mitigation of LIBs via externally applied suppressants; and (iii) the articles are identified whether they are experimental-based or review-based.

Exclusion criteria in Step 3: (i) focus on the development and design of safer and more fire-retardant LIBs; (ii) study the thermal runaway characteristics; (iii) study the fire or combustion behaviours of LIBs without discussing the fire suppression or thermal runaway mitigation; (iv) explore self-encapsulating fire suppressant materials for LIB electrodes or build-in cooling mechanism within LIBs; (v) discuss lithium polymer batteries; (vi) use numerical simulation of fire suppression approaches; (vii) full English text is not available; and (viii) two papers with relevant abstract descriptions, but the log-in credentials are unavailable to access the full text. One of the two papers could not be retrieved due to incomplete reference information. The other paper is from a popular science magazine and appears not to have any new information. Thus, the risk of missing essential or novel aspects is very low if these two papers are excluded from the detailed assessment.

After the abstract screening and skimming of the main texts in Step 3, the search results are further refined from n_{Step2}=167 to n_{Step3}=83.

Step 4 – Detailed Assessment of each article from Step 3

In Step 4, the detailed assessment categorizes the 83 selected articles into 17 review-based articles and 66 experimental-based articles, as shown in Appendices B1 and B2, respectively. The review-based articles are used to gain an overview and trend of relevant published journals and reports on the research of fire suppression on LIB fires and mitigation of thermal runaways. Concurrently, from the review-based articles and literature review sections of the experimental-based articles, citation search or backward snowballing technique is deployed to discover additional relevant technical or research reports/white papers/journal papers that were not published in major journals or not discovered in the previous steps. Likewise, additional articles from the citation search are also gone through the screening process in Steps 2 and 3. As a result of the citation search, an additional 3 review-based and 16 experimental-based articles are identified, as highlighted in yellow in Appendices B1 and B2, respectively.

Furthermore, in Step 4, the additional exclusion criteria are set for those experimental-based articles that (i) use only extractive lithium-ion electrolytes or vent gases for the fire suppression experiments; (ii) discuss firefighting techniques only applicable to fire services, e.g. use firefighting lance to pierce through EV battery box and inject the water directly onto batteries; (iii) experiment only FM200 extinguishing agent which is phasing down; and (iv) present only the experimental proposal without results. After further exclusion of 17 articles, the final number of articles collated for detailed review in Step 4 is

$$n_{\mathrm{Step4}} = n_{\mathrm{Step4(review)}} + n_{\mathrm{Step4(experimental)}} = (17+3) + (66+16-17) = 85$$

The flow chart in Figure 18 summarises the screening process from Steps 1 to 4.

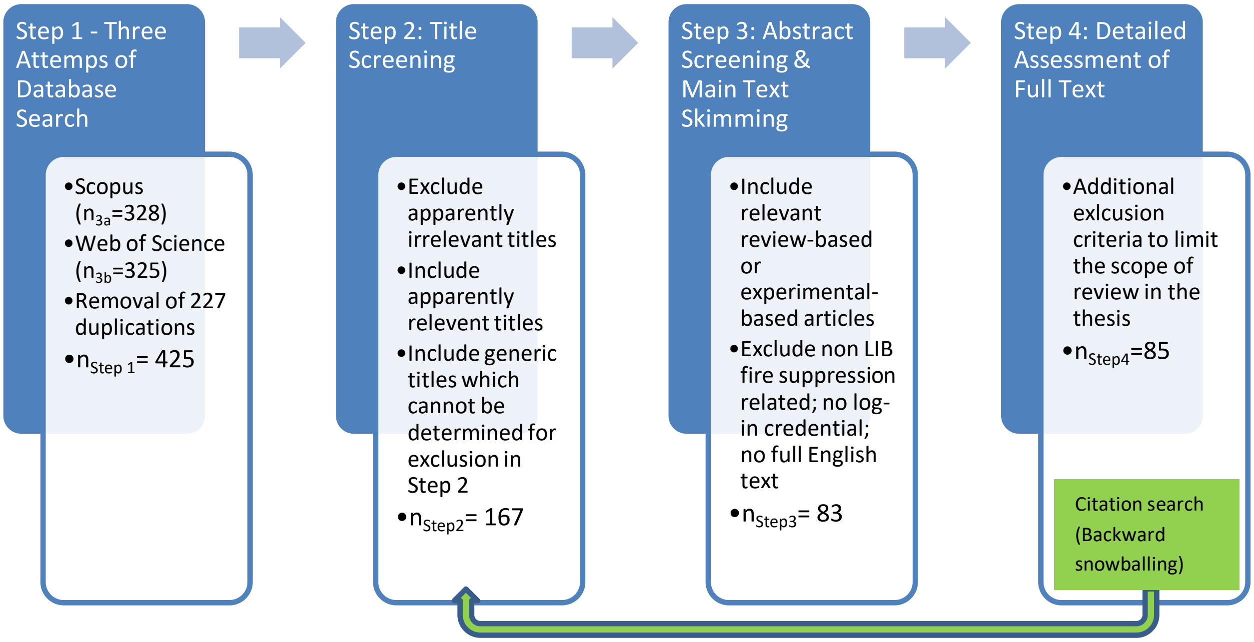


Figure 18 Summary of the literature screening process.

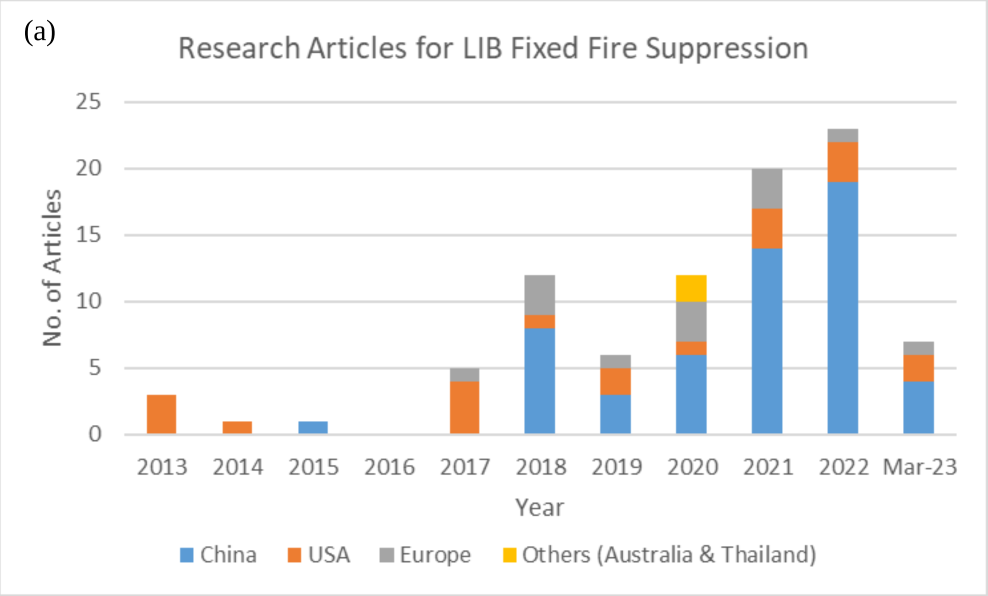
The detailed assessment further categorises the experimental-based articles according to the dispersion modes, types of extinguishing agents, types of batteries and test methods. The experimental approaches and key results are presented in Chapter 4 and Appendix B2. Following that, the detailed assessment, comparison and key findings are discussed in Chapter 5.

4 Results

This chapter summarises the results and findings from the gathered literature data, including the overview of research trends, types of extinguishing agents, dispersion modes and categorisation of experiments into cell-level, module-level, EV pack-level, BESS rack-level and warehouse storage.

4.1 Bibliometric Analysis

In order to gain insight into the related research from the collected literature data, a bibliometric analysis is carried out. As there is no restriction on the years of publications in the database search, it is found that the earliest research on LIB fire suppression started in 2013, when NASA started their first fire experimental works using portable fire extinguishers with fine water mist and CO_2 agents on the efficacy to suppress LIB fires [64]. At the same time, FM Global started looking into sprinkler protection for the warehouse storage of LIBs [65]. Also that year, one of the largest automotive manufacturing countries, an Automobil company from Germany performed experiments on firefighting techniques on high-power LIB cells used on electric vehicles [66]. US Federation Aviation Administration, in 2014, started systematic fire suppression experiments and experimental set-up for cell-level testing using 10 different extinguishing agents, including water-, gas- and powder-based agents [67]. It is noticed that this experimental set-up model could be the first reference model for the LIB cell-level testing that was subsequently utilised and developed by other researchers in the following years. As shown in Figure 19 (a), between 2013-2016, there were only a handful of publications, most of which came from the US. From 2017 onwards, the research and publication in this field were booming steadily, particularly from Chinese higher institutions and laboratories. To date, more than 60% of the related publications are from China, followed by the US, as shown in Figure 19 (b). There were also several non-English but related articles in Chinese and Korean which are not listed in the chart below.



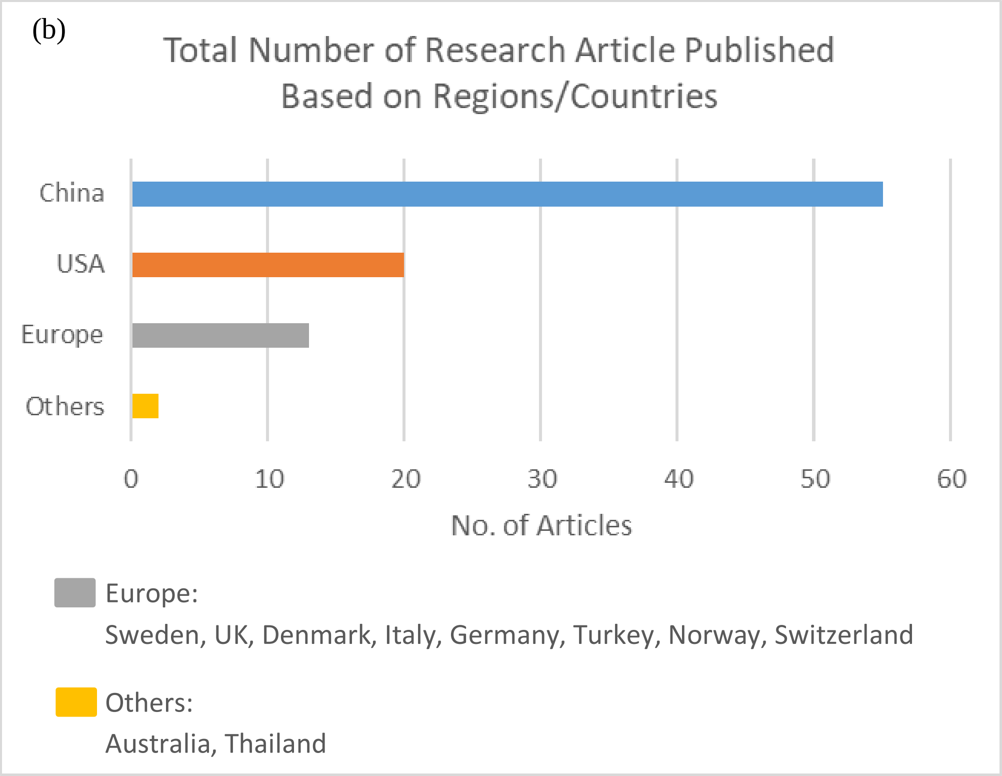


Figure 19 (a) Research articles for LIB fixed fire suppression from 2013 to March 2023; and (b) Total number of research articles based on countries.

The publications above are further categorised into 20 review-based and 65 experimental-based articles. Twenty (20) review-based articles are utilised as a benchmark to check any vital or novel findings are not missed out in the thesis. Sixty-five (65) experimental-based articles are then categorised based on the levels of experiments according to LIB configurations, as shown in Figure 20. Cell-level experiment refers to extinguishing agents aimed directly at single or multiple exposed cells. Module-level experiment refers to extinguishing agents aimed at the battery module box housing multiple cells. EV pack-level experiment refers to the battery pack cabinet used on a standard electric vehicle/bus containing either multiple battery modules or multiple large-size battery cells. Extinguishing agents are injected directly into the pack cabinet or applied externally. BESS rack-level experiment refers to a LIB energy storage system room/container housing battery racks, and multiple battery modules are mounted in each battery rack. Extinguishing agents are typically discharged above the battery racks within the energy storage system room/container. Warehouse storage experiment refers to extinguishing agents discharged in a battery storage space where battery cells are packed in carton boxes, stacked and stored. From the chart in Figure 20, the majority of the publications (about 67%) conducted cell-level experiments only. The conclusions drawn from the cell-level experiments might be beneficial for EV application because the mode of agent dispersion is similar to EV pack-level experiments. However, it clearly shows that the research on the large-scale BESS rack-level experiment is lagging. A major distinction between the BESS rack-level experiment and the others is the dispersion mode of extinguishing agents, in which the rack-level experiment tests the efficacy of a fire suppression system dispersing an extinguishing agent into a room or space where a large quantity of battery cells and modules is housed in racks. The other levels only test the efficacy of an extinguishing agent dispersed directly onto cell(s) or module(s). Warehouse storage has a similar mode of dispersion as the

BESS rack-level experiment, but the main differences are the battery cells are idling with 50% SOC and packed densely in carton packaging in vertical stacks. The following sub-sections in this chapter will further elaborate on the four levels of experiments and warehouse storage experiments. The key findings of each publication are also summarised in Appendix B.

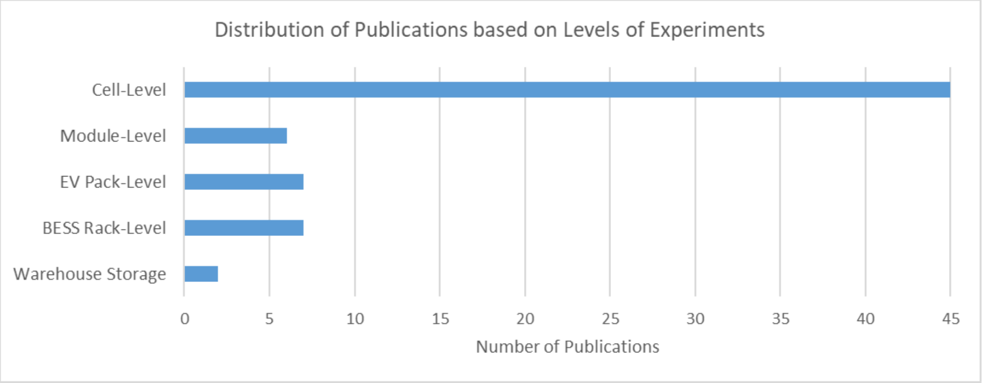


Figure 20 Distribution of publications based on levels of experiments.

4.2 Cell-Level Experiment

In cell-level experiments, the extinguishing agents act directly on the burning surface of LIB cell(s). Compared with other levels of experiment, the cell-level experiment does not encounter the accessibility problems of the extinguishing agents reaching a deep-seated fire. From the collated literature data, 45 publications present more than 20 different extinguishing agents on this level, and the experimental setups in these research are relatively similar. Due to a large number of publications and similarity among them, the results of cell-level experiments are presented according to the type of extinguishing agent (water, gas, powder and synergistic) in the following subsections following a general description of the experimental procedures and agents.

4.2.1 Overview of Cell-Level Experiment

The experimental setup for the cell-level experiment generally takes place in a controlled combustion chamber, as shown in Figure 21. The tested battery cells (single or multiple) are housed with or without an explosion-proof tank positioned in the middle of a combustion chamber. An electrical heater attached to the cells or a burner underneath the cells is usually deployed to initiate the thermal abuse leading to thermal runaway. The extinguishing agents are stored in a cylinder or tank and connected to the explosion-proof tank or the combustion chamber. The discharge nozzles are located strategically to ensure the discharged agents cover the exposed battery cells entirely. The moment of agent activation depends on the intent of the research, i.e. when a vent gas smoke is observed, a flame is started, or a critical temperature is exceeded. Multiple thermocouples (TC) are attached to and near the cells to monitor the temperature trend during the experiments.

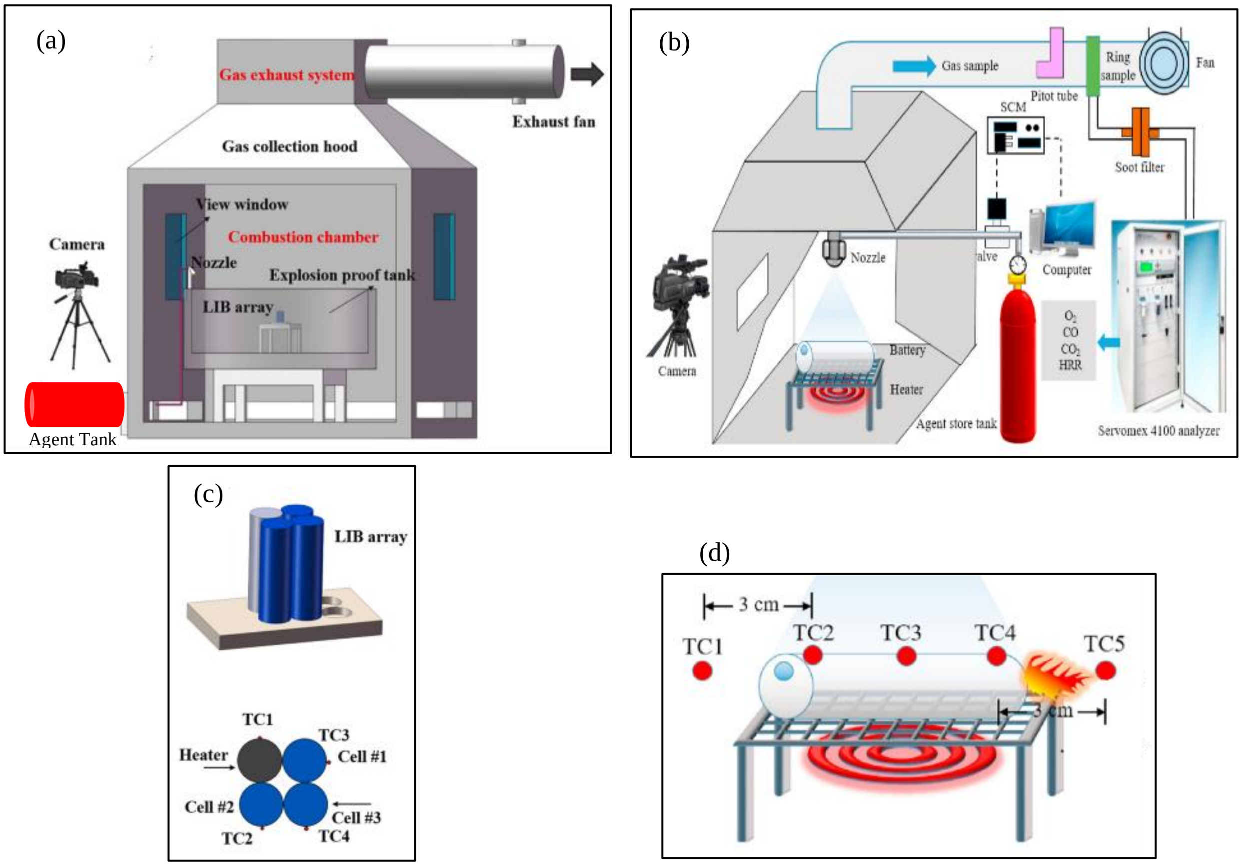


Figure 21 Examples of typical experimental set-up for the cell-level experiment (a) with an explosion-proof tank; (b) without an explosion-proof tank; (c)&(d) placement of thermocouples (TC) and heaters [68,69].

The extinguishing agents tested in the cell-level experiments are categorised in Figure 22. From the graph, water mist (WM) with and without additives and $C_6F_{12}O$ agents attracted the most research attention. Some novel researches using synergistic agents also focus on improving the performance of WM and $C_6F_{12}O$ [70–74].

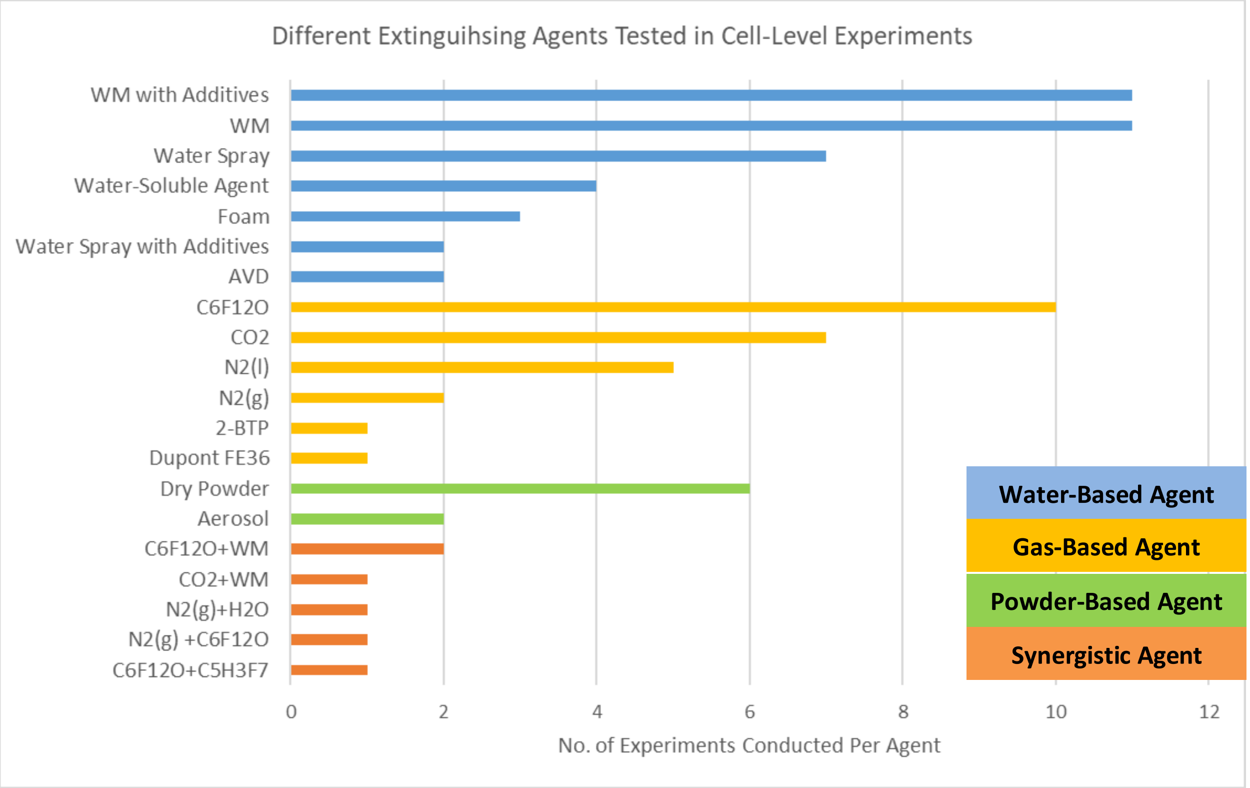


Figure 22 Number of experiments conducted for different extinguishing agents in cell-level experiments.

4.2.2 Water-Based Extinguishing Agent

From the literature data, the tested water-based extinguishing agents include pure water, water with additives, pure WM, WM with additives and foam. Among these agents, the research on WM with and without additives is the most popular, as shown in Figure 22. A variety of tested additives includes F-500, AVD, K_2CO_3, KCl, $KHCO_3$, $K_2C_2O_4$, Na_2CO_3, $NaHCO_3$, NaCl, $C_{12}H_{26}O$, CH_4N_2O, SDBS, SDS, APG, AEO-9, DMMP, FC4330, EL90, EL20, KEOA, PFAB, FMEE, AEC, MAEPK, etc. [72,75–86].

In general, for the cell-level experiments, WM with additives almost combines all necessary fire suppression effects of a “fire tetrahedron”, which comprise two or more of the following advantages: a good cooling effect due to high heat capacity of water; fine mists float in the air to perform gas cooling, reduce adiabatic flame temperature and also deplete the oxygen concentration; and additives can reduce the surface tension of fine water droplets to increase the penetration ability, form an isolation film to separate the fuel from oxygen and/or inhibit the chemical reaction of combustion. Thus, the overall fire suppression performance of WM with additives is better than pure WM in terms of quicker fire extinguishment and cooling [75,78–80,82,84,86]. Although WM with additives can extinguish LIB cell fires in all tests, not all of them effectively stop thermal runaway (TR) and cell-to-cell TR propagation, probably due to different mixes and concentrations of additives, battery chemistries and capacities, which require future studies.

4.2.3 Gas-Based Extinguishing Agent

The gas-based extinguishment agents focus only on clean agents that have minimal harm to the environment. From the literature data, the tested clean agents include Type 1 – gas-based agents such as N_2(g) and CO_2; and Type 2 – agents stored as liquid and discharged as gases such as $C_6F_{12}O$ (e.g.

Novec1230 or FK-5-1-12), liquid N_2(l), 2-BTP and FE36. Type 1 agents extinguish fires mainly by reducing the adiabatic flame temperature with an appropriate concentration of inert gases but without surface and gas cooling capability. For Type 2 agents, some additional gas cooling effect is introduced when converting from liquid to gas phases. On top of that, $C_6F_{12}O$, 2-BTP and FE36 extinguish fires by inhibiting chemical reactions and N_2(l) by reducing adiabatic flame temperature.

Among all available research, studies of $C_6F_{12}O$ are ranked 2nd highest in popularity. Compared with water-based agents at cell-level experiments, gas-based agents offer a clear advantage of fast fire extinguishment but less or no surface cooling, i.e. LIB fire can be extinguished rapidly, but prevention of TR is not guaranteed [67,70,87–91]. N_2(l), as a novel LIB fire extinguishing agent, has attracted research attention since 2021 due to its excellent cooling capacity as a key factor in mitigating TR and cell-to-cell propagation [92–96]. However, the pack- and rack-level experiments for N_2(l) are unavailable, which might be a promising area for future studies.

4.2.4 Powder-Based Extinguishing Agent

From the literature data, the tested powder-based extinguishing agents include ABC ultra-fine dry powder, BC ultra-fine dry powder, ABC dry powder, superfine powder, purple-k, aluminium ammonium sulfate dodecahydrate (AASD) composited ABC dry powder and aerosol. Though all these agents can extinguish LIB fires, none can prevent TR and cell-to-cell propagation due to their poor surface cooling effect [67,91,97–99], except for the novel AASD [$NH_4Al(SO_4)_2\cdot 12H_2O$]] composited ABC dry powder [100]. AASD is an inorganic phase change material with a melting point of 93.5°C and a latent heat of 269J/g. When it applies onto a TR LIB, AASD powders melt and change from a solid to a liquid phase by absorbing a lot of heat. Thus, it can potentially cool a TR LIB and mitigate TR propagation [100]. So far, there is only one publication on LIB fire suppression experiment using AASD composited ABC dry powder, in which the AASD composite enhances the surface cooling performance of ABC dry powder. Nevertheless, this is still in the infant stage and requires more research to establish its usage and application.

4.2.5 Synergistic Extinguishing Agent

The previous sections demonstrate that any single agent has its limitations in mitigating a LIB fire and preventing TR propagation. Since 2020, researchers have been exploring the synergistic extinguishing approach by combining two agents to complement the shortfall and enhance the performance of a single agent. Zhang et al. [71] studied the efficacy of N_2(g)+$C_6F_{12}O$ and N_2(g)+WM and found that both could suppress the LIB fire and stop TR. The former exhibited 51.2% higher extinguishing efficiency and the latter increased the cooling rate by 20% compared with N_2(g) alone. Tian et al. [74] added $C_5H_3F_7$ to $C_6F_{12}O$ with a 1:1 ratio so that the synergistic agent has both a cooling effect and extinguishing capability. Liu et al. [72] and Zhang et al. [70] found that $C_6F_{12}O$+WM synergistic agent performed better in fire extinguishment and cooling than $C_6F_{12}O$ or WM alone. Zhang et al. [70] also determined $C_6F_{12}O$+WM was better than CO_2 + WM. Like N_2(l) and AASD composited ABC dry powder, the pack- and rack-level experiments for synergistic extinguishing agents are also unavailable, which might be a promising area for future studies.

4.3 Module-Level Experiment

In the module-level experiments, multiple battery cells are housed in a battery module box. The extinguishing agent is applied over the battery module box to investigate extinguishing capability, cooling effect and TR propagation. The literature review resulted in three conference papers, one white paper and two technical reports on this level. Key findings from each publication are presented in the following subsections.

4.3.1 Conference Paper: *“Experimental Study on Fire and Explosion Characteristics of Power Lithium Batteries with Surfactant Water Mist”*

Zhu et al. [85] conducted a battery module fire experiment using four 20Ah LFP cells connected in series to form an 80Ah module capacity and housed in a battery module box, as illustrated in Figure 23. The SOC was not reported. The battery thermal runaway was initiated by an external burner, and the extinguishing agent was activated when a stable flame was observed. The agent used was LPWM with a combination of different additives – fatty methyl ester ethoxylate (FMEE), alkyl glucoside (APG) 06, APG08, APG10, sodium dodecyl sulfate (SDS), sodium fatty alcohol polyoxyethylene ether carboxylate (AEC) and potassium monoalkyl ether phosphate (MAEPK).

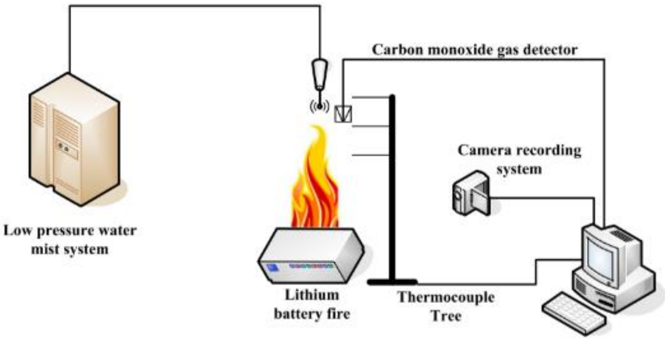


Figure 23 Illustration of the experimental setup by Zhu et al. [85].

This study demonstrated that the LPWM with a 5% concentration of the proposed mixture of additives could effectively cool the flame and suppress the fire. The proposed agent cooled the flame temperature at a rate twice as fast as pure WM. However, what happened to the battery cells in the module box and whether the proposed extinguishing agent could mitigate TR propagation were not presented in this paper.

4.3.2 Conference Paper: *“Research and Development of Fire Extinguishing Technology for Power Lithium Batteries”*

Luo et al. [86] conducted a similar battery module fire experiment as Zhu et al. [85] but used 50% SOC batteries and the thermal runaway was initiated by mechanical abuse, i.e. puncturing with a steel needle. The extinguishing agents used were direct water spray, WM with 5% F-500 additive and WM with 5% self-made anionic nonionic additive. The study concluded that WM with additives could reduce the flame temperature and extinguish the flame more rapidly than pure water spray. Furthermore, the fire suppression performance of self-made additive was better than F-500. However, what happened to the battery cells in the module box and whether the proposed extinguishing agent could mitigate TR propagation were not presented in this paper.

4.3.3 Conference Paper: *“Development of a Standard Test Scenario to Evaluate the Effectiveness of Portable Fire Extinguishers on Lithium-ion Battery Fires”*

This conference paper by Juarez et al. [64] in 2013 is one of the earliest publications looking into the fire suppression of LIBs. In this paper, the field application was the LIB fire suppression technique onboard an international spacecraft. The experiments used two battery modules stacked vertically, and each module contained four cylindrical battery cells with 4Ah per cell. The battery chemistry and SOC are unknown. The thermocouples were attached to each cell and to each module's plastic casing. Thermal runaway of the bottom battery module was initiated by an external heating element. Fine WM and CO_2 extinguishers were applied 15s after the bottom module was fully involved in a fire. The experimental setup is shown in Figure 24.

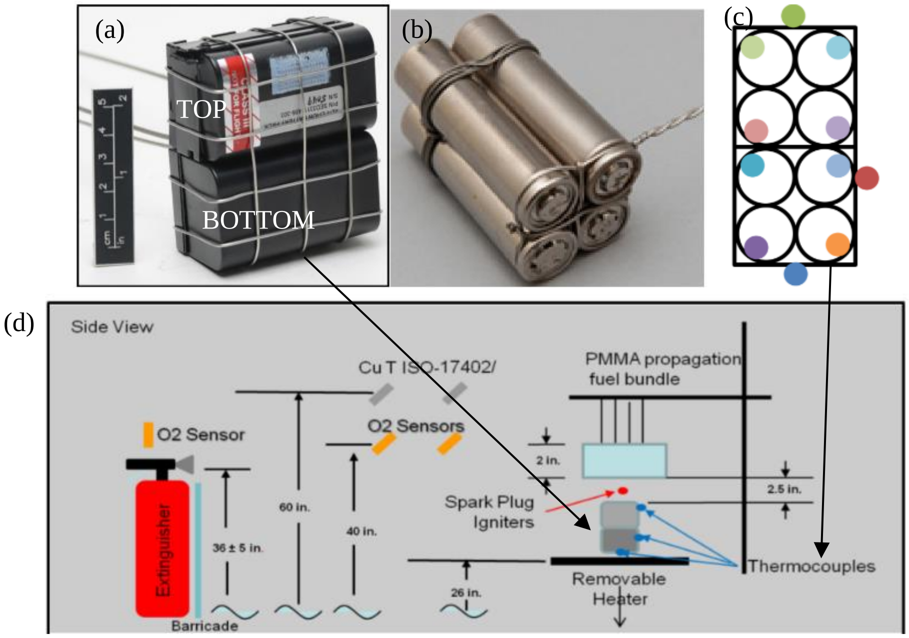


Figure 24 (a) Two stacked battery modules; (b) Four battery cells in each module; (c) Placement of thermocouples represented by colour dots; and (d) Experimental setup [64].

The study showed that in a fully involved fire, fine WM extinguisher could extinguish the flame but could not stop cell-to-cell TR propagation and module-to-module propagation. CO_2 extinguisher was worse, which could not even completely extinguish the flame. It was also found that the battery module casing retained the heat and hindered the cooling process.

4.3.4 White Paper: *“Fire Protection for Li-ion Battery Energy Storage Systems”*

The experiment (shown in Figure 25) [50] was conducted by Siemens company using three NMC battery cells in an original battery module housing. The battery capacity and SOC are unknown. The test was conducted in an N_2(g)-flooded chamber with an 11.3% O_2 concentration and an ambient 20.9% O_2 concentration. The cell TR was initiated by the internal short circuit of battery cell No.1.

Figure 25 (a) Battery module; (b) Battery module in N_2 chamber; (c) Aftermath @ 20.9% O_2 concentration; and (d) Aftermath @ 11.3% O_2 concentration [50].

The study demonstrated that if $N_2(g)$ with 45.2% extinguishing concentration flooded an air-tight space as early as the TR initiated (i.e. upon the vent gas released), with a depleted O_2 concentration of 11.3%, cell-to-cell TR propagation within a partially enclosed battery module could be mitigated, as compared with complete TR propagation at an ambient O_2 concentration of 20.9%.

4.3.5 Technical Report: *"Consideration of ESS Fire Safety"*

Hill et al. from DNV [101] conducted cell-level and module-level experiments using NMC, LFP and LTO battery cells, ranging from 1.2 to 200Ah. The module capacity ranged from 7.5 to 55 kWh. The SOC was 90%. The extinguishing agents used were sprinkler water, water-soluble gel (FireIce), foam (Pyrocool), water-soluble agent (F-500) and aerosol. The experiments were conducted in a partially enclosed containerised outdoor burn facility, as shown in Figure 26. TR was initiated by a propane torch. The agents were activated immediately upon a rapid thermal increase.

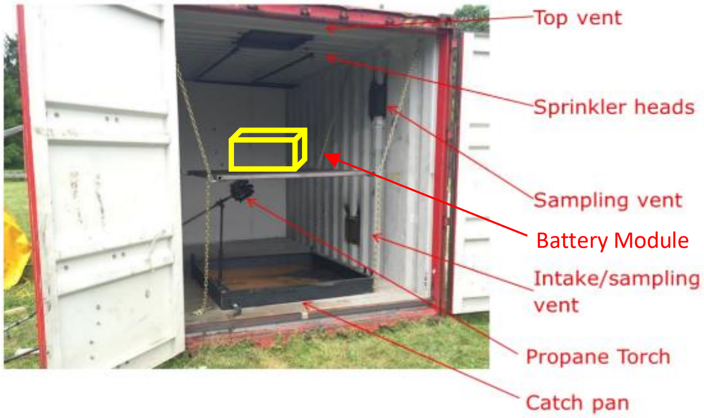


Figure 26 Outdoor burning facility for the module-level experiment [101].

The study found that all proposed extinguishing agents could put out the flames in cell- and module-level experiments. However, TR propagation could not be mitigated by Pyrocool and aerosol in the module-level experiments because re-ignition occurred after the agents were consumed. Water was found to have a better surface cooling effect than all other water-based agents in the experiment. The aerosol was the least effective in cooling but the most effective in quenching the flame. Thus, DNV suggested aerosol system be backed up by water-based suppression for better extinguishment and cooling effects.

4.3.6 Technical Report: *"Lion Fire – Extinguishment and Mitigation of Fires in Li-ion Batteries at Sea"*

Andersson et al. from RISE [102] conducted LIB fire experiments using a 20Ah LFP pouch cell with 90% SOC housed within a purpose-built battery module box. TR was initiated by heating a battery cell with an electric heating element and a pilot flame ignited the battery off-gas within the battery module box. A plate thermometer acted as a dummy cell to record the temperature of cell-to-cell TR propagation. The perforated steel sheets partially hindered a direct injection agent from reaching the seat of the fire, mimicking a packed battery module/pack in real life, as shown in Figure 27 (a).

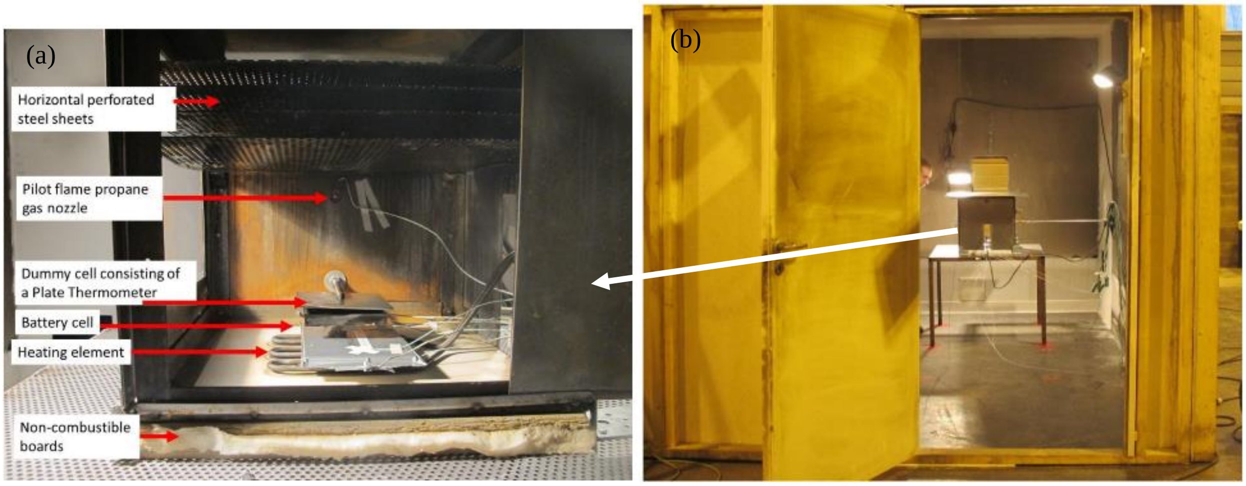


Figure 27 (a) Purpose-building battery module box; and (b) Total flooding dispersion [102].

Two different experimental setups were presented in the report: (i) Total flooding and (ii) Direct internal injection.

In a total flooding dispersion, the battery module box was placed within the containerised test compartment. Sprinkler water spray and water mist were applied outside the module box in the test compartment, as shown in Figure 27 (b). Water spray used a medium velocity water spray open-nozzle with a k-factor of 43.2 l/min/bar$^{1/2}$ and operating pressure of 2.4 bar). LPWM nozzle (k-factor of 3.5 L/min/bar$^{1/2}$, operating pressure of 15 bar and nominal water flow rate of 13.6 L/min) and HPWM nozzle (k-factor of 3.5 L/min/bar$^{1/2}$, operating pressure of 50 bar and nominal water flow rate of 24.7 L/min) were also utilised in the experiments. Respective nozzles were installed at the centre of the compartment ceiling vertically above the battery module box. The test results showed that none of the three methods in the total flooding could extinguish the fires from the LIB because the agents could not penetrate the module casing to reach the seat of the fire.

In a direct internal injection dispersion, the different extinguishing agents were connected into the battery module box with a spray nozzle located above the perforated sheets, as shown in Figure 28. The direct internal injection dispersion mode in this experiment is considered similar to the EV pack-level experiment in the following Section 4.4. The tested agents were water, Class A foam (also known as “wildfire foam” or “wetting agent” for Class A solid fires), Class F foam (aqueous solution of high activity salts and stabilisers for Class F cooking oil, fat and grease related fires), compressed air foam system (CAFS: water mixed with Class A foam with compressed air), N_2(g) and AVD. The test results showed that water, Class A foam and Class F foam could penetrate the perforated sheets, reach the fire, extinguish the fire quickly and exhibit a cooling effect on the adjacent dummy cell. The performance of these three agents was similar. N_2(g) could extinguish the fire rapidly but had a minimal cooling effect. For CAFS, the performance of extinguishment and cooling was similar to water in two of three CAFS tests using low-expansion foam. The remaining CAFS test using high-expansion foam failed to extinguish the fire because the high-expansion foam could not cover the battery cell due to a higher air-to-solution ratio than the low-expansion foam leading to the high-expansion foam being repelled by the released pressure from the battery vent gas. Lastly, AVD, with its higher viscosity, took a long time to penetrate through the perforated sheet and eventually extinguished the fire when the AVD agent fully covered the battery cell.

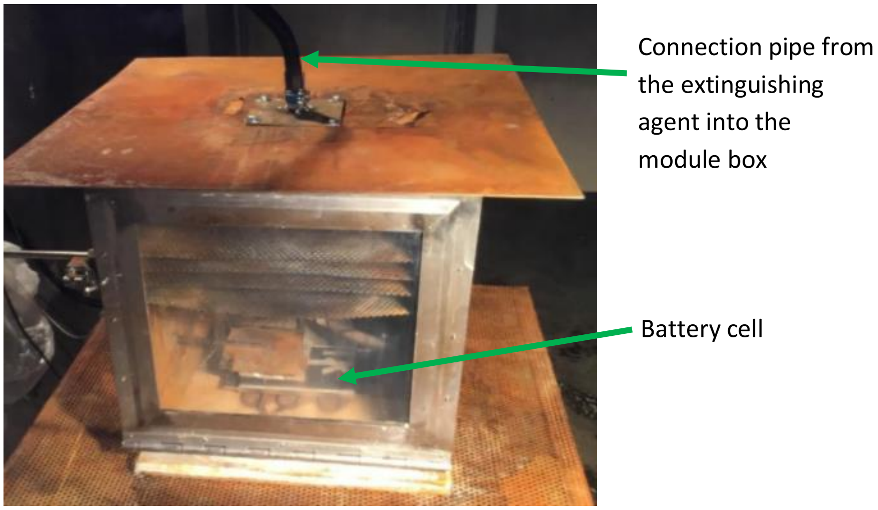


Figure 28 Direct internal injection of extinguishing agents within the battery module [102].

4.4 EV Pack-Level Experiment

In electric vehicles, multiple large-size battery cells or battery modules containing many smaller cells are housed in a large enclosed battery cabinet forming a battery pack. The fixed fire suppression system on the EV battery pack is possible for electric buses due to space available onboard to house the fire protection appliance. On the other hand, it is unlikely for electric cars due to space limitations. The extinguishing agent can be injected directly into the battery pack cabinet or applied externally where the battery packs are located. In addition to the battery pack-level alike experiment by RISE in Section 4.3.6 above, the literature review resulted in four journal papers and two conference papers related to the pack-level experiment. Four of six identified publications used $C_6F_{12}O$ extinguishing agent directly injected into the battery pack cabinet, mimicking the dimensions of a typical battery pack cabinet used for electric buses. One publication compared the efficacy between $C_6F_{12}O$ and water spray using direct internal injection dispersion. The remaining one studied WM and water spray with additives for both external spray and direct internal injection dispersion. Thus, the following subsections present the findings based on the types of agents tested for better grouping of the identified publications.

4.4.1 Experiments Using $C_6F_{12}O$ Agent (Novec1230 or FK-5-1-12)

In all pack-level experiments using the $C_6F_{12}O$ agent with direct internal injection, the flame could be knocked out quickly. However, TR propagation could only be mitigated in one of five experiments and could not be stopped in two of five experiments, while the remaining two experiments were inconclusive.

Table 8 summarises these experiments and key findings from the respective publications, while Figure 29 to Figure 33 illustrate each experimental setup.

Table 8 Summary of $C_6F_{12}O$ fire suppression experiments from five papers.

Reference	Battery	Pack Arrangement	Start of Agent Activation	Flame Extingu-ishment	Prevention of TR Propagation
Liang et al., 2023 [103] Figure 29	Prismatic/271Ah/ LFP/100%SOC	7 live cells + 26 dummy cells	3min after TR vent gas is ignited	Yes	Yes
Han et al., 2022 [104] Figure 30	Prismatic/24Ah/ LFP/100%SOC	9 modules x 28 cells	Immediately upon TR vent gas is ignited	Yes	No
Sun et al., 2022 [105] Figure 31	Prismatic/117Ah/ NMC/100%SOC	2 cells	Immediately upon TR vent gas is ignited	Yes	No
Zhou et al., 2021 [106] Figure 32	Prismatic/202Ah /LFP/100%SOC	3 cells	20s after the TR vent gas is ignited	Yes	Inconclusive. The authors suggested injecting the agent continuously to mitigate TR propagation.
Yu et al., 2019 [107] Figure 33	Prismatic/20Ah /LFP/100%SOC	1 live module (12 cells) + 8 dummy modules	Immediately upon TR vent gas is ignited	Yes	Inconclusive. The temperature of the adjacent cell continued to rise slowly after the agent was completely discharged.

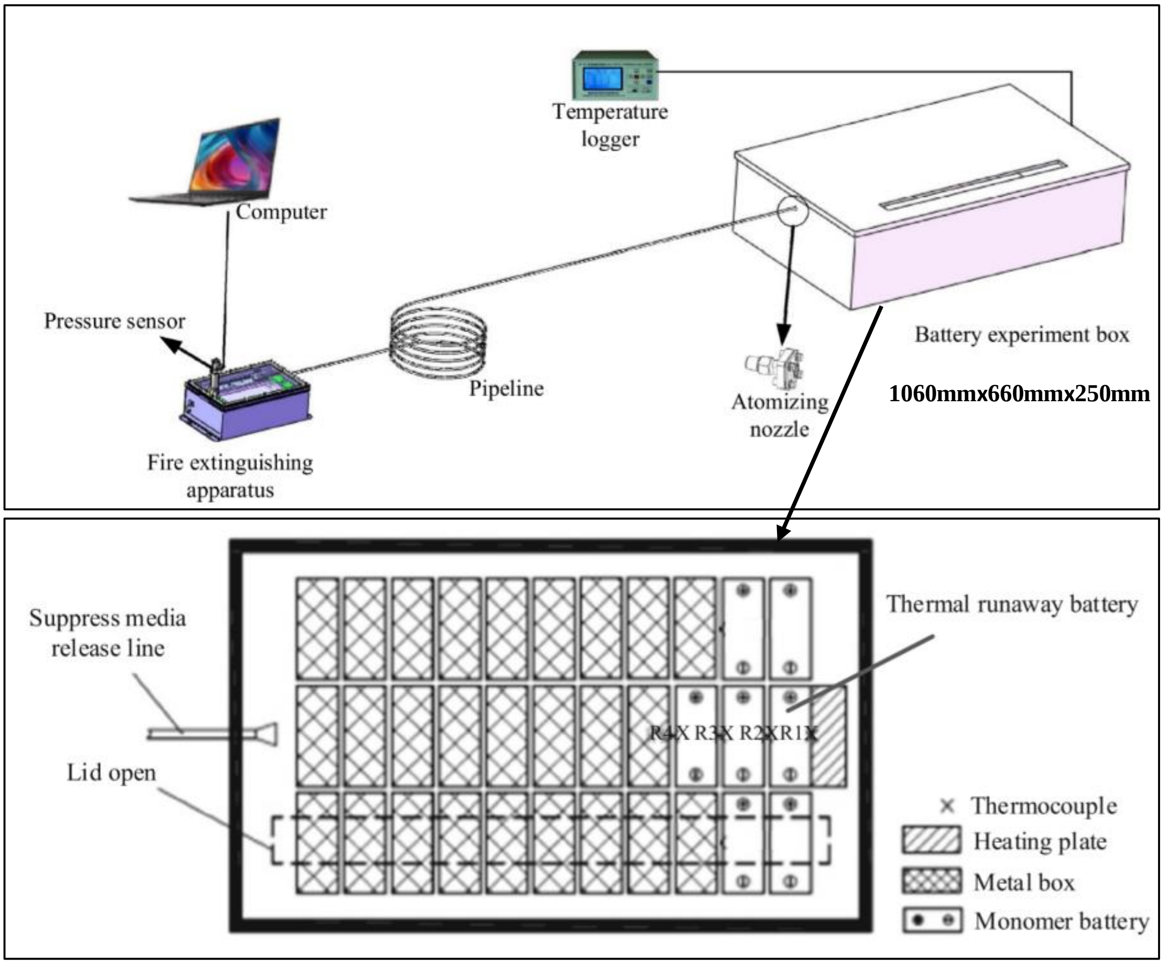


Figure 29 Illustration of experimental setup by Liang et al. [103].

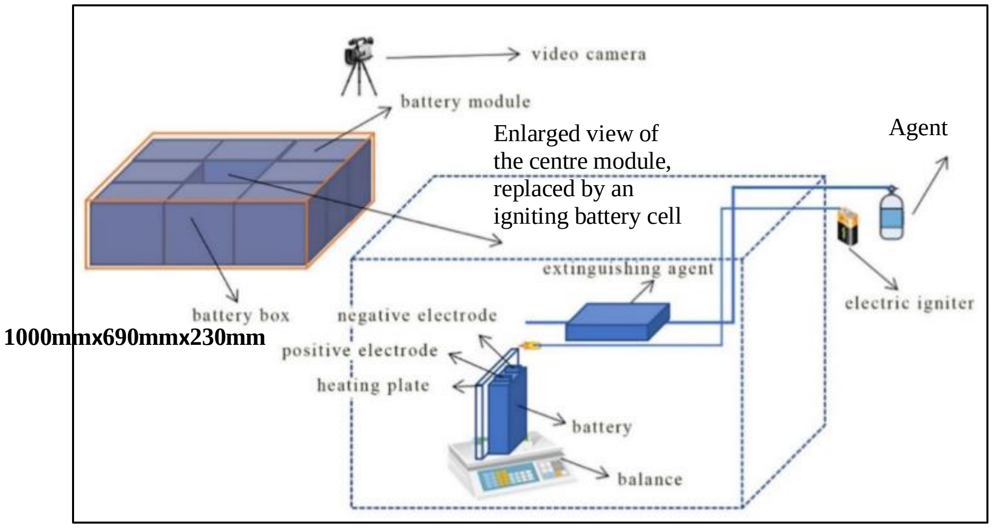


Figure 30 Illustration of experimental setup by Han et al. [104].

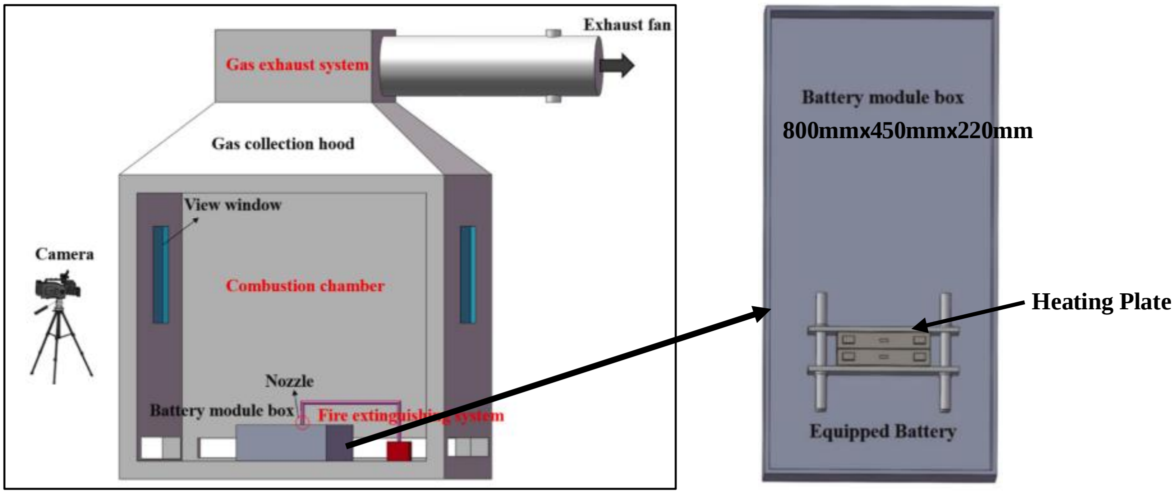


Figure 31 Illustration of experimental setup by Sun et al. [105].

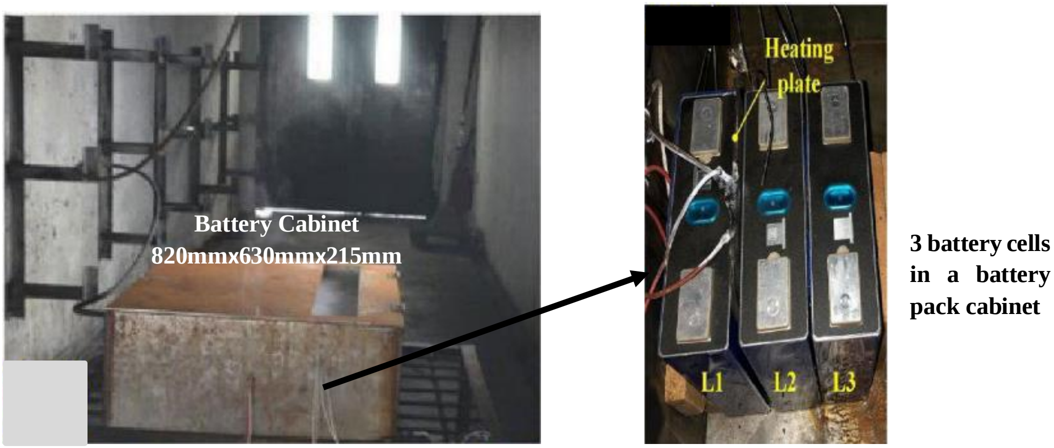


Figure 32 Illustration of experimental setup by Zhou et al. © 2021 IEEE [106].

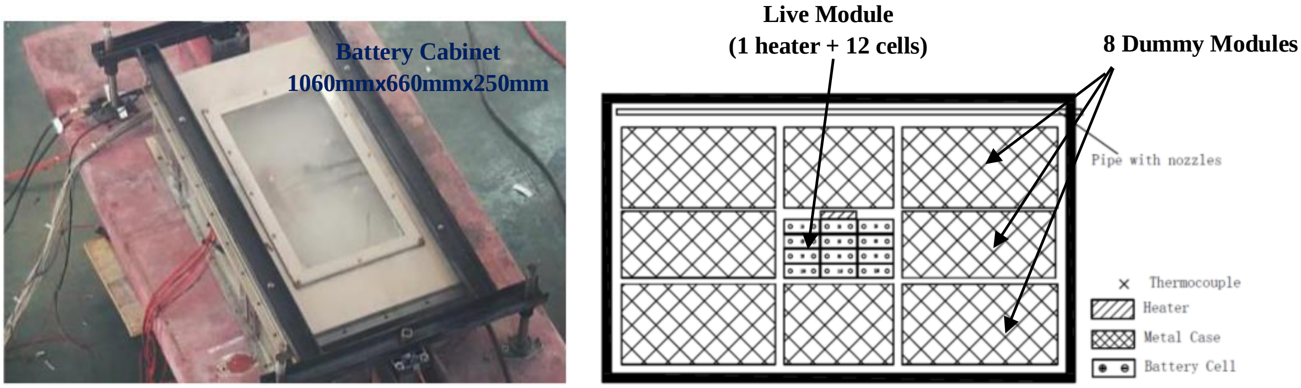


Figure 33 Illustration of experimental setup by Yu et al. © 2019 IEEE [107].

4.4.2 Experiments Using Water-Based Agent

Sun et al. [105] used the same experimental setup with direct internal injection dispersion in Figure 31 to compare the efficacy of $C_6F_{12}O$ and water spray. They found that water had a better cooling effect which could extinguish the fire and prevent TR propagation.

Bisschop et al. [108] conducted EV pack-level experiments using prismatic 28Ah NMC cells 100%SOC with two water-based extinguishing agents: (i) WM+5% foam additive and (ii) water spray+5% foam additive. The battery pack cabinet contained two live modules (housing 12 cells each) and six dummy modules. The two agents were directly injected into the pack cabinet, as shown in Figure 34 (a)(b), similar to the above $C_6F_{12}O$ experiments. In addition, they also examined the efficacy of water spray + 5% foam additive agent dispersing outside the battery pack cabinet, as shown in Figure 34 (c). TR was initiated by a gas burner impinging the flame onto a live battery cell in Module 1, and the extinguishment started 30s after the TR was observed. Given a similar volume amount (i.e. approximately 12-13L) of WM and water spray, WM could last for 3-4min with 4 full-cone nozzles at a flow rate of 1.7 L/min, but water spray lasted for only 30s with three full-cone nozzles at a flow rate of 7.2 L/min.

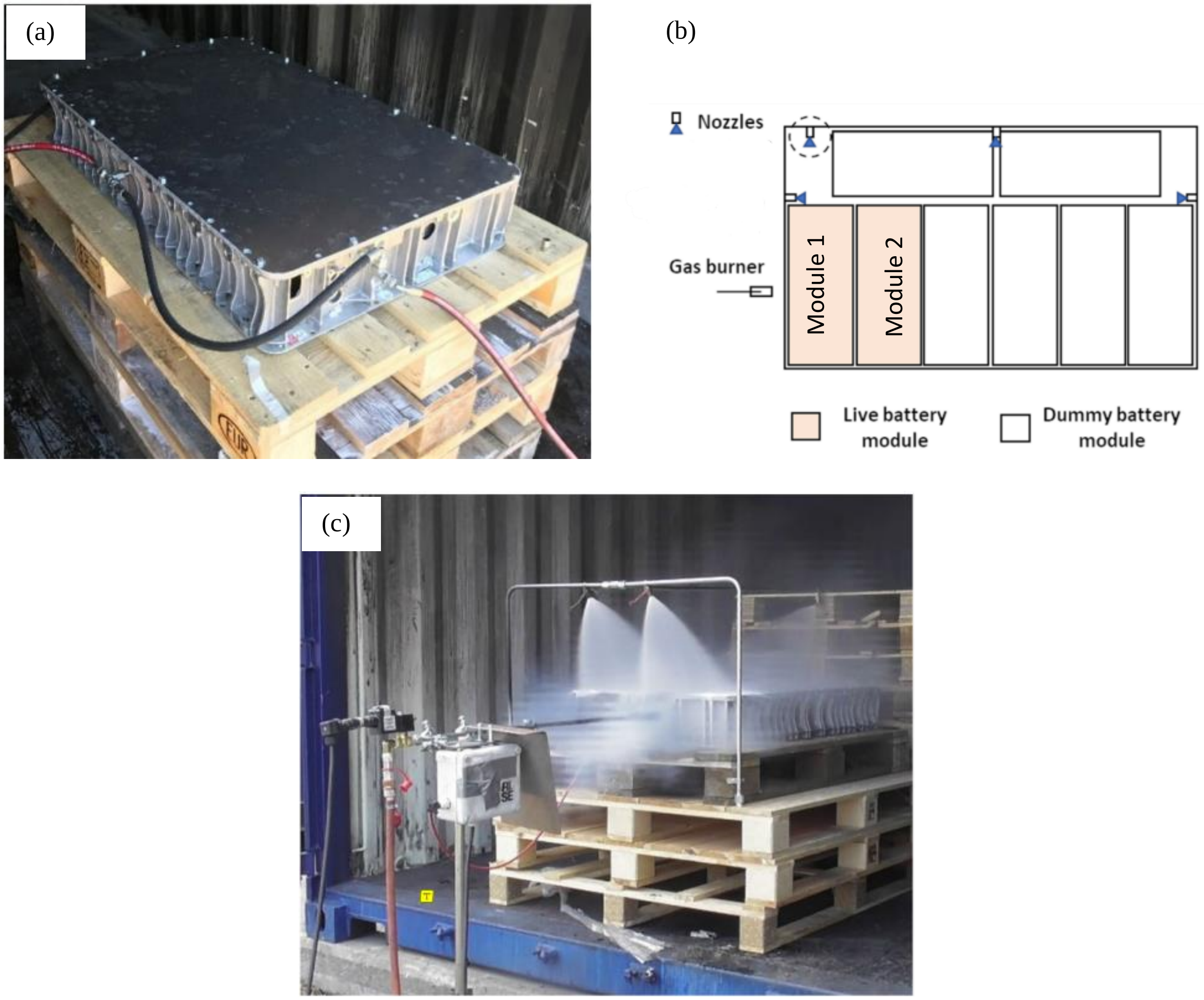


Figure 34 (a) Experimental setup of direction internal injection; (b) Illustration of battery modules within the battery pack cabinet; and (c) Experimental setup of external water spray [108].

The study demonstrated that both direct internal injection and external water spray could rapidly extinguish the flame gushing from the battery pack cabinet. However, the external water spray did not contribute to any internal cooling of the battery cells and modules due to little or no penetration of the water spray into the battery pack cabinet, and TR propagation went on internally. For direct internal injection, WM and water spray both exhibited their cooling effects and prevented the module-to-module TR propagation. Furthermore, the internal cooling performance of the WM is marginally better than the water spray in terms of cell-to-cell TR propagation in the TR initiating module (Module 1) because the slower propagation rate was observed. Finally, the experiment suggested that for an internal direct injection of water-based suppressants, a low flow rate and long release time would be the most effective way to hinder TR propagation for cells and modules.

4.5 BESS Rack-Level Experiment

In the BESS rack-level experiment, battery modules containing battery cells are densely mounted on battery racks, mimicking a battery energy storage system in a test room or an outdoor container. The experiments using fixed fire suppression systems applied outside the battery rack to examine the efficacy of fire control, suppression and mitigation of TR propagation. The literature review resulted in one journal paper, one white paper and five technical reports related to the BESS rack-level experiments. Key findings from each research are presented in the following subsections in two categories. The first category is the single-rack experiments examining module-to-module propagation. The second category is the multi-rack experiments examining both module-to-module and rack-to-rack propagations.

4.5.1 Single-Rack Experiment

Three publications report fire suppression experiments on a single rack with only one live battery module and multiple dummy modules to examine module-to-module TR propagation.

4.5.1.1 Journal Paper: *"Experimental Study on the Efficiency of Dodecafluoro-2-Methylpentan-3-One ($C_6F_{12}O$) on Suppressing Large-Scale Battery Module Fire"*

Zhang et al. [109] conducted a rack-level experiment using 243Ah prismatic LFP battery cells with 100%SOC. A battery rack with dimensions of 1.65m (width) X 0.8m (depth) X 2.2m (height) was placed in a BESS container. An open battery module containing 12 exposed battery cells was positioned in the middle of the rack, with 20 other dummy modules arranged in seven rows of three modules, as shown in Figure 35. TR was initiated by an electric heater attached to the battery cell, and a propane burner ignited the released battery vent gas. After 30s of burning, 4kg $C_6F_{12}O$ extinguishing agent was discharged via a nozzle near the top-centre shelf of the battery rack.

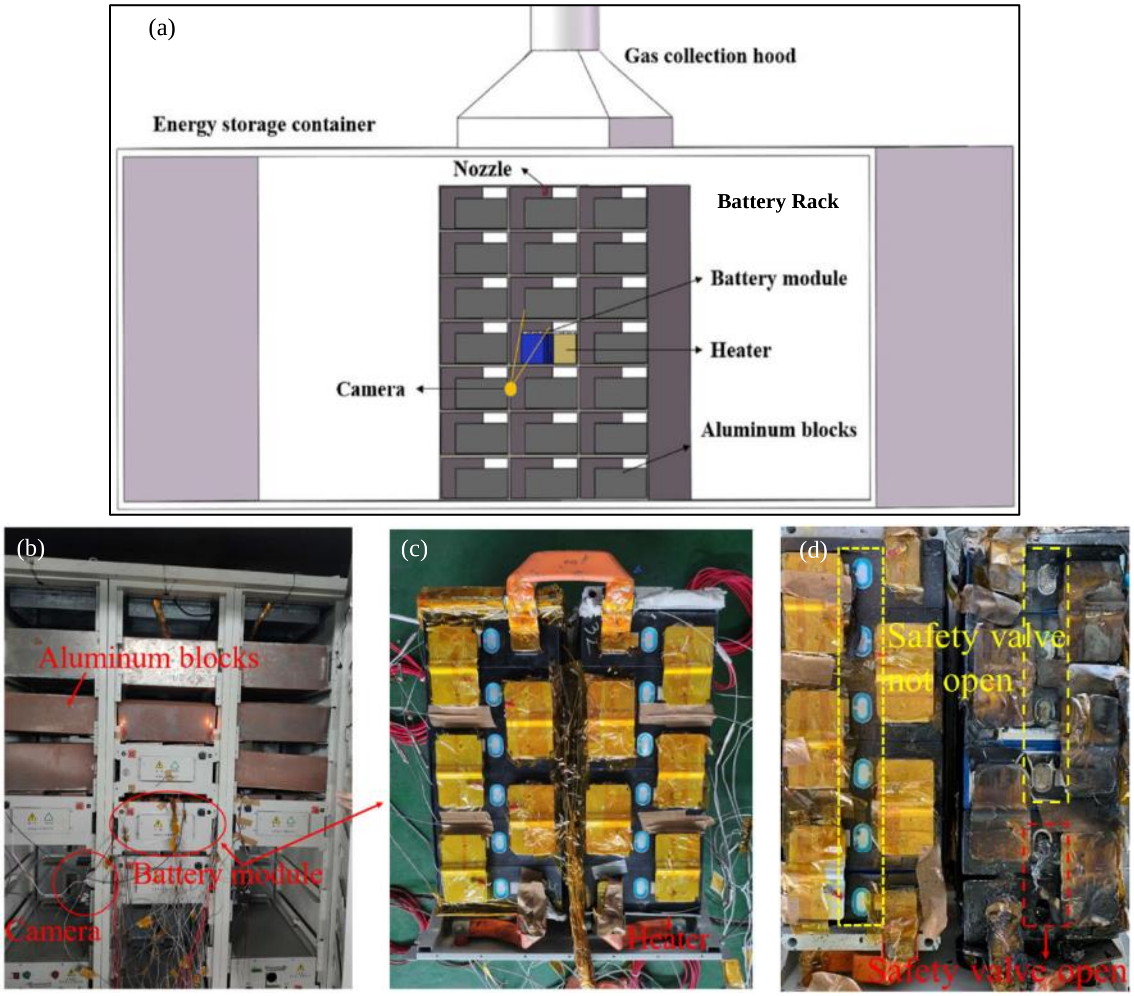


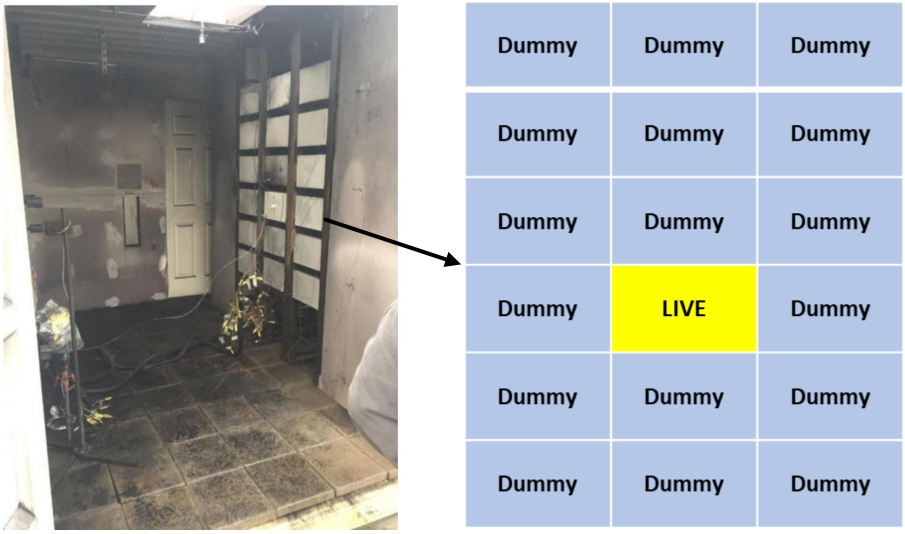
Figure 35 (a) Experimental setup of the battery rack; (b) Overview of battery rack; (c) Twelve battery cells in the battery module; and (d) Aftermath [109].

The experiment demonstrated that a sufficient amount of $C_6F_{12}O$ (i.e. 4kg) in the experimental setup could extinguish the battery module fire rapidly in 16s and exhibited a certain cooling effect. The TR propagation was halted in the second battery cell adjacent to the TR initiating cell without propagating further. The temperature of the remaining ten cells remained below 75°C one hour after the experiment. The study concluded that $C_6F_{12}O$ with high concentration could effectively extinguish the fire and inhibit TR propagation. In the experiment, the battery cells were not mounted in a module box. Thus, $C_6F_{12}O$ agent could penetrate the gaps between modules and reach the exposed battery cells.

4.5.1.2 Technical Report: *"Technical Reference for Li-Ion Battery Explosion Risk and Fire Suppression"*

Gully et al. [110] conducted rack-level experiments using 63Ah pouch NMC battery cells with 100% SOC. In a standard container, a battery rack contained one live battery module and 17 dummy modules arranged in six rows of three modules, as shown in Figure 36. The live module was located in the middle of the fourth row and had a rating of 417Ah of five pouch cells. The actual dimensions of the battery rack are unknown. TR was initiated by a resistive heating element attached to battery cells in the live module. The experiments examined two dispersion modes and four extinguishing agents: (i) Total flooding with $C_6F_{12}O$

(Novec1230), HPWM and sprinkler water; and (ii) Direct internal injection into the battery module with water spray and compressed air foaming system (CAFS). However, the report does not provide additional information regarding the mode and duration of the agent activation and nozzle specifications of the sprinkler and WM. The objective of the fire suppression systems in this study was to investigate the efficacy in module-to-module TR propagation by measuring the temperature changes of the neighbouring dummy modules but not examining cell-to-cell TR propagation in the live module.



Dummy	Dummy	Dummy
Dummy	Dummy	Dummy
Dummy	Dummy	Dummy
Dummy	LIVE	Dummy
Dummy	Dummy	Dummy
Dummy	Dummy	Dummy

Figure 36 Battery modules mounted on a battery rack in a standard container [110].

In the total flooding experiments, HPWM and $C_6F_{12}O$ could effectively extinguish the visible flames, but the sprinkler could not. HPWM and sprinkler exhibited similar cooling capabilities on the neighbouring dummy modules and performed better than $C_6F_{12}O$ in this regard. Thus, the overall performance of HPWM was better than the sprinkler and $C_6F_{12}O$.

In the direct internal injection experiments, both water and CAFS could extinguish the visible flames. In addition, they could also reduce the temperature inside the initiating module significantly, e.g. below 80°C compared with 900°C in the total flooding experiments. The temperature reduction of the neighbouring dummy modules was also lower than the total flooding experiments. Compared between water and CAFS, water could further reduce the temperature of the neighbouring dummy modules.

Overall, the authors recommended CAFS with direct internal injection because it exhibited the best heat-mitigating performance among all tested methods and agents and had limited conductivity and corrosion effects when compared with water.

4.5.1.3 Technical Report: *"Lion Fire II – Extinguishment and Mitigation of Fires in Lithium-ion Batteries at Sea"*

Bisschop et al. [36] conducted rack-level experiments using 2.55Ah NMC cylindrical and 50Ah LFP prismatic battery cells with 100% SOC, respectively. The NMC battery module contained 507 battery cells, made up to a rating of 100Ah, and the LFP battery module contained 30 battery cells, made up to the same rating of 100 Ah. In a standard shipping container, a battery rack contained one live battery module and 11 dummy modules arranged in four rows of three modules, as shown in Figure 37. The dimensions of the rack were 1.8m(width) x 0.66m(depth) x 1.2m(height). The live module was located in the middle of the third row. TR was initiated by an external gas burner impinging flame on the rear side of the live battery module, and two spark igniters ignited the TR battery vent gas from the front side of the live battery module. The experiments examined two dispersion modes and seven extinguishing agents: (i) Total flooding dispersion with LPWM, LPWM with 3% F-500 additive, sprinkler water, sprinkler water with 3% F-500 additive and Inergen inert gas IG541; and (ii) Local external dispersion with WM and WM with AVD additive. The conventional sprinkler nozzle delivered a water flow of 800 L/min and the LPWM nozzle delivered a water flow of 12 L/min at 12 bar. Q-fog system [111] was used in the local external dispersion with a flow of 10 L/min. The respective nozzles were placed at 2.1m height and 0.6m horizontal distance from the front face of the rack. The nozzle pointed vertically downwards in the total flooding dispersion, while the nozzle pointed towards the rack in the local external dispersion, as illustrated in Figure 38.

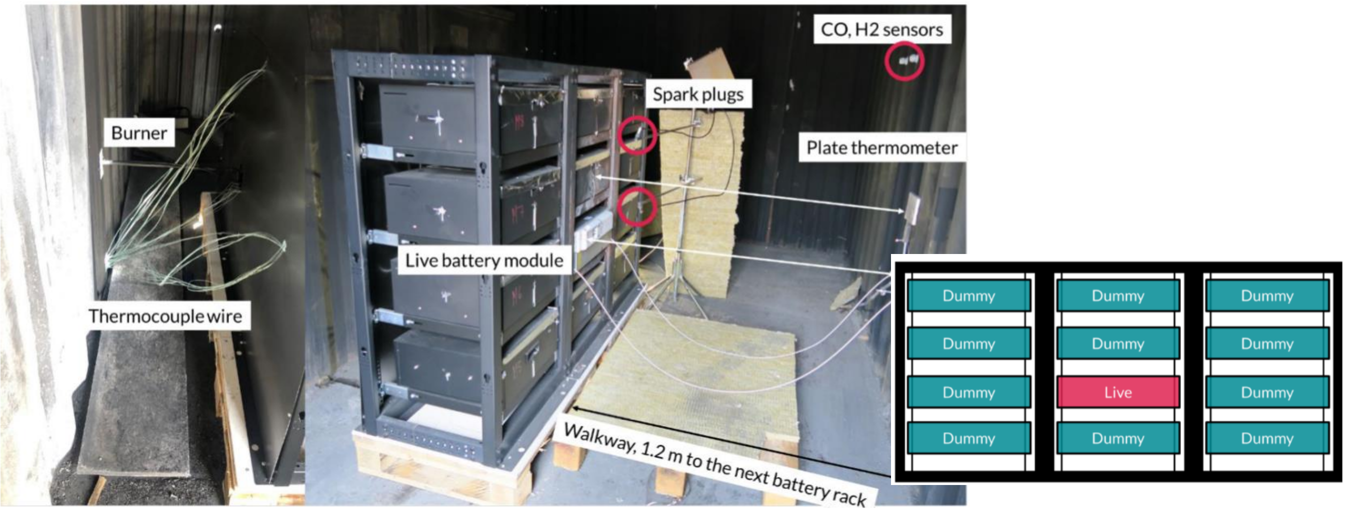


Figure 37 Battery modules mounted on a battery rack in a standard container [36].

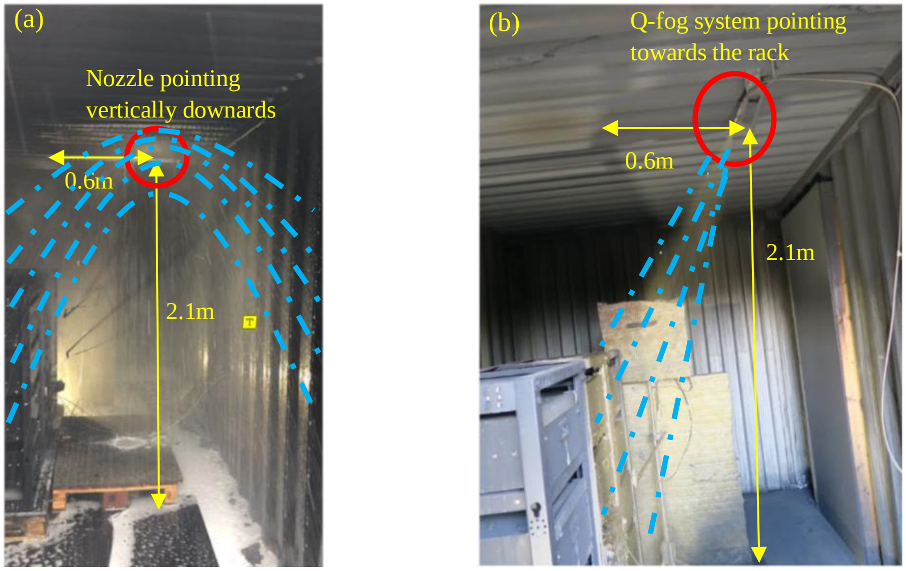


Figure 38 Nozzle setting for (a) Total flooding; and (b) Local external dispersion [36].

For all experiments, a 30s delay was applied to activate the suppression systems upon the temperature of the top neighbouring dummy module exceeding 70°C on the bottom and 100°C on the sides. In the total flooding dispersion, sprinkler and WM (with or without F-500) were sustained for 10 min and IG541 for 2 min. In the local external dispersion, WM was sustained for 3 min and AVD for 5.5 min.

The tests concluded that none of the suppression systems in the experiments could mitigate cell-to-cell propagation in the live battery module, which was also not the objective of the experiments. All systems were able to reduce the temperature of neighbouring modules and decrease flames to some extent upon activation of the systems but were still insufficient to completely prevent module-to-module propagation. The usage of additives F-500 and AVD also provided a positive effect on LIB fires, though the degree of its effectiveness is minor. The over-designed IG541 system (i.e. 2 min discharge) significantly lowered the immediate risk of module-to-module propagation (i.e. extinguishing the visible flame quickly) but poorer in long-term surface cooling than water-based agents. Between LFP and NMC, LFP took a longer time to reach the thermal runaway state and exhibited lower fire hazards than NMC in all experiments. Separately, the authors also stated that the comparison between the total flooding dispersion and local external dispersion was inconclusive due to a slight increment of the energy rating of the live battery modules in the latter experiment.

4.5.2 Multi-Rack Experiments

Four publications on fire suppression experiments use two to three live battery racks, fully or partially filled with live battery modules, to examine module-to-module and rack-to-rack TR propagation.

4.5.2.1 Technical Reports: *“Development of Sprinkler Protection Guidance for Lithium Ion Based Energy Storage Systems”*

There were two similar technical reports identified on this title. The original experimental report was developed by Ditch and Zeng [112] from FM Global, and its results were subsequently adopted by Long and Misera [113] from NFPA in another similar technical report. The rack-level experiments were conducted using 20Ah LFP and 32.5Ah NMC prismatic and 95%SOC battery cells with water-based sprinkler systems, mimicking the installation of battery energy storage systems in commercial facilities. The sprinkler system tests were performed individually for the LFP and NMC battery rack systems.

For the LFP system, two battery racks (one TR initiating rack and one target rack) with dimensions of 0.77m (width) x 0.66m (depth) x 1.76m (height) each were located side-by-side in a non-confined space with an unobstructed ceiling. Each rack housed 16 battery modules arranged in eight rows of two modules, and each battery module with a 120Ah rating contained 78 LFP cells, as shown in Figure 39. The NMC system had the identical configuration, except for the rack dimensions of 0.768m (width) x 0.76m (depth) x 2.4m (height) and each battery module with a 130Ah rating contained 64 NMC cells.

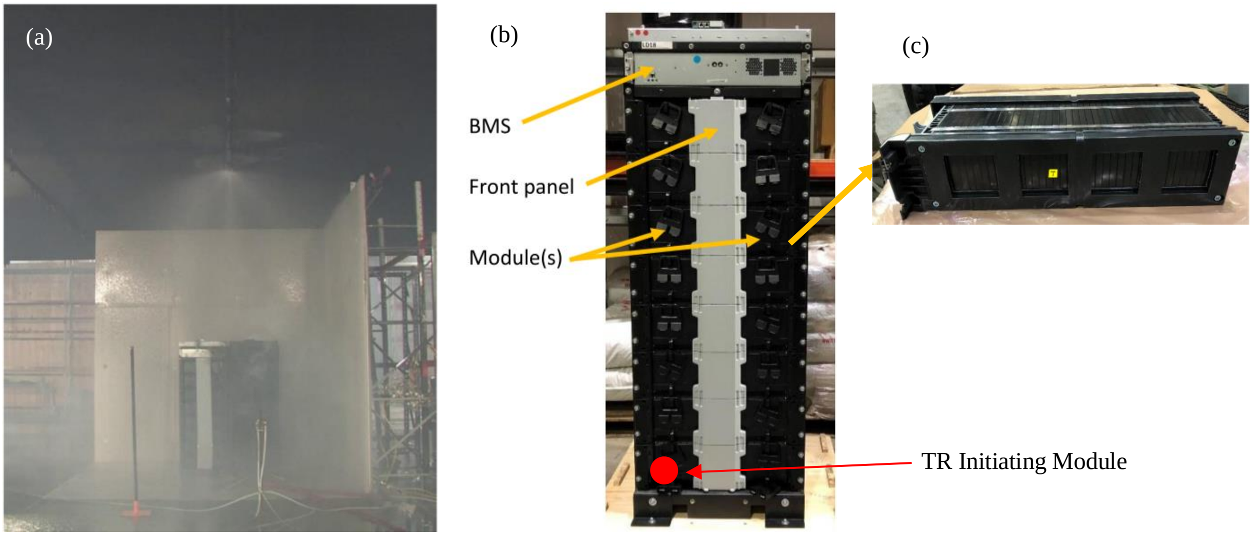


Figure 39 (a) Photo of LFP sprinklered test during fire decay phase; (b) Photo of LFP rack; and (c) Photo of LFP module with front face of module © 2020 FM Global All rights reserved [112].

TR was initiated by three flat bar hearing elements attached to the bottom-left battery module. A pilot flame was used to ignite the LFP vent gas but was not required for the NMC battery because NMC's self-produced sparks could ignite the NMC vent gas. Four sprinkler heads with 3.0m by 3.0m spacing were installed at 4.3m from the floor and 0.3 below the ceiling. The front-facing of the racks was directly underneath a sprinkler head, while the other 3 sprinkler heads were 3.0m away.

The tests observed that (i) a single sprinkler activation was capable of containing the fire within the TR initiating rack and preventing the fire from spreading to an adjacent rack for the LFP rack system, as shown in Figure 40 (a); (ii) For the NMC rack system, four sprinkler heads were activated and fire also spread to the adjacent rack, as shown in Figure 40 (b). Both LFP and NMC tests demonstrated that the ceiling-sprinkler suppression system could reduce the overall fire intensity and control the fire but could not completely suppress the fire and cool the internal battery modules inside the racks due to rack/module casings and tight module space leading to limited or no penetration of sprinkler water to the deep-seated fires from cells. Thus, cell-to-cell and module-to-module TR propagation could not be mitigated by the ceiling sprinkler system for both LFP and NMC rack systems. Only rack-to-rack TR propagation was prevented in the LFP rack system because LFP was tested to have lower fire hazards than NMC batteries in the experiments.

The report also recommended a set of sprinkler parameters to achieve a good level of fire protection in a similar environment, such as a minimum discharge density of 12 mm/min, a minimum K-factor of 81 L/min/bar$^{1/2}$, a nominal temperature rating of 74^{o}C and a response time index (RTI) of 27.6 m$^{0.5}$s$^{0.5}$(i.e. quick response). In addition, a minimum demand area and duration of sprinkler operation were also suggested to enable the design of an appropriate sprinkler protection system. For the LFP rack system, the sprinkler water supply should be designed based on a minimum demand area of 230m^{2} with at least 90min duration with a recommended rack separation distance of 1.5m. For the NMC rack system, the sprinkler water supply should be designed based on the total room area with a duration of 45min multiplied by the number of adjacent racks with a rack separation distance of less than 2.7m (e.g., if three racks are positioned less than 2.7m from each other, the sprinkler duration will be 45min x 3racks=135min). The test data and results by FM Global were subsequently used to support the development of NFPA's new standard, NFPA855:2020, for the installation of stationary energy storage systems [114] and the revision of the existing standard, NFPA13:2022, for the installation of sprinkler systems [115].

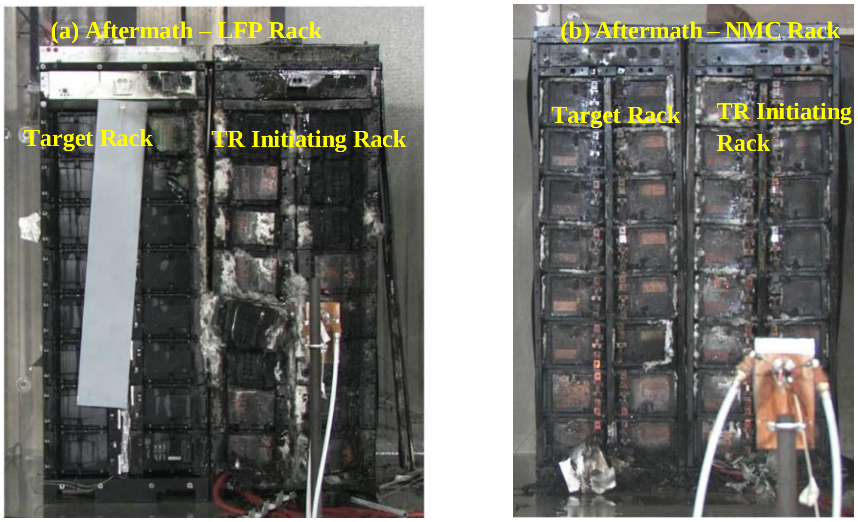


Figure 40 (a) Photo of LFP sprinklered test at burnout; and (b) Post-test photo of NMC showing complete burnout of main and target rack © 2020 FM Global All rights reserved [112].

4.5.2.2 Technical Report: *"UL9540A Installation Level Tests with Outdoor Lithium-ion Energy Storage System Mockups"*

Barowy et al. [116] conducted rack-level experiments using 3.2Ah cylindrical NCA battery cells with 100% SOC. One TR initiating rack, two target racks and several dummy racks (for visual aid only) were placed in an ISO intermodal container. The dimensions of each rack were 0.368m(width) x 0.61m(depth) x 1.4m (height). The TR initiating racks housed nine battery modules arranged in nine rows of a single module. Each module with a rating of 891Ah contained 270 battery cells. The two target racks were loaded to a one-third capacity of the initiating rack. Target Rack 1 rack was directly adjacent to the initiating rack. Target Rack 2 was 0.9m opposite the initiating rack, as shown in Figure 41. TR was initiated by a flexible film heater wrapped around two cells inside the module from the bottom third row. The experiments tested two types of extinguishing agents/systems: (i) 8.5 vol% design concentration $C_6F_{12}O$ (Novec1230) total flooding system upon activation of two smoke detectors about one minute after the first TR; and (ii) sprinkler water spray above the battery racks by four open nozzles with a uniform spray density of 20.4 L/min/m^2 upon activation of a standard response sprinkler link about 10 min after the first TR.

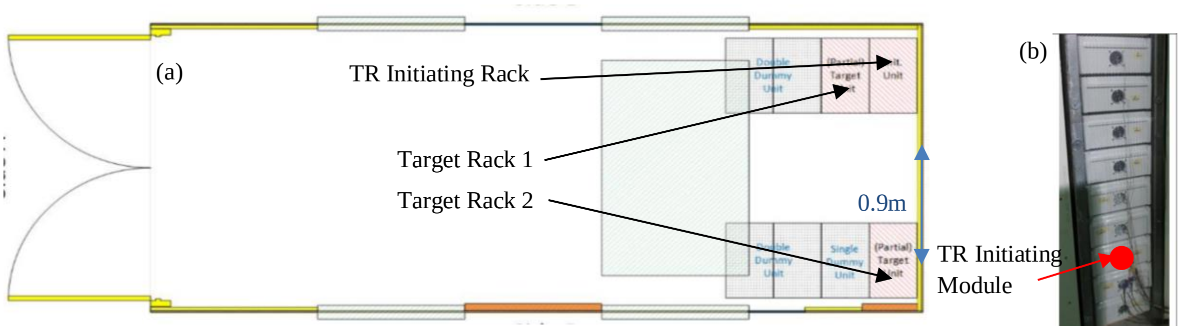


Figure 41 (a) Tested battery racks in an ISO container; and (b) Battery rack [116].

In the $C_6F_{12}O$ total flooding experiment, the suppression system was activated by the smoke detectors detecting the TR battery vent gases. However, TR propagation continued 7 min after the agent was completely discharged, followed by ignition and deflagration in the initiating rack. Eventually, TR propagated to all modules in the initiating rack and Target Rack 1 (shown in Figure 42), while no TR propagation impacted Target Rack 2 at 0.9m away.

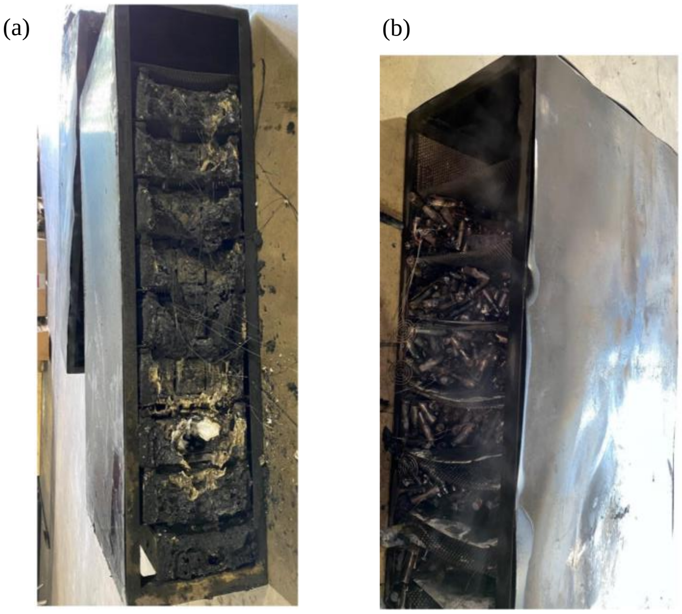


Figure 42 Aftermath of $C_6F_{12}O$ experiment (a) Target Rack 1; and (b) TR Initiating Rack [116].

In the sprinkler water spray experiment, the suppression system was turned on upon activating the sprinkler link by the ceiling jet of the fire plume about 10 min after the first TR. Within 5s, the visible flame was extinguished by the sprinkler. The suppression system remained operational for about 55 min. However, 8 min after the sprinkler operation stopped, TR propagation continued in the initiating rack and spread to Target Rack 1, but no further visible flame was reported. Eventually, seven of nine modules in the initiating rack and one of nine modules in Target Rack 1 experienced TR in the sprinkler water spray experiment, as shown in Figure 43.

Given that the experimental observation of both $C_6F_{12}O$ and sprinkler water spray experiments were terminated after approximately 3 hours from the first TR, the extent of rack damage in the sprinkler water spray experiment was much more moderated than the $C_6F_{12}O$ experiment.

Figure 43 Aftermath of sprinkler water spray experiment. Left: Target Rack 1 and Right: TR Initiating Rack [116].

Therefore, the study concluded that neither $C_6F_{12}O$ total flooding nor sprinkler water spray could prevent module-to-module TR propagation in the initiating rack because the agents could not deliver sufficient cooling to the deep-seated and encased battery cells. Sprinkler water spray performed much better than $C_6F_{12}O$ in preventing rack-to-rack TR propagation, as shown above. Furthermore, early and continuous operation of the sprinkler water spray could potentially inhibit rack-to-rack TR propagation.

4.5.2.3 White Paper: *“Fixed Firefighting Solutions for Stationary Energy Storage Systems”*

Rothe et al. [117] conducted rack-level experiments using LMO prismatic battery cells with 100% SOC. One TR initiating rack, two target racks (on the right and left of the initiating rack) and eleven dummy racks were placed in a standard container, as shown in Figure 44. The dimensions of each rack were approximately 0.6m(width) x 0.66m(depth) x 2m (height). Each rack housed seven battery modules arranged in seven rows of a single module. Two adjacent modules in the middle of the initiating rack contained eight LMO battery cells as the TR initiating modules. All other target modules in the initiating rack and target racks contained several cylindrical LIB cells (unknown chemistry and capacity) at the bottom of the module box and were filled with sand. TR was initiated by two special glow plugs (heating elements) attached to the cells in the LMO live module. The suppression systems / extinguishing agents tested in the experiments were HPWM (60 to 200 bar), N_2(g) (design concentration of 45.7% for 60 s) and aerosol (concentration of 100 g/m^3) systems. All of them were built according to manufacturers' requirements and triggered upon activating two detecting systems (i.e. aspirating smoke detectors and point detectors). The HPWM system operated for 30 min, and the holding time of N_2(g) and aerosol systems was also 30 min.

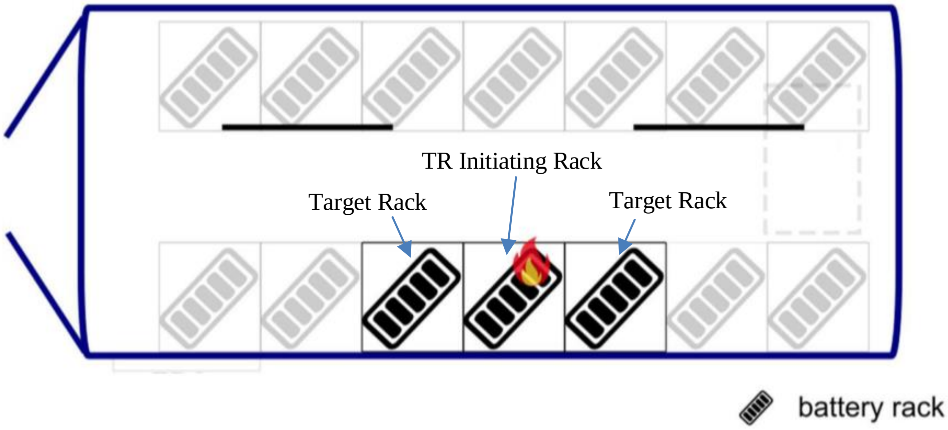


Figure 44 Placement of battery racks in a standard container [117].

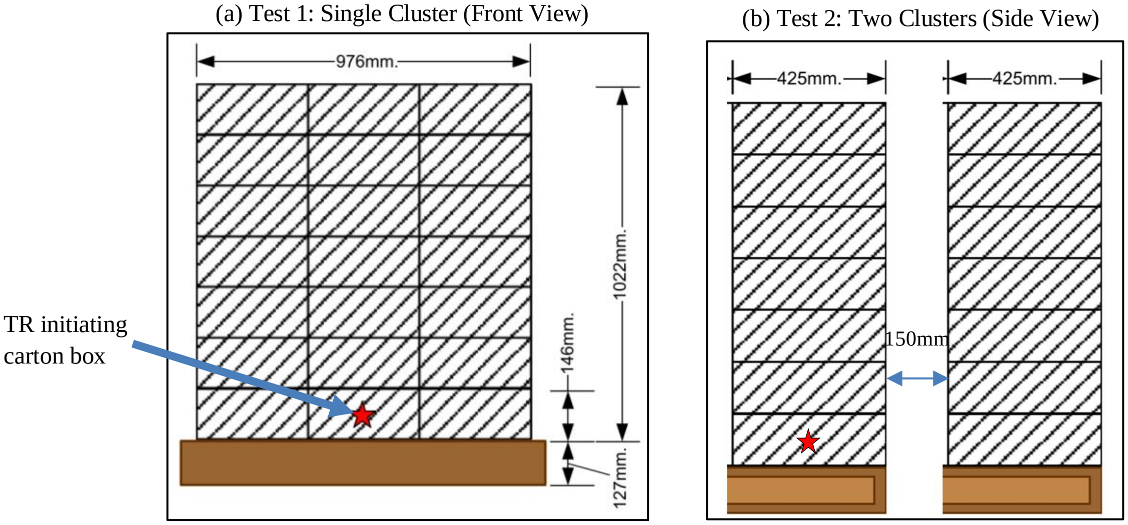
The study demonstrated that the HPWM exhibited the best cooling effect in slowing the cell-to-cell TR propagation in the initiating module (i.e. TR stopped at the last cell in the initiating module). For N_2(g) and aerosol systems, the cooling effect was limited as all cells in the initiating module were damaged by the TR. In all three experiments, all battery cells in the adjacent live module and target modules remained intact, except for the minor damage in the target modules under the aerosol system. From the experimental results, it appears that the module-to-module and rack-to-rack TR propagations in all three experiments were prevented, which differed from other rack-level experiments. This could probably be due to the early activation of the suppression systems by the more sensitive dual smoke detection systems in the experiments.

Nevertheless, the authors concluded from their experiments that HPWM showed the best cooling effect in tackling LIB fires, slowing down cell-to-cell TR propagation and preventing module-to-module and rack-to-rack TR propagation. N_2(g) and aerosol systems could stop the fire glow but deliver insufficient cooling to the batteries, in which the temperatures detected on the batteries and internal space of the container under the aerosol system were significantly higher than N_2(g) and HPWM.

4.6 Warehouse Storage Experiment

In the warehouse storage experiment, battery cells are densely packed in carton boxes with a certain amount of plastic dividers, which are stacked and stored in a warehouse environment. The experiments examine the efficacy of sprinkler suppression system only to investigate the extent of damaged battery cells in the fire, which the objective is different from module-to-module or rack-to-rack propagation in the above experiments. The literature review resulted in one technical report and one journal paper. These two publications were from the same institution (FM Global). The technical report by Ditch and Vries [65] in 2013 was inconclusive in establishing the effectiveness of the sprinkler system due to unfamiliarity with the LIB's fire behaviours when using the cartoned unexpanded plastic (CUP) commodity as a substitute testing material for LIB batteries. The experiment provided some good reference points for subsequent research, such as the specifications and ceiling height of the sprinkler heads and the estimated fire load and storage height of the stacked LIB carton boxes. Therefore, Ditch in 2016 & 2017 [118] conducted warehouse storage fire suppression experiments using real LIB cells. The tested battery cells were 20Ah pouch LFP cells with 50% SOC for long-term storage. Twenty battery cells were packed in each carton box and internally separated by nested polystyrene plastic dividers. The author indicated that in such a cartoned configuration, the batteries only contributed to 20% of the combustible loading, while the remaining 80% were from the plastic dividers and carton box.

The sprinkler heads installed at 12.2 m ceiling height were the quick-response type with an RTI of 27.6 $m^{1/2}s^{1/2}$, K-factor of 320 L/min/bar$^{1/2}$, activating temperature of 74°C and operating pressure of 2.4 bar. Two experimental setups of sprinkler suppression tests were conducted: (Test 1) a single cluster of 21 cartons arranged in three vertical stacks of seven carton boxes, as shown in Figure 45 [118]; and (Test 2) two such clusters facing each other, separated with a 150mm spacing. TR was initiated by a foil heater fixed to the cells within the carton box in the middle of the bottom level, as shown in Figure 45. Leaked liquid electrolytes were observed on the wetted exterior of the carton box as a sign of TR. However, the foil heater could not ignite the TR flammable content within the carton box until an external pilot flame was pushed against the carton box.


(a) Test 1: Single Cluster (Front View)

(b) Test 2: Two Clusters (Side View)

Figure 45 (a) Test 1: Single cluster of 21 carton boxes; and (b) Test 2: Repeat Test 1 with two such clusters [118].

The sprinkler systems were activated approximately 18 min after the surface burning started in Test 1 and approximately 8 min after the surface burning started in Test 2. The earlier sprinkler activation in Test 2 was due to the fire plume column created by the space between the two clusters. For both tests, fires were extinguished in 5 min.

In Test 1, the sprinkler discharge time was about 10 min. Approximately 30% of the battery cells were damaged during the fire upon the termination of the experiment without further investigation of re-ignition.

In Test 2, the sprinkler operation lasted for 20 mins. Fires re-ignited and re-grew after the stoppage of the sprinkler operation. Approximately 70% of the battery cells were damaged during the fire upon the termination of the experiment 15 min later.

The study concluded that there was insufficient air within the densely packed carton box to start the combustion of the TR battery cells. The initiation of the fire propagation for such settings requires an external ignition source. The sprinkler system could control a growing storage fire and a developed battery fire, while re-ignition remained as a major threat in such settings. A suggestion made by the author was to sufficiently pre-wet the surrounding carton boxes with the sprinkler system to prevent fire and TR propagation.

5 Discussion

This chapter aims to discuss and analyse the effectiveness of an extinguishing agent or a fire suppression system on LIB fires depending on different LIB configurations as well as the protection objectives in the actual field applications. The author also reflects on the uncertainties in his review methodology, experimental setups and interpretation of experimental results from literature reviews.

5.1 Effectiveness

The levels of battery configurations and choice of a dispersion mode on battery cells/modules/packs/racks will determine the inherent objective of a fire protection system to achieve its effectiveness in a LIB field application. For instance, the objective of a BESS rack-level installation could be reasonably set to prevent rack-to-rack TR propagation and reduce module-to-module TR propagation, but unrealistic to achieve mitigation of cell-to-cell TR propagation. Thus, if an extinguishing agent can meet the objective even without mitigating the cell-to-cell TR propagation, it will still be considered effective.

On the other hand, if an extinguishing agent is claimed to be effective without understanding the LIB configurations, it may fail the objective of fire protection in a field protection. For example, the AVD manufacturer [53] demonstrated AVD's effectiveness in flame extinguishment and TR mitigation by dispersing the AVD agent directly onto the exposed LIB cells. However, in a direct internal injection module-level independent experiment by RISE [102], the perforated sheets (mimicking dummy cells) were placed between the discharge nozzle and the TR cell. As a result, the AVD agent having a high viscosity took a long time to seep through the perforated sheets to reach the TR cell, leading to the interaction between the agent and the TR cell being significantly delayed.

Hence, effectiveness is discussed below according to different battery configurations. Comparisons among different levels of battery experiments are utilised to identify the potential use of appropriate extinguishing agents/suppression systems in field applications.

5.1.1 Comparison at Cell-Level

The cell-level is the most basic unit in a LIB battery system. At this level, extinguishing agents have direct contact with exposed TR battery cell(s) to suppress a battery fire and/or cool the cell(s). In general, all tested agents, including water-, gas-, powder-based and synergistic agents, were able to suppress the LIB-cell fires with a wide range of different chemistries (NMC, LFP, NCA, LCO, LNO) and capacities (1.2-300Ah) tested, except that the CO_2 agent could not suppress the cell fires of the higher capacity NMC batteries at 50Ah [119] and 94Ah [120].

However, different agents exhibited different cooling effects to slow or inhibit the cell-to-cell TR propagations. Although the absolute cooling effect of each agent could not be derived directly from different experiments due to different test conditions such as battery chemistries, capacities and experimental setups and test procedures, if a specific experiment compared the cooling effect of several agents and the same agents were also compared with other agents in other specific experiments, the relative cooling effects could still be ranked among different extinguishing agents. For example, in Experiment 1, Agent A performed better than Agent B. In Experiment 2, Agent B performed better than Agent C. Though

Agents A and C were not tested in the same experiment, Agent B is a common factor in bridging up Agents A and C. Hence, it is still possible to deduce that Agent A > Agent B > Agent C. Therefore, Table 9 below compares the surface cooling effect at the cell level and aims to deduce the ranking of surface cooling effects among different extinguishing agents at the cell-level.

Table 9 Comparison of surface cooling effect at the cell-level.

Reference	**Battery Tested**	**Comparison of Cooling Effect**
Zhang et al., 2023 [96]	LFP 1.2Ah	$N_2(l) > N_2(g)$
Yuan et al., 2022 [75]	LFP 15Ah	WM with 3% F500 additive > WM
Sun et al., 2022 [105]	NMC 117Ah	Water > $C_6F_{12}O$
Wang et al., 2022 [78]	NMC 2.6Ah	WM with additives > WM
Zhang et al., 2022 [71]	NCA 3.4Ah	$N_2(g)$+WM > $N_2(g)+C_6F_{12}O > N_2(g)$
Yuan et al., 2022 [79]	NCA 3Ah	WM with 3% F500 additive > WM
Liu et al., 2022 [80]	LFP/LCO/NMC 1.3-1.5Ah	WM with NaCl additive > WM
Zhao et al., 2021 [91]	NMC 2.6Ah	Water > ABC ultra-fine dry powder > BC ultra-fine dry powder > $C_6F_{12}O$
Guo et al., 2021 [73]	NMC 4Ah	WM > AVD
Wang et al., 2021 [82]	LFP 20Ah	WM with additives > WM
Wang et al., 2021 [121]	NMC 26Ah / 4.2Ah LFP 20Ah	AVD > $C_6F_{12}O$ > 2-BTP
Xu et al., 2020 [120]	NMC 94Ah	WM > CO_2
Liu et al., 2020 [72]	NMC 38Ah	WM+ $C_6F_{12}O$ > WM with additives > WM > $C_6F_{12}O$
Zhang et al., 2020 [70]	LFP 243Ah	WM+ $C_6F_{12}O$ > WM+ CO_2 > WM > $C_6F_{12}O$
Russo et al., 2018 [122]	LNO 20Ah	Water > Foam > WM > CO_2 > Dry Powder
Zhuang et al., 2018 [89]	LFP 30Ah	$CO_2 > N_2(g)$
Li et al., 2018 [84]	LFP 30Ah	WM with additives > WM
Wang et al., 2018 [119]	NMC 50Ah	$C_6F_{12}O > CO_2$
Luo et al., 2018 [86]	LFP 20Ah (50%SOC)	WM with additives > WM
Rao et al., 2015 [98]	LFP 100Ah	CO_2 > Superfine Powder
Maloney, 2014 [67]	Unknown chemistry 2.6Ah (50%SOC)	Water > AF31 > AF21 > Aqueous A-B-D > $C_6F_{12}O$ > Purple-K > FE36

Note: Unless otherwise stated, the battery cells tested are all 100% SOC.

From the comparative results, the ranking of the cooling effect can be deduced as follows:

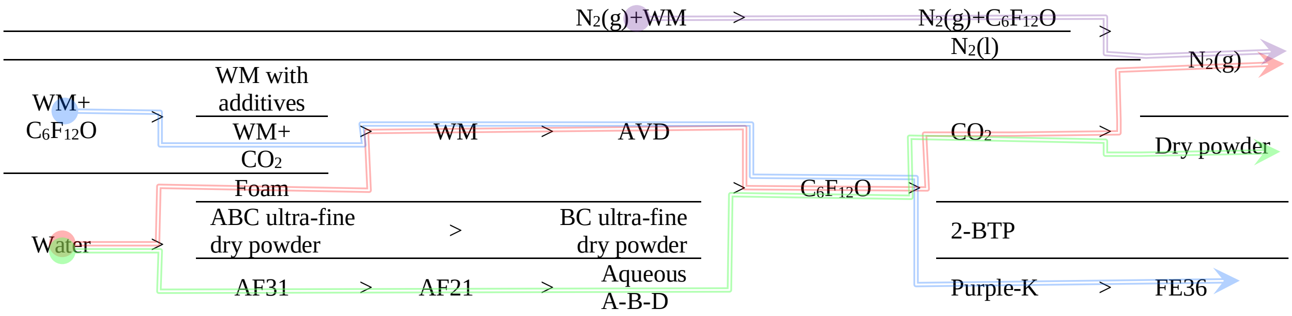


Figure 46 Ranking of the cooling effect of different extinguishing agents at the cell-level.

The order of higher cooling to lower cooling agents is from left to right and then forward, upward or downward as long they are not separated by black horizontal lines. Examples of interpreting Figure 46 are represented in red/blue/green/purple lines above. For the agents separated by the black lines, it means the comparative cooling effects among these agents were not experimented with. As can be seen in Figure 46, water-based agents generally exhibit better cooling performance than other agents for LIB-cell fires.

Furthermore, for battery cells with different chemistries at similar capacities, Liu et al. [80] conducted the WM and WM with NaCl additive experiments on cylindrical LFP (1.53Ah), NMC (1.45Ah) and LCO (1.33Ah) battery cells. They concluded that the extinguishing agents could cool a TR LFP more than NMC and LCO. Thus, LFP was easier to suppress than NMC and LCO at a similar capacity, while there is no apparent difference between NMC and LCO. Wang et al. [121] conducted AVD, $C_6F_{12}O$ and 2-BTP experiments on pouch NMC (26Ah) and LFP (20Ah) battery cells. The cooling effect on TR LFP was better than NMC. Therefore, the two comparative studies both concluded that LFP battery cell is safer than NMC.

The cell-level experiment could be considered the smallest-scale EV pack-level experiment. The outcomes derived from the cell-level experiments could provide useful background information that benefits research development at the EV pack-level, which has a similar mode of agent dispersion as the cell-level.

5.1.2 Comparison at Module-Level

At the module-level, multiple battery cells are housed in a battery module box. The extinguishing agents applied externally are hindered by the box casing, and the agents could either not, or only to a limited degree, penetrate the casing to reach TR battery cells. Thus, the flame extinguishment and cooling effect from the cell-level experiments could be compromised if the same extinguishing agents are applied at the module-level.

As deduced from the cell-level experiments, water-based agents have good flame extinguishment and cooling capabilities. The cell-level experiments with WM [123,124] and water spray [91,125] could suppress cell fires and mitigate cell-to-cell TR propagation. In contrast, even the high-performing water-based agents tested at the cell-level could not achieve similar performance at the module-level. From the module-level experiments by Juarez et al. [64], the battery module casing was made of plastic. WM could extinguish the external flame but could not stop cell-to-cell and module-to-module TR propagation. In another experiment by Andersson et al. [102], the battery module casing was made of steel. Sprinkler water, LPWM and HPWM all could not even penetrate the steel module casing to suppress the battery fire and stop cell-to-cell TR propagation within the module box. Thus, the materials used for battery module boxes, their combustibilities or water ingress protections will inevitably affect the performance of an extinguishing agent at the module-level.

The module-level experiment could be considered a reduced-scale rack-level experiment to reflect what could and could not be achieved at the BESS rack-level when an extinguishing agent is applied externally. Therefore, the main fire suppression objective in the module-level or BESS rack-level battery configurations should not be preventing cell-to-cell TR propagation but rather extinguishing the visible flames, slowing and preventing module-to-module / rack-to-rack TR propagation. Alternatively, if a battery module box can be designed with sufficient perforations (e.g., small holes, slots) to allow fine or gaseous extinguishing agents to penetrate through it, this could undoubtedly enhance the flame extinguishment and/or cooling effect on battery cells as what was presented in Siemens' experiment [50] in Section 4.3.4. However, such a design might compromise the integrity of dust ingress protection of a battery module, which requires design collaboration with LIBs' manufacturers.

5.1.3 Comparison at EV Pack-Level

Pack-level battery configuration is usually implemented on electric vehicles. Multiple large battery cells or modules containing smaller cells are housed in a large battery cabinet. The battery cabinets are located in the different parts of an electric vehicle, depending on the manufacturer's design. Typically, up to 13 L of extinguishing agent could be installed in a heavy vehicle such as an electric bus [108], but need to be much smaller if applied to smaller vehicles such as electric cars. If an external fire suppression system is applied over a battery pack cabinet, even the high-performing water-based agents can only extinguish the external flame but not contribute to any internal cooling due to little or no penetration of the extinguishing agent into the relatively enclosed battery pack [108]. This phenomenon is similar to the module-level experiments. Thus, most pack-level experiments from the literature review focused on the direct internal injection of extinguishing agents into the battery pack cabinets (similar to the cell-level experiments but with more densely packed batteries). The extinguishing agents could gain more direct contact with the affected batteries to slow down and prevent internal TR propagation.

Following the literature review results presented in Sections 4.3.6 and 4.4, the tested batteries included prismatic NMC and LFP with capacities ranging from 20 to 271Ah, with extinguishing agents including $C_6F_{12}O$, water spray, water spray with 5% foam additive and WM with 5% foam additive, Class A foam, Class F foam, CAFS foam, N_2(g) and AVD [102–108]. Among these, all direct injecting agents could extinguish the visible flames quickly, except for the high-expansion CAFS foam, which was too light and repelled by the TR battery vent gas [102] and the high-viscosity AVD took a long time to reach the TR battery [102]. Regarding the cooling effect to curb the internal TR propagation, N_2(g) had a minimal internal cooling effect [102] and the internal cooling performance of $C_6F_{12}O$ was not guaranteed because the prevention of TR propagation failed in two of three experiments [104,105]. All water-based agents tested, excluding high-expansion foam, exhibited their cooling effect to curb the internal TR propagation. WM with 5% foam performed slightly better than water spray with 5% foam in terms of cooling rate [108]. The internal cooling performance among water spray, Class A foam, Class F foam and low-expansion CAFS foam were similar [102]. The cooling effect of various extinguishing agents derived from the pack-level experiments generally aligns with the cell-level comparison discussed in Section 5.1.1. Therefore, presently, water-based agents with direct internal injection systems, especially WM with 5% foam additive, could be a more viable implementation for electric buses. Furthermore, those novel combinations of extinguishing agents explored at cell-level experiments with an enhanced cooling performance require future large-scale pack-level experiments to prove their effectiveness, such as WM+$C_6F_{12}O$, WM+CO_2, WM+N_2(g), $C_6F_{12}O$+N_2(g), $C_6F_{12}O$+$C_5H_3F_7$, N_2(l) and AASD composited ABC dry powder. If any of these novel combinations of agents could achieve lesser carrying capacities of suppressants onboard electric vehicles for a desirable fire suppression performance, it will benefit the future development of electric buses and cars.

5.1.4 Comparison at BESS Rack-Level

The battery configuration at the rack-level is typically implemented in a battery energy storage system. Many battery racks mounted with densely stacked battery modules are lined up in rows in a system room or container. Thus, a fixed fire suppression system provided for BESS also typically protects the entire BESS space (i.e. total flooding), and the design of such a system shall evenly cover the entire room/container space. At this level, the reach of the extinguishing agents to a fire load is even more challenging due to more layers of hindrance by the rack cabinet as well as the stacking battery modules.

The total battery capacity at the rack-level is also much higher, which increases the fire hazards drastically. Alternatively, a direct internal injection could be considered, similar to the EV pack-level application.

From the literature reviews, the majority of the rack-level experiments were conducted with total flooding systems, except for one experiment using direct internal injection. The tested fixed suppression systems / extinguishing agents in the total flooding were sprinkler system (water and additives), HPWM system (water), LPWM system (water and additives), Novec1230 system ($C_6F_{12}O$), inert gas system (IG541 and N_2), aerosol system (fine alkaline-salt particles), and AVD system (semi-total flooding covering the front face of the rack only). The objective of the total flooding system is not to prevent cell-to-cell TR propagation in a fire module but to prevent module-to-module and/or rack-to-rack TR propagation. One experiment used a direct internal injection system with water spray and CAFS foam aimed at mitigating cell-to-cell TR propagation. A comparison of BESS rack-level experiments is shown in Table 10.

Table 10 Comparison of BESS rack-level experiments.

Reference	Battery Chemistry	Suppression System	Extinguishing Agent	Flame Extinguishment	Cell TR Propagation Mitigation	Module TR Propagation Mitigation	Rack TR Propagation Mitigation
Zhang et al. [109]	LFP	Total Flooding	$C_6F_{12}O$	Yes	To a certain extent	Yes	Not Applicable
Gully et al. [110]	NMC	Total Flooding	$C_6F_{12}O$	Yes	No	No	Not Applicable
			HPWM	Yes	No	Yes, similar module surface cooling effect between HPWM and sprinkler	
			Sprinkler water	No	No		
		Direct Internal Injection	Water spray	Yes	To a certain extent	Yes, better than HPWM and sprinkler	
			CAFS	Yes	To a certain extent		
Bisschop et al. [36]	LFP and NMC	Total Flooding	LPWM	No	No	1. All agents to a certain extent. 2. IG541 performed best in flame extinguishment. 3. Agents with additives and AVD were a little better. 4. LFP was easier to be cooled than NMC. 5. Module surface cooling effect of LPWM and water were very similar.	Not Applicable
			LPWM with 3% F500	No	No		
			Sprinkler water	No	No		
			Sprinkler water with 3% F500	No	No		
			Inergen gas IG541	Yes	No		
		Local external dispersion (Semi-total flooding)	Water spray	No	No		
			AVD	No	No		
Ditch and Zeng [112] Long and Misera [113]	Total Flooding	LFP and NMC	Sprinkler water	No	No	No	Yes for LFP; No for NMC
Barowy et al. [116]	Total Flooding	NCA	$C_6F_{12}O$	No	No	No	No for the adjacent rack; Yes for

							the rack separated at 0.9m away
			Sprinkler water	No	No	No	Slight propagation to the adjacent rack. Yes for the rack separated at 0.9m away
Rothe et al. [117]	Total Flooding	LMO	HPWM	Yes	Slight effect	Yes	Yes
			N_2(g)	Yes	No	Yes	Yes
			Aerosol	Yes	No	Slight propagation	Slight propagation

Some of the rack-level experiments above give different outcomes even though the same extinguishing agent was used. This is probably because of the different experimental setups, testing procedures and battery chemistries/capacities. When using $C_6F_{12}O$, Zhang et al. [109] could achieve flame extinguishment and mitigate cell and module TR propagation. However, this is totally opposite in Barowy et al.'s experiment [116] and partially true in Gully et al.'s experiment [110]. Some possible reasons are (i) Zhang et al. [109] did not mount the battery cells in an enclosed battery module box, and the agent could reach the partially exposed TR battery cells; (ii) Barowy et al. [116] used all live battery modules without dummy modules in their experiment leading to a much higher energy capacity and fire load.

When using sprinkler, it is generally true that it could not fully suppress the visible flame and prevent cell TR propagation (due to the inability to reach the deep-seated fire and TR cells), but it could reduce fire intensity and provide a certain cooling effect. Whether the sprinkler can mitigate module and/or rack TR propagation also depends on the battery chemistries and capacities. For instance, LFP (120Ah/module) is easier to be cooled than NMC (130Ah/module) [112,113], and NCA (891Ah/module) is much harder to be cooled [116].

Comparing water-based agents in total flooding systems, HPWM is more effective than LPWM and sprinkler in flame extinguishment. The module surface cooling effects are similar among HPWM, LPWM and sprinkler, which could mitigate module/rack TR propagation to a certain extent. Bisschop et al.'s experiment [36] also demonstrated that water-based agents with additives (F500 and AVD) exhibit a slightly improved cooling effect.

Rothe et al.'s experiment [117] was a bit unique compared with other experiments, as they used very sensitive smoke detection systems to activate the agents, i.e. the agents were discharged early upon detecting TR battery vent gases. Flame extinguishment, module and rack TR propagation were significantly mitigated by all three test agents (HPWM, N_2(g) and Aerosol).

Besides the total flooding dispersion, Gully et al. [110] also conducted experiments with direct internal injection into battery modules (similar to the EV pack-level approach). When an agent can get into the battery cells, the performance of flame extinguishment and cooling is enhanced and better than the total flooding.

To summarize, some tentative conclusions can be derived from these BESS rack-level experiments:

(i) An extinguishing agent using direct internal injection or acting on exposed battery cells is more effective in flame extinguishment and TR mitigation than a total flooding system. An extinguishing agent can be effective in flame extinguishment and cooling to inhibit TR propagation if the agent can reach a deep-seated fire and have sufficient contact with battery cells, for example, direct agent dispersion in cell-level experiments and direct internal injection in EV pack-level experiments and a few BESS rack-level experiments. However, as compared with the most BESS rack-level (total flooding) experiments, if the access of the same extinguishing agent to the encased battery cells is hindered by a battery module box or a rack cabinet, the agent cannot achieve a similar flame extinguishment and cooling performance as good as in the cell-level and EV pack-level experiments.

(ii) Among water-based agents, HPWM is more effective in flame extinguishment. The module surface cooling effect of the tested water-based agents are similar and slightly better when additives are used.

(iii) $C_6F_{12}O$, IG541, N_2(g), HPMW and aerosol are generally effective in flame extinguishment, in which $C_6F_{12}O$ and over-designed inert gases can extinguish the flame quicker than HPWM. However, the long-term cooling effects of gas-based agents and aerosol are relatively poorer than those water-based agents. Therefore, gas-based agents and aerosol alone may not be suitable for TR mitigation. This matches 3M's declaration [52] that Novec1230 ($C_6F_{12}O$) *"cannot stop thermal runaway once initiated"* and Inergen's declaration [126] that IG541 *"cannot control thermal runaway in batteries"*. Therefore, DNV [101] suggests that gas-based suppression or aerosol systems are to be backed up by a water-based suppression system for better extinguishment and cooling effects. Some ships using LIB ESS as a power supply to the propulsion systems were already equipped with the aerosol system to protect BESS onboard and backed up with an additional water-based suppression system [36].

(iv) The effectiveness of suppression systems/extinguishing agents also depends on battery chemistries and capacities, as well as an appropriate separation distance between racks.

(v) A sensitive smoke detection system enabling early activation of extinguishing agents enhances the effectiveness of suppression systems.

5.2 Uncertainty

As no actual LIB fire suppression experiments have been conducted by the author, the results and discussions presented in the thesis are based on the author's interpretation of the available published experimental results according to the author's best knowledge. In this subsection, the author reflects on uncertainties in his literature review methodology, experimental set-up, test procedures, interpretation of experimental results and conclusions. Some suggestions are made to address the uncertainties but will not be implemented in this thesis.

5.2.1 Uncertainty in Literature Review Methodology

A sizable number of journal and conference papers were obtained through Scopus and Web of Science. Around 60% of the publications were first filtered away through the title screening, and the next 20% were filtered away through the abstract screening. However, the author did the screenings individually based on his own discretion, according to his best knowledge. There might be uncertainty in that he might have filtered away some relevant publications. Thus, this will be an area of improvement if a peer can participate in the screenings to close the gap.

Nevertheless, the author still had a certain confidence in his methodology through citation searching (or backward snowballing) when the detailed assessment was carried out on the remaining 20% chosen publications. A small number of additional publications, including relevant technical reports and white papers (not published in any journals), were then added to the detailed assessment.

5.2.2 Uncertainty in Experimental Setup

As there is no formal terminology to categorise the experimental setup into different levels of battery configurations, the author assessed and interpreted the experimental descriptions and figures in each publication and categorised them into cell-, module-, EV pack- and rack-level and warehouse storage experiments to best describe the consolidated data from the literature review. A reader should note that there are other terminologies of battery configurations in a LIB battery system seen in various publications, such as string, array and installation, which may or may not be interchangeable with what the author defined in the thesis. Thus, it should always refer to the definitions stated in Section 4.1.

For the module-level experiments and above, most publications do not explicitly state whether the battery module boxes used in the experiments were combustible or non-combustible and what the percentages of openings of module boxes or rack cabinets are. Such differences will affect the penetration of extinguishing agents onto the battery cells, thus influencing the effectiveness of extinguishing agents. In addition, in the single-rack experiments, only one live module was used. Thermocouples were attached to the adjacent non-combustible dummy modules to examine TR propagation. However, such an experimental setup did not take into consideration of the battery thermal reaction of the adjacent modules if live battery cells were also used in the adjacent modules, which might underestimate the TR propagation. At least two live adjacent battery modules should probably be used in the experiment for a more realistic result.

Ideally, these uncertainties can be addressed by clarifying the details with the original authors of the publications. Nevertheless, it is expected that convincing them to spend extra time and effort to provide more detailed information will be difficult.

5.2.3 Uncertainty in Interpretation of Experimental Results and Conclusions

Interpretation of experimental results largely depends on the test procedures, which include (i) the moment an extinguishing agent is triggered; (ii) the duration of an agent acting on batteries; and (iii) the length of post-fire observation. For example, if an agent is triggered early, it will be more effective in flame extinguishment. If the duration of agent discharge is long enough, it will be more efficient in cooling. If the length of post-fire observation is not long enough, one may not conclude the mitigation of TR propagation accurately because of the inherent nature of the LIB's internal thermal reaction, which may take hours or days to re-ignite.

These test procedures are different from one experiment to another, and incomplete information is provided in some publications. The author tried to extract the available information for *(i)* and *(ii)*. However, *(iii)* is not mentioned explicitly in most publications. The author did not differentiate the effectiveness in mitigating TR propagation by evaluating the length of post-fire observation but directly took the written conclusions from the original publications. The uncertainty in this aspect is difficult to address because there is no formal test method providing specific guidance to ensure a consistent length of post-fire observation to define the successful mitigation of TR propagation.

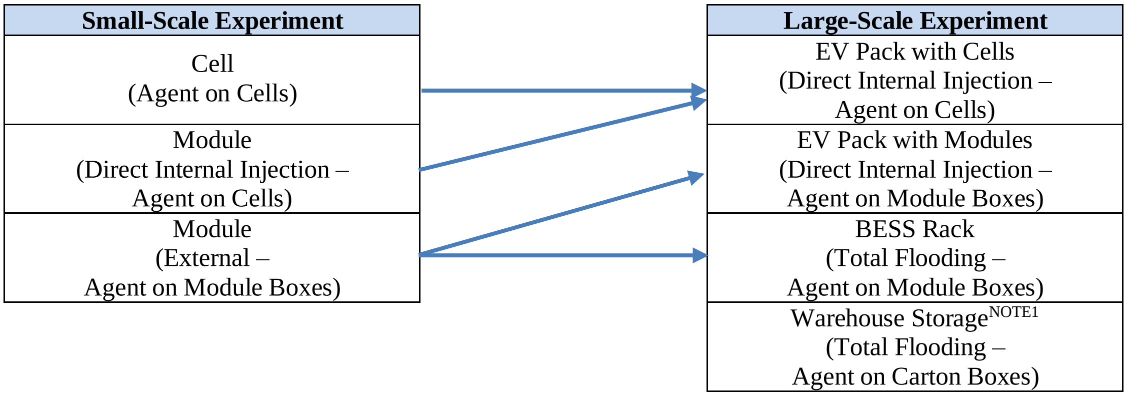
Therefore, the absolute effectiveness of an extinguishing agent in cell-level experiments could not be derived directly due to these uncertainties of test procedures. Instead, the author adopted the relative comparisons (refer to Section 5.1.1 on how this was derived) to rank the cooling efficiency of different extinguishing agents when the test procedures in a specific experiment were the same. This comparison approach was also adopted in the discussions for module-, EV pack- and BESS rack-level experiments.

Separately, a reader should also note that the thesis does not discuss another key aspect of the effectiveness of an extinguishing agent in a LIB fire, which is the ability to absorb explosive and toxic gases. This requires additional review to supplement the current one.

6 Conclusions

A systematic literature review of fire suppression of lithium-ion batteries was conducted, and a total of 85 relevant publications across the past ten years (2013 to March 2023) were evaluated in the thesis.

The experimental results from the past publications were categorised into cell-, module-, EV pack- and BESS rack-level and warehouse storage experiments according to different battery configurations. It is worth mentioning that no previously published review utilised such an approach to clearly present the effect of fire suppression systems/extinguishment agents based on LIB configurations. An extinguishing agent can be effective in flame extinguishment and mitigation of TR propagation in cell-level experiments because it acts on the exposed LIB cells to maximise its effectiveness. This is considered a small-scale experiment. However, in a LIB battery system, the battery configurations are not simply bare LIB cells but in a larger scale. The cells hindered by the module boxes, pack cabinets or rack cabinets are not directly exposed or have limited exposure to extinguishing agents, impacting the effectiveness of extinguishing agents. Thus, the results from a small-scale experiment cannot be directly applied to a LIB battery system without understanding the mode of agent dispersion and battery configurations. Some relevancy between small-scale and large-scale experiments derived from the review is illustrated in Figure 47, showing the applicability between them.



NOTE1: The warehouse storage experiment is unique by itself because about 80% of the fire load comes from carton boxes and internal plastic dividers, and only 20% is from LIB cells. The LIB fire hazard in the warehouse storage setting is similar to the fire hazard of the cartoned unexpanded plastic, except for the special consideration of TR propagation.

Figure 47 Applicability of small-scale experiments for large-scale experiments.

Until March 2023, about 67% of the publications focused on cell-level and 9% on module-level experiments. Figure 47 links the applicability of a small-scale experiment to a large-scale experiment. The outcomes derived from an applicable small-scale experiment could provide a useful reference point and background information for research development of the large-scale experiment and also potential cost and time savings based on the lessons learnt from the small-scale experiments to avoid failed experiments at the large-scale.

Regarding the types of extinguishing agents for LIB fires, more than 20 agents comprising water-, gas-, powder-based and synergistic agents are found from past research (refer to Figure 22). They possess one or more of the following fire suppression properties: surface cooling, gas cooling, flame cooling (reducing adiabatic flame temperature), suffocating (diluting oxygen concentration), inhibiting combustion chemical reaction and smothering (separating the fuel from the air). Generally, water-based agents exhibit a better overall cooling effect to slow down or mitigate TR propagation than gas-based and power-based agents at all levels of experiments. Gas-based and ultrafine powder (aerosol) agents have a quicker extinguishment capability of visible flame but give poorer overall cooling, mainly because they lack a surface cooling effect compared with water-based agents in which surface cooling plays a vital role in the mitigation of TR propagation in cells, modules, packs or racks. Synergistic agents are found to be more effective than any single participating agents in cell-level experiments, but they have yet to be tested in large-scale experiments.

There are two agent dispersion modes in large-scale experiments: direct internal injection and total flooding. The experiments demonstrate that direct internal injection is more effective in flame extinguishment and mitigation of TR propagation than total flooding system mainly because of the direct contact of extinguishing agents with battery cells or modules with little hindrance. The tight space within a battery box or cabinet also increases the volume percentage concentration of the directly injected agents. Generally, most EV pack-level experiments used a direct internal injection system, which better suits the installation on electric vehicles. Most BESS rack-level experiments used a total flooding system, mainly protecting adjacent racks and BESS room/container with a bonus to slow down or mitigate module TR propagation. Key findings from the large-scale experiments are as follows:

a) From EV pack-level experiments, water-based agents (water spray, water spray with foam additive, WM with foam additive, Class A foam, Class F foam, low-expansion CAFS foam, AVD) and gas-based agents (N_2 and $C_6F_{12}O$) were tested using direct internal injection systems. All tested agents could extinguish the visible flames quickly, except for the high-viscosity AVD which took a bit longer. Ranking of the cooling effect for internal TR propagation within the battery pack from high to low is derived as follows:

WM with foam additive > Water Spray with foam additive > [Water spray; Class A foam; Class F foam, low-expansion CAFS foam] > $C_6F_{12}O$ *>* N_2(g)

b) From BESS rack-level experiments, water-based agents (HPWM, LPWM, LPWM with additive, sprinkler water, sprinkler water with additive, water spray and AVD), gas-based agents (IG541, N_2, and $C_6F_{12}O$) and powder-based agent (aerosol) were tested using total flooding systems. Gas-based agents, aerosol and HPWM could extinguish the visible flames outside the battery modules or racks, but other water-based agents could not. However, gas- and powder-based agents were poorer than water-based agents in the surface cooling of battery modules or racks. Thus, gas-based agents and aerosol alone may not be suitable for TR mitigation for modules and racks. All water-based agents had similar cooling effects, and those with additives performed slightly better.

Overall, HPWM with additives appears to be the best-performing suppression system/extinguishing agent for BESS rack-level installation since it both suppresses the flame and provides surface and gas cooling. If gas-based or aerosol suppression systems are used, it is suggested to be backed up by a water-based suppression system for better flame extinguishment and cooling.

c) The effectiveness of suppression systems/extinguishing agents also depends on battery chemistries and capacities.

> *An LFP LIB fire is easier to be suppressed and cooled than NMC and LCO (based on what had been tested and compared).*
>
> *A LIB with higher capacity also comes with a higher fire load, making its fire more difficult to be suppressed and cooled. Thus, the volume of extinguishing agents should increase correspondingly with an increased battery capacity.*

d) Early activation of suppression systems enhances the effectiveness of flame extinguishment and the ease of mitigation of TR propagation.

> *Having a sensitive smoke detection system and/or a good battery thermal management system to detect the early stage of TR increases the effectiveness of the suppression system.*

7 Future Research

Research development of LIB fire suppression systems / extinguishing agents is still ongoing. At the end of the report, some potential areas are suggested for future research, derived from the systematic literature review.

a) In the most recent cell-level experiments, several agents were combined (WM+$C_6F_{12}O$, WM+CO_2, WM+N_2(g), $C_6F_{12}O$+N_2(g), $C_6F_{12}O$+$C_5H_3F_7$, N_2(l) and AASD composited ABC dry powder) to provide two or more fire suppression working mechanisms (refer to Figure 13 and Table 5). However, their effectiveness in large-scale installations has not yet been proven. Thus, EV pack-level and BESS rack-level experiments using these novel combinations of agents are suggested for future research, aiming to improve the agents' performance in flame extinguishment and cooling and reduce the volume required of suppressants. The latter is important to support the future development of electric vehicles, particularly electric cars, by having a more efficient suppressant with EV-compatible carrying capacity to maximise the usable space onboard.

b) Direct internal injection of extinguishing agents has been proven more effective for LIB fires than the total flooding system or external agent dispersion in most EV pack-level experiments and a few BESS rack-level experiments. Therefore, researchers may consider collaborating with LIB battery system manufacturers to conduct rack-level experiments by integrating the direct internal injection system with battery modules and racks. The total flooding system could still be a backup or extend its discharge nozzles into the battery modules and racks.

   Direct internal injection in a large-scale installation also requires the integration of the agent discharge pipeworks and nozzles within the battery racks, packs or modules and interlink with the built-in fire and gas detectors, which pinpoint the location of TR modules or cells. In addition, the battery modules or cells should also be physically partitioned into different zones to achieve proper coverage when the direct internal injection is triggered.

c) Lastly, only one publication was found to test the effectiveness of $C_6F_{12}O$ extinguishing agent under extreme ambient temperatures at -40^oC and 85^oC [103]. An operable fire suppression system and extinguishing agent under extreme temperatures is vital for mobile electric vehicles under different climate conditions in four seasons. Thus, when conducting an EV-related fire suppression experiment, the boiling and freezing points of an extinguishing agent shall be carefully considered to ensure the performance of the extinguishing agent is not compromised during extremely hot and cold climates.

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Finally, I want to dedicate the thesis to my family, especially my spouse, for their unwavering support throughout the program. The encouragement, patience, understanding and love I received made it possible for me to complete this program successfully.

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Appendix A Search Strings for Scopus and Web of Science

Search results as of 26 March 2023:

<u>1st Attempt</u>

Scopus (n_{1a}=78):
(TITLE-ABS-KEY(lithium-ion) OR TITLE-ABS-KEY(li-ion)) AND TITLE-ABS-KEY(batter*) AND TITLE-ABS-KEY(fire) AND TITLE-ABS-KEY(suppression)

Web of Science (n_{1b}=67):
(TS=(lithium-ion) OR TS=(li-ion)) AND TS=(batter*) AND TS=(fire) AND TS=(suppression)

<u>2nd Attempt</u>

Scopus (n_{2a}=381):
(TITLE-ABS-KEY(lithium-ion) OR TITLE-ABS-KEY(li-ion) OR TITLE-ABS-KEY(lib)) AND TITLE-ABS-KEY(batter*) AND (TITLE-ABS-KEY(fire*) OR TITLE-ABS-KEY(flame*)) AND (TITLE-ABS-KEY(suppress*) OR TITLE-ABS-KEY(extinguish*) OR TITLE-ABS-KEY(mitigat*))

Web of Science (n_{2b}=403):
((TS=(lithium-ion) OR TS=(li-ion) OR TS=(lib)) AND TS=(batter*) AND (TS=(fire*) OR TS=(flame*)) AND (TS=(suppress*) OR TS=(extinguish*) OR TS=(mitigat*))

<u>3rd Attempt</u>

Scopus (n_{3a}=328)
((TITLE-ABS-KEY(lithium-ion) OR TITLE-ABS-KEY(li-ion) OR TITLE-ABS-KEY(lib)) AND TITLE-ABS-KEY(batter*) AND (TITLE-ABS-KEY(fire*) OR TITLE-ABS-KEY(flame*)) AND (TITLE-ABS-KEY(suppress*) OR TITLE-ABS-KEY(extinguish*) OR TITLE-ABS-KEY(mitigat*))) AND (EXCLUDE(EXACTKEYWORD, "Lithium Metal Battery"))

Web of Science (n_{3b}=325):
((TS=(lithium-ion) OR TS=(li-ion) OR TS=(lib)) AND TS=(batter*) AND (TS=(fire*) OR TS=(flame*)) AND (TS=(suppress*) OR TS=(extinguish*) OR TS=(mitigat*)) NOT TS=(metal))

Appendix B1 Selected Publications – Reviewed-Based

S/N	Reference		Article Title	Country
1	Conzen et al., 2023	[127]	*“Lithium ion battery energy storage systems (BESS) hazards”*	USA
2	Sebastian, 2022	[128]	*“A review of fire mitigation methods for li-ion battery energy storage system”*	USA
3	Zhang et al., 2022	[129]	*“A review of fire-extinguishing agents and fire suppression strategies for lithium-ion batteries fire”*	China
4	Zhang et al., 2022	[130]	*“A Review on Fire Research of Electric Power Grids of China: State-Of-The-Art and New Insights”*	China
5	Qiu & Jiang, 2022	[131]	*“A review on passive and active strategies of enhancing the safety of lithium-ion batteries”*	China
6	Snyder & Theis, 2022	[132]	*“Understanding and managing hazards of lithium-ion battery systems”*	USA
7	Yuan et al., 2021	[133]	*“A review of fire-extinguishing agent on suppressing lithium-ion batteries fire”*	China
8	Sun et al., 2021	[134]	*“Progress on the research of fire behavior and fire protection of lithium ion battery”*	China
9	Cui & Liu, 2021	[135]	*“Research progress of water mist fire extinguishing technology and its application in battery fires”*	China
10	Li et al., 2021	[136]	*“Research progress on fire protection technology of containerized Li-ion battery energy storage system”*	China
11	Sun et al., 2020	[137]	*“A review of battery fires in electric vehicles”*	China & Sweden
12	Ghiji et al., 2020	[35]	*“A review of lithium-ion battery fire suppression”*	Australia
13	Chombo & Laoonual, 2020	[138]	*“A review of safety strategies of a Li-ion battery”*	Thailand
14	Diaz et al., 2020	[139]	*“Meta-review of fire safety of lithium-ion batteries: Industry challenges and research contributions”*	UK
15	Wang et al., 2019	[140]	*“A review of lithium ion battery failure mechanisms and fire prevention strategies”*	China
16	Kong et al., 2018	[141]	*“Li-ion battery fire hazards and safety strategies”*	USA & China
17	Ingram, 2013	[142]	*“Lithium-ion batteries: A potential fire hazard”*	USA
Citation Search				
18	Hill, 2020	[143]	*“McMicken battery energy storage system event technical analysis and recommendations”*	USA
19	Wilkens et al., 2017	[144]	*“Assessment of existing fire protection strategies and recommendation for future work”*	Denmark
20	Warner, 2017	[145]	*“Overview of a year of battery fire testing by DNV GL”*	USA

Appendix B2

Appendix B2 Selected Publications – Experimental-Based

Note: 1. Unless otherwise stated, experiments with single-cell or multiple-cells bundled in the table below are directly exposed to the extinguishing agents. 2. Battery used for experiments are with 100% state-of-charge (SOC) unless otherwise stated. Comparison of the suppression efficacy of different SOCs is not discussed in the thesis.

S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
2023							
1	Li et al.	[100]	Cylindrical 3.5Ah NMC	Two cells bundled in an explosion-proof box	Aluminium ammonium sulfate dodecahydrate (AASD) composited ABC dry powder	China	AASD has high heat absorbing capacity (10 times higher than Novec1230). It can extinguish LIB fire and suppress thermal runaway propagation.
2	Zhang et al.	[68]	Cylindrical 4Ah NMC	Three cells bundled in an explosion-proof tank	Intermittent water spray	China	Duty cycles and spray time are proposed for the intermittent water spray, which can extinguish the fire, accelerate the cooling and prevent thermal runaway (TR) propagation.
3	Zhang et al.	[96]	Cylindrical 1.2Ah LFP	Single-cell in an accelerating rate calorimeter chamber	1. N_2(g); 2. Liquid N_2	USA	Both N_2(g) (slow cooling) and liquid N_2 (fast cooling) can mitigate TR by setting the activation temperature at 130°C. No visible flame is involved in the experiment.
4	Liang et al.	[103]	Prismatic 271Ah LFP	EV Pack-Level: A standard electric bus battery box containing 7 live cells and 26 dummy cells	$C_6F_{12}O$ gas discharge into the battery box	China	$C_6F_{12}O$ can extinguish the fire and prevent thermal runaway propagation. The temperature of the adjacent batteries does not exceed 90°C within 30mins after the fire is extinguished and no re-ignition is observed. $C_6F_{12}O$'s performance is affected by the extreme ambient temperatures at -40°C and 85°C. Details are also presented in Chapter 4.
5	Cao et al.	[92]	Cylindrical 3.5Ah NMC	Single-cell in an open space without an enclosure	Liquid N_2	China	Liquid N_2 exhibits a superior cooling effect, drastically reducing the surface temperature of a thermal runaway battery to -170°C. Thus, it can effectively extinguish the fire and inhibit the thermal runaway of LIBs.
6	Rothe et al. (White paper from citation search)	[117]	Prismatic 40Ah LMO and Cylindrical cells	BESS Rack-Level: Three live battery racks and 11 dummy racks in a 20' sea container	1. HPWM fixed firefighting system (FFS) 2. N_2(g) FFS 3. Aerosol FFS	Germany	Details are presented in Chapter 4.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
2022							
7	Yuan et al.	[75]	Cylindrical 15Ah LFP	Three cells bundled in a cuboid combustion chamber	1. WM with 3% F-500 additive 2. WM	China	WM can extinguish the fire but cannot stop TR propagation. WM with F-500 additive can both extinguish the fire and stop TR propagation. The cooling capacity of WM with F-500 additive is estimated 3 times of pure WM.
8	Han et al.	[104]	Prismatic 24Ah LFP	EV Pack-Level: A standard electric bus battery box contains 9 modules and 28 cells in each module, for a total of 252 cells.	FK-5-1-12 ($C_6F_{12}O$) gas discharge into the battery box	China	The cooling effect of $C_6F_{12}O$ gas increases with more $C_6F_{12}O$ gas being released into the battery box. $C_6F_{12}O$ gas can extinguish the fire but cannot completely inhibit the TR propagation in this experiment. Details are also presented in Chapter 4.
9	Zhang et al.	[146]	Cylindrical 4Ah NMC	Single-cell in an explosion-proof tank	Intermittent water spray	China	Intermittent water spray can extinguish the fire and has a higher water utilisation frequency and a better cooling effect than continuous spray. The paper compares the efficacy of short-pulse and long-pulse sprays but does not report if the intermittent water spray can effectively stop the TR.
10	Meng et al.	[69]	Cylindrical 14Ah LFP	Single-cell in an ISO9705 full-scale room	Intermittent $C_6F_{12}O$ gas spray	China	The intermittent $C_6F_{12}O$ spray extinguishes the fire successfully, lengthens the low-temperature duration and decreases the rate of temperature rise after the agent is exhausted. For the tested 14 Ah LFP battery, the optimal duty cycle of 55.4% for the intermittent spray is proposed to achieve the best suppression and cooling effect.
11	Sun et al.	[105]	Prismatic 117Ah NMC	EV Pack-Level: Two cells in an EV battery module box	1. $C_6F_{12}O$ gas 2. Water spray 3. HFC-227ea (not discussed in this thesis) Agents are discharged into the battery module box	China	$C_6F_{12}O$ gas cannot prevent TR propagation but prolong the TR propagation by decreasing the battery temperature and reducing the heat transfer. Water spray achieves a better cooling effect and prevents TR propagation. Details are also presented in Chapter 4.
12	Zhang et al.	[109]	Prismatic 273Ah LFP	BESS Rack-Level: A battery rack in	$C_6F_{12}O$ gas	China	Details are presented in Chapter 4.

Appendix B2

S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
				an energy storage container. The rack contains 1 live battery module and 20 dummy modules. The live battery module contains 12 live battery cells.			
13	Wang et al.	[93]	Cylindrical 3.5Ah NMC	1. Single-cell 2. Two cells bundled in a confined space	Liquid N_2	China	Liquid N_2 can extinguish the fire and effectively inhibit TR propagation in the confined space.
14	Zhou et al.	[76]	Cylindrical 3.5Ah NMC	Two cells bundled without an enclosure	Fine WM with additives containing urea (CH_4N_2O), AEO-9, FC4330 and DMMP	China	The low conductivity fine WM with additives containing the optimal concentration of 0.36% urea, 2% AEO-9, 0.25% FC-4330 and 3.5% DMMP is proposed to achieve efficient inhibition of TR and its propagation and reduce the risk of short-circuiting.
15	Huang et al.	[94]	Cylindrical 2.2Ah LCO	Five cells bundled in an explosion-proof chamber	Liquid N_2	China	Liquid N_2 has an excellent cooling capacity, which can prevent TR propagation when the activation of the agents starts before the batteries reach critical temperatures, as proposed in the paper.
16	Wang et al.	[77]	Prismatic 30Ah LFP	Single-cell in an explosion-proof box	WM with different combinations of additives containing SDBS, APG0810, K_2CO_3, Na_2CO_3, $C_{12}H_{26}O$, FC4330, EL90 and urea (CH_4N_2O)	China	The study finds that WM with SDBS-FC4430-Na_2CO_3 solution with a mass ratio of 1:2:1.5 has the highest fire-extinguishing efficiency, followed by EL90 as an additive. The TR propagation is not discussed in the paper.
17	Wang et al.	[78]	Cylindrical 2.6Ah NMC	Five cells bundled in a combustion chamber	Fine WM with additives containing $NaHCO_3$ and urea (CH_4N_2O)	China, UK & USA	Fine WM with additives is more effective in extinguishing fires than pure WM without additives. The additives improve heat absorption, cooling effect, oxygen depletion and breakage of the chemical reaction. The compound agent can also stop TR propagation.
18	Zhang et al.	[71]	Cylindrical 3.4Ah NCA	Single-cell in an enclosed combustion chamber	1. N_2-twin-fluid $C_6F_{12}O$ mist 2. N_2-twin-fluid H_2O mist	China	The N_2-twin-fluid liquid mist synergistic technology proposed in this paper can extinguish the fire and suppress TR. N_2-twin-

Appendix B2

S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
							fluid $C_6F_{12}O$ mist exhibits 51.2% higher extinguishing efficiency than applying $N_2(g)$ alone, and N_2-twin-fluid H_2O mist increases the cooling rate by 20%.
19	Liu et al.	[87]	Prismatic 300Ah LFP	Single-cell in a combustion chamber scaled to ½ of ISO9705 room.	$C_6F_{12}O$ gas	China	Higher doses of $C_6F_{12}O$ gas achieve more efficient extinguishment. However, it increases the toxicity level. The study proposes the optimal doses of 2.9g/Wh under the experimental conditions for this battery cell. The thermal runaway cannot be wholly mitigated for such high-power LIB.
20	Yuan et al.	[79]	Cylindrical 3Ah NCA	Six cells bundled in an enclosed stainless steel tank	WM with 3% F-500 additive	China	WM with 3% F-500 additive could absorb the main explosive gases. It exhibits better cooling capacity and more water penetration than pure WM. The agent can also suppress LIB fires but cannot prevent TR propagation with 100% SOC.
21	Liu et al.	[80]	Cylindrical 1.5Ah LFP; 1.3Ah LCO; 1.5Ah NMC	Single-cell without an enclosure	WM with 5% NaCl additive	China	WM with 5% NaCl additive demonstrates better fire suppression efficiency and cooling effect than pure WM. Both WM with 5% NaCl additive and pure WM can extinguish the fire and inhibit TR for LFP. However, the inhibition effect of TR for LCO and NMC is unsatisfactory.
22	Xu et al. (Journal paper from citation search)	[123]	Cylindrical 2.5Ah NMC	1. Single-cell 2. Three cells bundled in an enclosed box	WM	China	The study demonstrates a good cooling efficiency of WM. The paper also quantifies the critical onset temperature of TR is increased by 36°C due to WM, which prolongs the TR propagation and will ultimately suppress the TR propagation if the duration of WM release increases.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
2021							
23	Zhao et al.	[91]	Cylindrical 2.6Ah NMC	Four cells bundled in an experimental box	1. Water spray 2. ABC ultra-fine dry powder 3. BC ultra-fine dry powder 4. Novec1230 ($C_6F_{12}O$)	China	The study is based on 70% SOC for the fire suppression test. The results show that water spray exhibits the best cooling efficiency and prevents TR propagation. The other 3 agents cannot effectively prevent TR propagation.
24	Said & Stoliarov	[88]	Cylindrical 2.6Ah LCO	12 cells bundled in a bench-scale wind tunnel test	Novec1230 ($C_6F_{12}O$) with 8.5% and 15.2% design concentration	USA	8.5 vol% concentration of Novec1230 cannot extinguish the fire and fails to prevent TR propagation. With the increased %vol concentration, 15.2% of Novec1230 can prevent thermal runaway propagation in 4 out of 6 tests, with 57% of battery cells (out of a total of 72 cells in 6 tests) not suffering from the thermal runaway during the tests. The combustion efficiency is reduced to below 18% by Novec1230.
25	Said et al.	[147]	Cylindrical 2.6Ah LCO	12 cells bundled in a bench-scale wind tunnel test	WM	USA	WM at the flow rates of 1.0 and 1.6g/s prevent TR propagation in 40%-50% of all tests. WM also delays TR propagation. The combustion efficiency is reduced to below 50% by WM.
26	Zhang et al.	[125]	Cylindrical 4Ah NMC	1. Single-cell 2. Three cells bundled in an explosion-proof box	Water spray	China	Water spray can efficiently suppress the fire. However, insufficient volume and low contact efficiency cannot prevent TR propagation. This can be resolved by increasing the volume of water spray and higher contact efficiency.
27	Huang et al.	[95]	Cylindrical 2.2Ah LCO	Single-cell in an explosion-proof combustion chamber	Liquid N_2	China	Liquid N_2 exhibits excellent cooling efficiency, which can cool a TR battery from approximately 700ºC to less than 100ºC within 80s. The TR could be prevented if the agent is applied before the critical TR temperature of 170ºC for this type of battery.
28	Zhou et al.	[106]	Prismatic 202Ah LFP	EV Pack-Level: Three cells bundled in a simulated battery box	$C_6F_{12}O$ gas discharge into the battery box	China	$C_6F_{12}O$ gas can quickly suppress the initial fire, and an extended spray of the agent is required to achieve a better cooling effect, thus preventing TR propagation. Details are also presented in Chapter 4.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
29	Guo et al.	[73]	Cylindrical 4Ah NMC	Two cells bundled in a combustion chamber	1. Low-pressure twin-fluid WM (mixing water and air) 2. AVD	China	The twin-fluid WM can quickly extinguish the fire. At an optimal working pressure of 1.2MPa, it performs better than AVD in cooling surface and flame temperatures. In contrast, AVD has a better asphyxiant capability to prevent re-ignition.
30	Zhou et al.	[81]	Cylindrical 3.5Ah LCO	Single-cell in a semi-enclosed box	WM with additives containing urea (CH_4N_2O), KEOA, KCl and FC-4330.	China	The experiment finds that the WM with additives of the optimal concentration of 0.17% FC-4330, 0.2% TEOA, 0.32% urea and 2.5% KCl can fire extinguishing and cooling effects to overcome a jet fire from the battery.
31	Wang et al.	[82]	Pouch 20Ah LFP	Single-cell in a combustion chamber	1. WM with SDS additive 2. WM with carboamide additive 3. WM	China	Compared among the three agents, all of them can suppress the LIB fires. The order of fire suppression capability is WM with 1% SDS > WM with 1% carboamide > pure WM. The ability to prevent TR is not tested, but the experiments show that WM with additives has better heat absorption, potentially beneficial to TR mitigation.
32	Tian et al.	[74]	Cylindrical 6.5Ah NMC	Six cells bundled in an explosion-proof box	Novec1230($C_6F_{12}O$) + heptafluorocyclopentane mixed solution	China	The mixed solution improves the cooling effect of Novec1230, which can extinguish the fire and keep the batteries cool. However, TR propagation is not further investigated in the paper.
33	Zheng et al.	[83]	Shape not mentioned 12Ah LFP	Single-cell without an enclosure	WM with additives containing PFAB, APG0810, K_2CO_3, SDBS, $C_{12}H_{26}O$ and Na_2CO_3	China	The experiment finds that WM with PFAB-APG0810-K_2CO_3 additive has a better extinguishment effect for an incipient fire, and WM with SDBS- $C_{12}H_{26}O$-Na_2CO_3 additive exhibits a better cooling effect to bring a TR battery below 200°C in a shorter time.
34	Wang et al.	[121]	1. Pouch 26Ah NMC 2. Pouch 20Ah LFP 3. Cylindrical 4.2Ah NMC	1. Individual cells for NMC and LFP 2. Three cells bundled for NMC in an explosion-proof chamber	1. AVD 2. Novec1230 ($C_6F_{12}O$) 3. 2-BTP	China	Compared AVD's cooling efficacy among the 3 types of batteries, the order is Pouch LFP(-220°C/s) > Pouch NMC(-84°C/s) > Cylindrical NMC(-23°C/s). Compared the three agents' cooling efficacy on LCO's battery, AVD outweighs Novec1230 (-9°C/s) and 2-BTP(-10°C/s). TR propagation is

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
							not further investigated in the experiment.
35	Un & Aydin	[148]	Cylindrical 2Ah LCO	15 cells bundled in an outdoor environment	Boron-based suppression agent	Turkey	Boron-based suppression agent can extinguish the fire and provide a cooling effect. No investigation of TR is in the paper.
36	Bisschop et al. (Technical report from citation search)	[36]	1. Cylindrical 2.55Ah NMC 2. Prismatic 50Ah LFP	BESS Rack-Level: 1. 39 NMC cells form a battery module 2. Two LFP cells form a battery module A rack consists of 1 live module and 11 dummy modules. The test is conducted in a standard shipping container.	1. Total flooding WM with 3% F-500 additive 2. Sprinkler water with 3% F-500 additive 3. Direct spray water + AVD 4. Total flooding IG541 gas	Sweden	Details are presented in Chapter 4.
37	Siemens (White paper from citation search)	[50]	Prismatic Unknown capacity and chemistry	Module-Level: Three cells bundled in an original module housing	N_2 gas with a 45.2% extinguishing concentration	Switzer-land	Oxygen concentration is reduced to 11.3% to prevent TR propagation, provided that the activation of N_2 gas starts at the earliest possible time during LIB's off-gassing.
38	Barowy et al. (Technical report from citation search)	[116]	Cylindrical 3.2Ah NCA	BESS Rack-Level: In a standard shipping container, one TR initiating rack consists of nine modules, each loaded with 270 cells. Two adjacent target racks are loaded with 1/3 capacity of the TR initiating rack.	1. Novec1230 ($C_6F_{12}O$) 2. Sprinkler	USA	Details are presented in Chapter 4.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
					2020		
39	Xu et al.	[120]	Prismatic 94Ah NMC	Single-cell in an explosion-proof chamber	1. CO_2 2. WM 3. FM200 (not discussed in this thesis)	China	WM exhibits a better cooling effect than CO_2 in the experiment. WM can effectively suppress LIB fires. However, CO_2 cannot completely suppress the fire. However, the experiment does not further investigate the efficacy of the agents for TR mitigation.
40	Liu et al.	[72]	Prismatic 38Ah NMC	Single-cell in a battery module box	1. $C_6F_{12}O$ gas 2. WM 3. $C_6F_{12}O$ gas + WM 4. WM with $KHCO_3$ & $K_2C_2O_4$-H_2O additives Discharge directly into the module box	China	The experiment shows that the cooling effect of the combined agents of $C_6F_{12}O$ gas and WM outweighs $C_6F_{12}O$ gas alone or WM alone. Early activation of agents also brings better cooling efficiency. WM at higher working pressure provides better cooling efficiency. Lastly, WM with additives exhibits better cooling and suppression effects.
41	Meng et al.	[97]	Prismatic 22Ah LFP	Single-cell in full-scale ISO9705 room	ABC dry powder	China	ABC dry powder can suppress LIB fire under appropriate conditions but with a limited cooling effect which cannot prevent TR of the LIB.
42	Zhang et al.	[70]	Prismatic 243Ah LFP	Single-cell in a combustion chamber	1. $C_6F_{12}O$ gas 2. WM 3. $C_6F_{12}O$ gas + WM 4. CO_2 + WM 5. HFC-227ea + WM (not discussed in this thesis)	China	$C_6F_{12}O$ gas alone can suppress the fire quickly but has a limited cooling effect. WM alone takes a long time to suppress the fire but eventually cools the battery and prolongs the TR. The combination of $C_6F_{12}O$ gas + WM exhibits the best performance, which can quickly suppress the fire and cool the battery temperature more significantly. The overall effect of $C_6F_{12}O$ gas + WM is better than CO_2 + WM.
43	Bisschop et al.	[108]	Prismatic 28Ah NMC	EV Pack-Level: An enclosed EV battery pack cabinet contains two live and six dummy modules. Each live module contains 12 cells.	1. WM with less than 5% foam additives (Internal only) 2. Water spray with less than 5% foam additives (Internal and External) Discharge internally into the battery box and externally onto the battery box	Sweden	Details are presented in Chapter 4.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
44	Liu et al. (Journal paper from citation search)	[124]	Cylindrical 2.6Ah NMC	Five cells bundled in a combustion chamber	WM	China	WM can extinguish the fire and exhibit an excellent cooling effect to prevent TR propagation. However, an insufficient amount of WM could not stop the TR of the initiating cell effectively.
2019							
45	Liu et al.	[149]	Cylindrical NMC 2.6Ah	Single-cell in a combustion chamber	WM	China	WM can prevent TR before the battery reaches the critical TR temperature. Although it cools the battery surface, it still cannot stop TR beyond the critical TR temperature.
46	Yu et al.	[107]	Prismatic 20Ah LFP	EV Pack-Level: A standard electric bus battery pack case contains one live and eight dummy modules. The live module contains 12 cells.	$C_6F_{12}O$ gas discharge directly into the battery case. The battery cells in the live module are exposed to the gaseous agent.	China	$C_6F_{12}O$ gas can extinguish the fire and has a certain cooling effect to block TR propagation with continuous injection. Details are also presented in Chapter 4.
47	Long & Misera (Technical report from citation search)	[113]	1. Prismatic 20Ah LFP 2. Prismatic 32.5Ah NMC	BESS Rack-Level: A rack contains 16 live battery modules. Each LFP live module contains 78 cells, and each NMC live module contains 64 cells.	Sprinkler system in a testing facility	USA	Details are presented in Chapter 4.
48	Ditch & Zeng (Technical report from citation search)	[112]					
49	Gully et al. (Technical report from citation search)	[110]	Pouch Unknown cell capacity NMC	BESS Rack-Level: A rack contains 1 live and 17 dummy modules in a testing facility.	1. Sprinkler 2. HPWM 3. Novec1230 ($C_6F_{12}O$) 4. Direct injection of FIFI4Marine CAFS 5. Direct injection of water	Norway	Details are presented in Chapter 4.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
2018							
50	Russo et al.	[122]	Pouch 20Ah LNO	Single-cell in an open outdoor space	1. CO_2; 2. Foam; 3. dry powder; 4. Water; and 5. WM	Italy	The experiment briefly investigates the extinguishing effect of each agent on the single cell. The order of extinguishing efficiency is water>foam>WM>CO2>Dry Powder. TR mitigation is not investigated.
51	Si et al.	[150]	Prismatic NMC	Single-cell in an explosion-proof tank	1. CO_2 2. HFC-227ea (not discussed in the thesis)	China	CO_2 can extinguish the fire and has a certain cooling effect on the battery. TR is not investigated in this paper.
52	Zhuang et al.	[89]	Pouch 30Ah LFP	Single-cell in a combustion chamber	1. N2 2. CO_2	China	CO_2 has better heat absorption capability than N_2 and exhibits a better cooling effect. However, both agents cannot prevent TR.
53	Liu et al.	[90]	Prismatic 38Ah NMC	Single-cell in an explosion-proof box	$C_6F_{12}O$ gas	China	$C_6F_{12}O$ gas can quickly extinguish the fire within 2-3s. However, it cannot effectively cool the battery below the TR temperature from the evidence that the vent gas continues releasing from the battery after the fire is extinguished.
54	Li et al.	[84]	Pouch 30Ah LFP	Single-cell in an enclosure	WM with additives containing SDS and EL-20	China	The experiment investigates the fire extinguishment capability of WM and WM with additives. The extinguishment efficiency is in the order of WM with SDS+EL-20 additives > WM with SDS additive > WM with EL-20 additive > pure WM. TR mitigation is not further investigated.
55	Wang et al.	[119]	Cylindrical 50Ah NMC	Single-cell in an enclosed cupboard with three layers of shelf	1. $C_6F_{12}O$ gas 2. CO_2	China & UK	$C_6F_{12}O$ gas can extinguish the battery fire within 30s. Whereas, CO_2 cannot entirely suppress the fire. TR mitigation is not investigated in this paper.
56	Andersson et al. (Technical report from citation search)	[102]	Pouch 20Ah LFP	Module-Level: one live cell, one dummy cell and four perforated metal sheets (mimicking densely packed battery cells) are placed in a battery module box.	Total compartment test: 1. LPWM 2. HPWM 3. Water spray Direct spray test over the module box: 4. Water spray 5. Class A foam 6. Class F foam 7. CAFS 8. N_2 9. AVD	Sweden	Details are presented in Chapter 4.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
57	Zhu et al. (Journal paper from citation search)	[85]	Unknown shape 20Ah LFP	Module-Level: Four cells bundled in a battery module box	LPWM with not more than 5% additives containing FMEE-APG-SDS-AEC-MAEPK	China	WM mist with the proposed additives can effectively and quickly extinguish the fire. TR mitigation is not investigated in this paper. Details are also presented in Chapter 4
58	Luo et al. (Journal paper from citation search)	[86]	Cylindrical 20Ah LFP 50% SOC	Module-Level: Four cells bundled in a battery module box	1. WM with 5% F500 2. WM with 5% self-made solution 3. Pure water	China	WM with additives exhibits more rapid suppression and excellent cooling effect than pure water. The overall performance of WM with the self-made solution is slightly better than WM with F500. Details are also presented in Chapter 4
2017							
59	Ditch	[118]	Pouch 20Ah LFP	Warehouse Storage: 20 cells packed in a single-wall corrugated carton box. Plastic dividers separate the cells. A maximum of 42 carton boxes contain a total of 840 cells. 50% SOC	Sprinkler system	USA	Details are presented in Chapter 4.
60	Hill et al.	[101]	1. NMC 2. LFP 3. LTO Ranged from 1.2 to 200 Ah	1. Cell test in an enclosed chamber 2. Module-Level test in a partially enclosed outdoor burn facility (metal container) 90% SOC	1. Water 2. Pyrocool 3. F-500 4. FireIce 5. Aerosol (Star-X)	USA	Details are presented in Chapter 4
61	Hill & Warner (Technical report from citation search)	[99]					
2015							
62	Rao et al.	[98]	Prismatic 100Ah LFP	Single-cell in an enclosed chamber	1. CO$_2$ 2. Superfine powder 3. Heptafluoropropane (FM200) (not discussed in this thesis)	China	The experiment shows that CO$_2$ and superfine powder can suppress the fire but cannot stop TR.

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S/N	Reference		Battery Type	Test Method	Extinguishant / Suppression Method	Country	Key Finding
2014							
63	Maloney (Technical report from citation search)	[67]	Cylindrical 2.6Ah (50% SOC) Unknown chemistry	Five cells bundled in an enclosed test chamber	Water-based agents: 1. Water 2. AF-21 3. AF-31 4. Aqueous A-B-D Gas-based agents: 5. Novec1230 ($C_6F_{12}O$) 6. Dupont FE36 7. CO_2 8. FM200 (not discussed in the thesis) 9. Halon (not discussed in the thesis) Dry chemical agent: 10. Purple-K	USA	Water-based agents are more effective in cooling than non-water-based agents. Water, AF21, AF31, Aqueous A-B-D and Novec1230 can extinguish the fire and stop the TR propagation. Whereas all the rest of the agents cannot prevent the TR propagation.
2013							
64	Juarez et al.	[64]	Cylindrical 4Ah Unknown Chemistry unknown	Module-Level: Two battery modules with four cells in each module. No enclosure is used.	1. Fine WM extinguisher 2. CO2 extinguisher Discharge over the surface of two battery modules.	USA	Details are presented in Chapter 4.
65	Ditch & Vries (Technical report from citation search)	[65]	Cylindrical Unknown capability and chemistry	Warehouse Storage: Carton boxes containing packed cells are arranged in a three-tier-high open-frame rack-storage (up to 4.6m) in a Large Burn Laboratory. 50% SOC	Sprinkler system	USA	Under the test storage environment, the ceiling sprinkler cannot extinguish the fires beyond the predicted experimental duration.

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Filtered articles based on the exclusion criteria in Step 4

S/N	Reference		Article Title	Reason of Exclusion
1	Han et al., 2023	[151]	*“Study on the minimum extinguishing concentration of $C_6F_{12}O$ for extinguishing synthesis gas flame of lithium-ion battery”*	The experiment uses extractive lithium-ion vent gases.
2	Wang et al., 2022	[152]	*“Fire and explosion characteristics of vent gas from lithium-ion batteries after thermal runaway: A comparative study”*	The experiment uses extractive lithium-ion vent gases.
3	Strum et al., 2022	[153]	*“Fire tests with lithium-ion battery electric vehicles in road tunnels”*	The experiment uses direct injection of water via a firefighting lance for fire services
4	Cui et al., 2022	[154]	*“Full-scale experimental study on suppressing lithium-ion battery pack fires from electric vehicles”*	The experiment uses direct injection of compressed air foam for fire services.
5	McKinnon et al., 2022	[155]	*“Full-scale walk-in containerized lithium-ion battery energy storage system fire test data”*	The paper only provides the proposed experimental settings without any results.
6	Fan et al., 2022	[156]	*“Numerical analysis on the combustion characteristic of lithium-ion battery vent gases and the suppression effect”*	The experiment uses extractive lithium-ion vent gases.
7	Liu et al., 2021	[157]	*“Experimental study on active control of refrigerant emergency spray cooling of thermal abnormal power battery”*	The experiment uses dummy battery cells to investigate the active control of the battery thermal management system, which is not directly related to fire suppression.
8	Egelhaaf et al., 2021	[158]	*“Firefighting of Li-Ion Traction Batteries - An Update”*	The experiment uses direct injection of water/CO_2/F-500 via a firefighting lance for fire services
9	Barelli et al., 2021	[159]	*“Oxygen reduction approaches for fire protection to increase grid Li-ion BESS safety”*	The paper discusses the conceptual study using the flammability limit of vent gases from LIBs. No experiment is carried out.
10	Un et al., 2021	[160]	*“Experimental study of fire suppression for Li-ion electric batteries with H_2O”*	The experiment uses direct injection of water for fire services.
11	Li et al., 2020	[161]	*“Full-scale experimental study on the combustion behavior of lithium ion battery pack used for electric vehicle”*	The experiment uses direct injection of water for fire services.
12	Liu et al., 2019	[162]	*“The inhibition/promotion effect of $C_6F_{12}O$ added to a lithium-ion cell syngas premixed flame”*	The experiment uses extractive lithium-ion vent gases.
13	Ghiji et al., 2019	[163]	*“Lithium-ion battery fire suppression using water mist systems”*	The experiment uses extractive lithium-ion electrolyte
14	Wang et al., 2016	[164]	*“The efficiency of heptafluoropropane fire extinguishing agent on suppressing the lithium titanate battery fire”*	The experiment uses FM200 for the fire suppression test.
15	Blum & Long, 2015	[165]	*“Full-scale fire tests of electric drive vehicle batteries”*	The experiment uses direct injection of water for fire service.
16	Hu et al., 2013	[166]	*“Effectiveness of heat insulation and heat dissipation for mitigating thermal runaway propagation in lithium-ion battery module”*	The paper discusses passive fire protection using a heat insulation approach. No experiment has been conducted on active fire protection methods.
17	Egelhaaf et al., 2013	[66]	*“Fire fighting of li-ion traction batteries”*	The experiment uses direct injection of water for fire service.