Lithium-ion Battery Fire Suppression in Submarine Battery Compartments

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ABSTRACT

Lithium-ion main storage batteries have the potential to improve the endurance of diesel-electric submarines through superior energy storage and charging capabilities when compared with traditional lead-acid batteries. A review of lithium-ion batteries has found that they pose a potential fire risk and conventional fire suppression systems may not provide an adequate level of safety in the event of a lithium-ion battery fire.

Studies have identified water-based fire suppression as effective for lithium-ion battery fires. Water extinguishes flames and cools the battery inhibiting exothermic reactions within the battery during a thermal runaway event. The application of liberal amounts of water or submerging the battery in water has been shown to achieve extinguishment of lithium-ion battery fires. However, these firefighting methods are not appropriate for submarines because the excessive volume and weight involved may result in submarine stability requirements not being met. Water mist fire suppression systems have the extinguishing and cooling capability of sprinklers or deluge systems whilst using a lower volume of water and are therefore potentially applicable for spaces such as submarine battery compartments.

In collaboration with Victoria University's Centre for Environmental Safety and Risk Engineering (CESARE), Defence Science and Technology Group is investigating the effectiveness of water mist fire suppression for lithium-ion battery fires. The aim of this work is to experimentally determine the extinguishing criteria for lithium-ion battery fires and develop Computational Fluid Dynamics models to predict the fire extinguishing capabilities of water mist on lithium-ion battery fires.

This paper describes why lithium-ion batteries are susceptible to fire, why water mist is seen as a promising fire suppression system for lithium-ion battery fires, and presents some of the preliminary experimental results of the collaborative research with CESARE.

INTRODUCTION

Lithium-ion batteries offer high energy and power density, light-weight and long lifespan [1, 2] and is the current preferred technology for mobile electronics, power tools, electric grid backup and aerospace applications [2]. Lithium-ion batteries are also gaining interest for use in diesel-electric submarine propulsion because their energy content could improve submarine range and endurance when compared to conventional lead-acid batteries [3]. In October 2018, the first of two lithium-ion battery equipped Soryu-class diesel-electric submarines was launched for the Japanese navy [4], these are the first submarines to be equipped with lithium-ion batteries. Lithium-ion batteries have also been developed for the second batch of three of the South Korean navy's next generation attack submarines [5].

A review [6] has found that, although occurrences are rare, lithium-ion batteries are a potential fire risk. Lithium-ion batteries are susceptible to thermal runaway, a complex combination of chemical reactions that are initiated by heat generated either internal or external to an individual cell. The reactions within the cells are exothermic resulting in a feedback loop that continues to produce heat until all reactive agents within the cell are consumed. The heat build-up can cause the combustible electrolyte within the cell to vapourise, vent and ignite resulting in heat transfer that could initiate thermal runaway in adjoining cells.

Studies [7, 8] have shown that water-based fire suppression is effective against lithium-ion battery fires as water extinguishes the combustion flames and cools the cells, inhibiting the exothermic reactions within the cell during thermal runaway. This has been achieved through the application of liberal amounts of water or by submerging the battery in water. This system of suppression is unlikely to be used on a submarine because of the restricted volume of water able to be carried, and stability requirements which may not be met upon the release of a large volume of water into a battery compartment. A system that has yet to be investigated for suppressing or extinguishing lithium-ion battery fires is water mist, a spray of fine water droplets that can provide both fire suppression and battery cooling. Water mist could extinguish burning electrolyte and potentially drive battery temperatures below the thermal runaway temperature and halt the reactions that generate heat. Water mist could be a viable extinguishing agent for submarine lithium-ion battery fire suppression because of its low water requirement and non-toxic nature.

Defence Science and Technology (DST) Group are currently collaborating with Victoria University's Centre for Environmental Safety and Risk Engineering (CESARE) to experimentally assess the thermal runaway and extinguishing processes and determine the criteria for lithium-ion battery fire suppression with water mist, criteria such as flow rate, orientation of the flow, water pressure and drop size distribution. This data will then be used to validate numerical analysis of lithium-ion battery fire suppression.

This paper describes lithium-ion battery chemistry, lithium-ion battery susceptibility to thermal runaway and why water mist could be the preferred choice for fire suppression. Also presented is an outline of the collaborative work being undertaken by DST Group and CESARE and some of the preliminary results.

LITHIUM-ION BATTERY COMPONENTS

Lithium-ion batteries are re-chargeable and comprise current collectors, electrodes (anode and cathode), flammable electrolyte, packaging materials, and separator. The term lithium-ion does not refer to singular cell chemistry but to a number of different chemistries. The choice of materials for the electrodes and electrolyte will affect the voltage, capacity, life, and safety of a lithium-ion battery. The following sections briefly describe lithium-ion battery components.

Current Collectors

The current collectors are the cell terminals and provide an even distribution of current across each of the electrodes. The anode and cathode materials are deposited onto copper and aluminium current collectors respectively so that the current collectors provide physical support to the electrode materials.

Electrodes

Typically, a metal oxide forms the cathode and graphite forms the anode. During discharge, lithium ions migrate from the anode and insert into voids in the cathode and upon charging, migrate from the cathode and insert into voids in the anode. The process is known as intercalation, the reversible insertion of ions into layered materials. The cell components and the intercalation processes are illustrated in *Figure 1*.

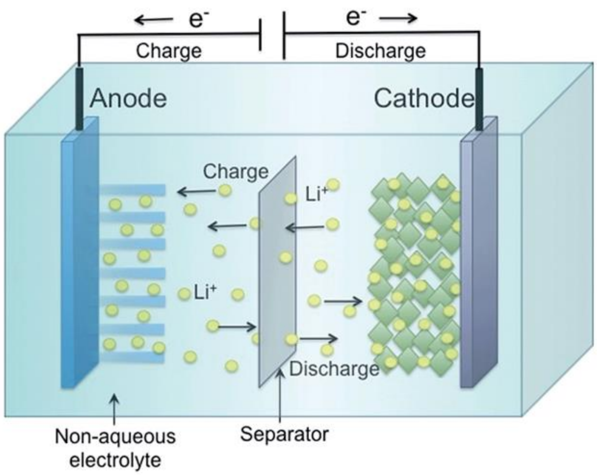

Figure 1. The insertion of lithium ions (yellow spheres) into the anode and cathode matrices during the charging and discharging processes [9].

Solid-Electrolyte Interface

During the initial battery charge, the intercalated lithium ions react with the electrolyte forming a passivating layer, the Solid-Electrolyte Interface (SEI), on the anode. The SEI allows lithium ion transport to the electrode but blocks electron flow to prevent electrolyte decomposition which consumes lithium ions and reduces the charge and discharge efficiency of the electrode material. The SEI forms mostly during the first charge, but continues gradually on further charging until the SEI layer is fully developed.

Separator

The separator is a thin porous membrane that physically separates the anode and cathode. The function of the separator is to prevent contact between the anode and cathode but allow lithium ion transport to and from the anode and cathode.

Electrolyte

The electrolyte is the medium that provides and facilitates the movement of lithium ions between the cathode and anode. The electrolyte in current technology lithium-ion batteries is flammable.

THERMAL RUNAWAY

If a lithium-ion battery temperature exceeds its safe operating temperature, the battery materials and electrolyte can lose their stability and generate heat which if not dissipated will generate more heat, a process known as thermal runaway.

Thermal runaway can be initiated by: internal defects producing an electrical short between the electrodes, elevated temperatures, over charging or discharging, or mechanical abuse. When a lithium-ion battery cell temperature exceeds the safe operating temperature of the cell, thermal runaway can take place in a multi stage process [10], typically

- the SEI layer begins to decompose exothermically at 90-120 °C (although this is dependent on the chemistry of the cell),
- exothermic reactions occur between the electrolyte and the anode above 120 °C and
- above 200 °C, thermal decomposition of the cathode evolves oxygen which can react with the electrolyte, followed by exothermic electrolyte decomposition.

The elevated temperatures produced during thermal runaway can induce electrolyte vapour production, pressurising the cell and triggering electrolyte venting or possibly rupturing the cell. Electrical equipment and wiring within the battery compartment can provide an electrical spark to ignite flammable liquids and gases however a fire can be started within lithium-ion batteries when the auto ignition temperature of the electrolyte is reached.

HAZARD AND RISK OF LITHIUM-ION BATTERY FIRES

Despite the extensive usage of lithium-ion batteries in electronic devices and vehicles, there is a fire risk associated with their use which is a concern in domestic electronic equipment [11], electric and hybrid electric vehicles [12, 13, 14, 15], and submarines [3, 16]. To achieve a desired voltage and energy content many small cells are closely packed in multi-cell batteries and the heat generated from a thermal runaway event in one cell can propagate to surrounding cells causing a cascading fire event.

Lithium-ion battery banks are generally safe under normal charge and discharge conditions. Battery Monitoring Systems (BMS) [17] are used to reduce the risk of thermal runaway by controlling lithium-ion battery characteristics such as current, temperature, and voltage within their safe operational window. However, due to the processes described above thermal runaway can still initiate.

To mitigate the risk of heat propagation to adjacent cells during a thermal runaway event, physical safety features such as an air gap between cells [18], thermal insulation [19] and heat absorbing phase-change and heat sensitive material between cells [20 , 21] can be incorporated within the battery compartment. However these features may add weight and volume and negate the advantages of using lithium-ion batteries. The development of new chemistry lithium-ion batteries, focusing on fire resistant electrolytes, is ongoing and these are not yet commercially available [22].

LITHIUM-ION BATTERY FIRE SUPPRESSION

Lithium-ion battery fires are primarily considered to be Class B (flammable liquids) fires as defined in Australian Standard AS1850:2009 [23] as they contain flammable liquid electrolytes, and can be extinguished like other Class B fires. However, if the cell is not sufficiently cooled, thermal runaway may continue and the combustible materials within the battery may re-ignite.

The total energy available for combustion within a lithium-ion battery is dependent on the stored electrical energy and the combustion load, consisting of the electrolyte and the flammable battery construction materials. The quantity of electrolyte in a cell can maintain combustion for a limited time but adjacent cells may undergo thermal runaway if heat transfer to the adjacent cells is not prevented.

Lithium-ion battery fire tests [7, 8] have shown that applying liberal quantities of water or by submerging in water, a lithium-ion battery fire can be extinguished and the cell cooled inhibiting ongoing combustion or cascading to adjacent batteries. For lithium-ion battery fire suppression on a submarine, water mist may be a suitable extinguishing agent because of its ability to provide cooling and extinguishment and low water requirement compared with other water based suppression systems.

WATER MIST FIRE SUPPRESSION

The term water mist refers to fine water sprays, a continuum of droplets in the range between aerosol (droplet diameter $\simeq$ 5 µm) and fog (10 µm $\leq$ droplet diameter $\leq$ 1000 µm) [24]. The United States National Fire Protection Association (NFPA) has defined water mist as a spray with a range of particle sizes smaller than 1000 µm [25]. Compared to gaseous agents and conventional sprinkler systems, water mist as an agent has the following advantages:

- no toxicity or asphyxiation concerns,
- no environmental concerns, and
- low water volume requirements.

Extinguishing Mechanisms

There are three mechanisms associated with the extinguishment of fires by water mist:

- Cooling

  The cooling mechanisms provided by water mist for fire suppression comprise cooling the flame and cooling the fuel surface. Water droplets can penetrate the flame, reducing the flame temperature below adiabatic as well as reducing the temperature of the fuel below its flash point. Each of these mechanisms is capable of halting combustion [24].

- Oxygen depletion

During a fire, water droplets are converted to vapour and the total volume occupied by the droplets increases by over three orders of magnitude [26]. The water volume expansion results in the disruption in the entrainment of air into the flame as well as the dilution of the oxygen to below the limiting oxygen concentration, halting combustion.

- Radiation attenuation

The presence of water mist significantly decreases the radiant heat flux to materials in the proximity of the fire, through heat absorption, which will limit the spread of fire. Water mist will also reduce the radiation feedback to the fuel surface, reducing the pyrolysis rate of the fuel.

Spray Characteristics

The effectiveness of water mist in suppressing fires is related to three main spray characteristics; the drop size distribution, the flux density and the spray momentum.

- Drop size distribution

The drop size distribution refers to the range of droplet sizes within a spray volume. Water mist contains droplets of different sizes which vary with time and location as the droplets collide, vapourise, or impinge on surfaces and drop out.

A volume of water divided into small droplets has a larger total surface area than an equivalent volume divided into larger droplets. Smaller droplets are therefore more efficient at heat absorption leading to flame cooling and oxygen depletion. The smaller drop sizes also exhibit gas like qualities and can be carried around the compartment to obstructed areas and provide extinguishing conditions where the larger droplets would not reach. Larger droplets can penetrate the fire plume, cooling the fuel and slowing the pyrolysis rate.

- Flux density

Flux density refers to the amount of water spray present in a unit volume. An increase in flux density will provide more water into a compartment and provide greater cooling, that cooling can reduce the flame temperature and fuel temperature, suppressing the fire.

- Spray momentum

Spray momentum refers to the spray mass, velocity and direction. The spray momentum will determine whether the water droplets have sufficient energy to penetrate the fire plume or reach the fuel surface. Without sufficient energy to penetrate the fire plume, the flame temperature will remain above the adiabatic flame temperature and extinguishment will not occur.

EXTINGUISHMENT EXPERIMENTS AND MODELLING

DST Group are currently collaborating with CESARE to assess the combustion behaviour associated with lithium-ion battery fires and determine whether water mist will suppress the fire and prevent thermal runaway. The fire and extinguishing experimental data will be used to validate a Computational Fluid Dynamics (CFD) analysis of lithium-ion battery fire and suppression. CFD packages such as Fire Dynamic Simulator, developed by the National Institute of Standards and Technology [27], are used to simulate fire scenarios by fire safety engineering and research communities. CFD will be used to model lithium-ion battery combustion and water mist interaction and simulate fire scenarios with different geometries, mist parameters, fuels, obstructions and construction materials. Once validated, CFD could be used to assess the design parameters of water mist systems and to contribute to the generation of firefighting standard operating procedures.

In order to validate the CFD modelling, experiments will be undertaken that focus on lithium-ion battery fire behaviour and water mist/lithium-ion battery fire interaction. The following sections present some preliminary results.

Lithium-ion Battery Fire Characterisation Studies

Studies have been conducted on used, lithium-ion polymer batteries, from Motorola two-way radios (battery type: PMMN4066). The batteries contain two flat cells connected in series but were separated into single cells. The cells were mounted vertically with a side mounted propane gas burner to apply heat to the cell which also acted as an ignition source for vented gases, as seen in *Figure 2*. Cell surface temperature and mass loss were measured.

The images in *Figure 2* represent typical stages that occurred during lithium-ion battery fire tests. A small gas jet (A) has released as a result of electrolyte vapourisation and is easily ignited. This develops into a large rapidly venting gas jet (B) which extinguishes the flame. As the venting gas velocity decreases, re-ignition occurs (C). Eventually the electrolyte gases are consumed but the packaging and internal combustibles maintain the fire (D).

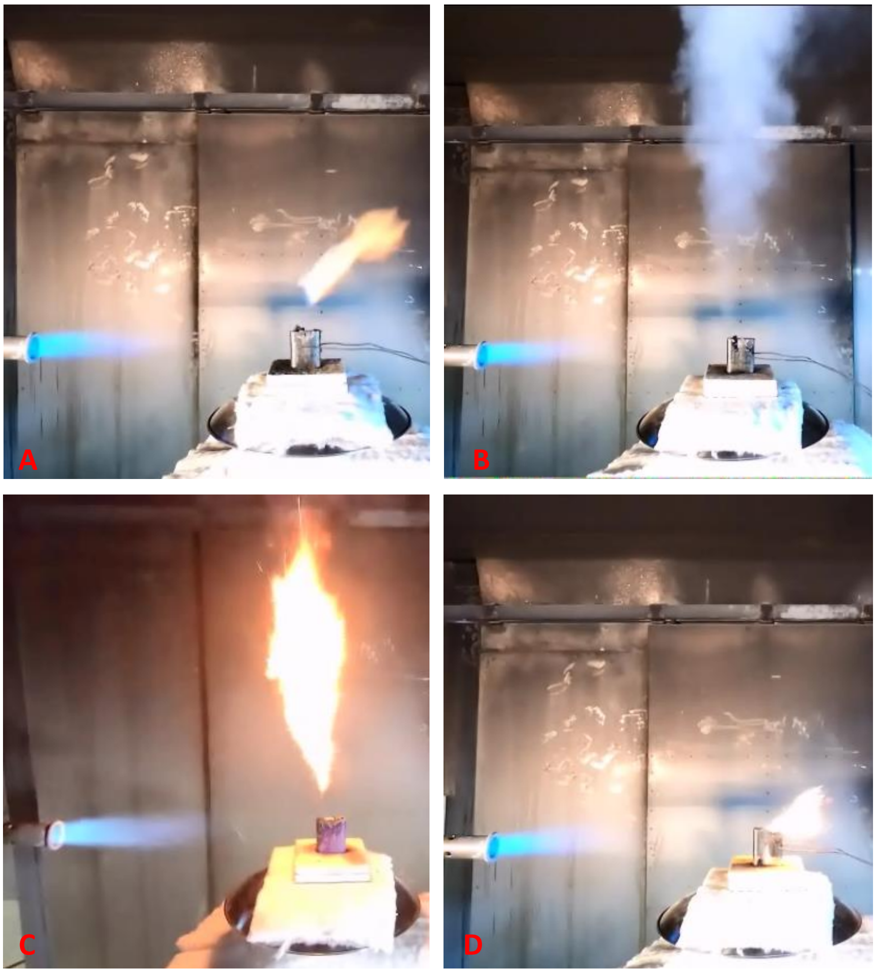

Figure 2. Typical stages of a lithium-ion polymer battery fire test. (A) A propane burner ignites a small vented gas jet. (B) The jet develops into a rapid venting prior to ignition that extinguishes the flame and (C) then re-ignites. (D) The combustible cell internal materials and packaging continue to burn after the electrolyte is consumed.

The stages of the fire in *Figure 2* correspond to distinct changes in the temperature and mass loss data shown in *Figure 3*. Firstly, there is a rise in cell surface temperature due to the action of the propane burner. Secondly, at 260 s (arrow A), a small jet venting through the pressure relief cap on the cell is seen as a reduction in mass. Ignition of the electrolyte gases by the propane burner occurred at this time. Thirdly, a marked increase in cell temperature transforms the jet into a rapid venting at 355 s (arrow B). This venting extinguishes the previous flame, and then is re-ignited about three seconds later by the burner flame, when the venting intensity has reduced. The rapid increase in temperature is indicative of thermal runaway which decreases after the internal reactions are complete. The battery continues to burn the combustible materials and packaging after the electrolyte is consumed. The spike increase in battery mass at arrow B in *Figure 3* is an idiosyncrasy of the load cell used to measure mass; the upward force of venting produces a transient downward reactive response, creating the illusion of greater mass.

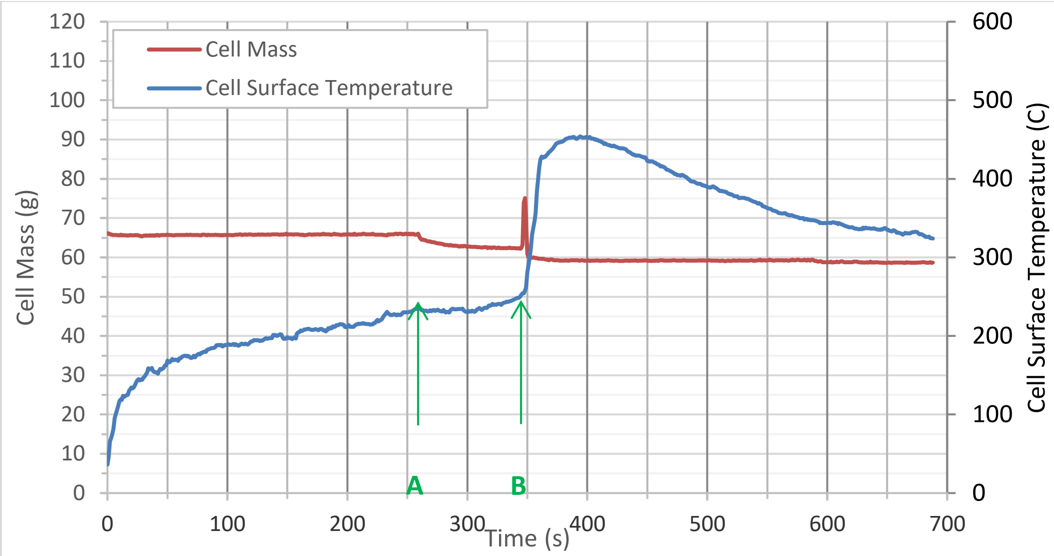

Figure 3. Mass and surface temperature behaviour resulting from heating a lithium-ion polymer cell using a side mounted propane gas burner.

A radiant panel was substituted for the gas burner to produce uniform cell heating to avoid localised heating produced by the propane burner. For these fire tests the cells were positioned with the large flat surface parallel to the radiant heater panel with a separate igniter used as an ignition source. Thermocouples are placed on the front and back surfaces of the cells.

Figure 4 shows the mass loss and the front and back surface temperatures of the cell when heated. Radiant heating results in an increase in cell temperature, and venting results in a loss of cell mass. The igniter was used at arrow A to ignite the gases and the panel heater was removed. This resulted in a drop in front surface temperature while the mass loss and back surface temperature remained stable. At arrow B major venting occurred extinguishing the flame. A short time later the temperature rises sharply - presumably thermal runaway has been initiated, and the mass drops (disregarding the load cell reactive spike). It was noted that the back surface temperature was higher than the front surface, possibly because the chemical reduction of electrolyte closer to the front surface had been more vigorous at an earlier time (100 s to 280 s) due to preferential heating of the front surface. After 380 s, there is no visible gassing.

It should be noted that not all tests resulted in two distinct outbursts of gas but the rapidly venting jet was always apparent.

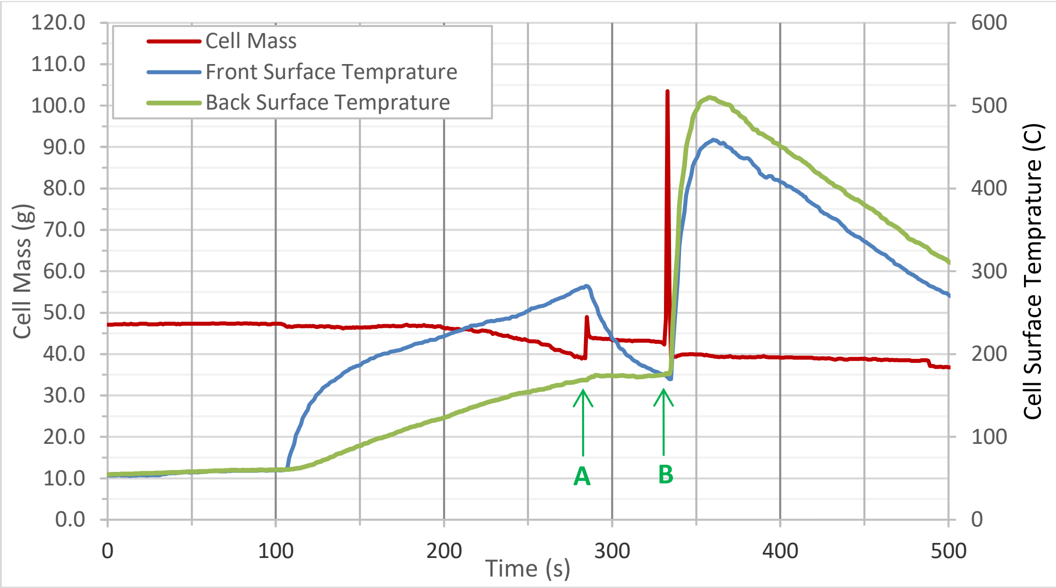

Figure 4. Mass and surface temperature behaviour resulting from heating the large surface of a lithium-ion polymer cell using a radiant burner.

Water Mist and Flame Interaction

To explore water mist fire suppression, tests were conducted with a water mist nozzle positioned above the flame of a propane fuelled Bunsen burner, a controllable fuel source compared to a battery venting event. The nozzle produced a hollow cone with droplet sizes ranging between 50 and 100 µm (NFPA defines water mist as having droplet diameters less than 1000 µm) and a flow rate of 0.8 ml/s. Different flame lengths were produced by adjusting either the air or propane flow rate and the extinguishing results are captured in *Table 1*. The results show that as the distance from the nozzle to the top of the Bunsen burner increased, or the flame length increased, the flame was more difficult to extinguish. The geometry of the experiment prescribes that greater distances between flame and nozzle result in lower mist flux density at the flame (due to both evaporation and greater cone volume), slowing the extinguishment process. The longer flame lengths require greater cooling to reduce the flame temperature.

Table 1. Effects of distance between the mist nozzle and Bunsen burner, and Bunsen burner's flame lengths and on the extinction time.

Distance (mm)	Extinction Time (s)		
	Flame Length = 80 (mm)	Flame Length = 140 (mm)	Flame Length = 200 (mm)
400	2.5	No	No
370	2	No	No
340	1	No	No
310	immediate	No	240
280	immediate	78	129
250	immediate	22.6	105
220	immediate	6	98
190	immediate	immediate	50
160	immediate	immediate	33

A Novel Water Mist Application Method

A different mist nozzle orientation has also been investigated for fire suppression. This mist system uses a flat spray positioned perpendicular to the flame of the propane fuelled Bunsen burner, rather than in the same plane as the flame. The nozzle was placed 150 mm horizontally and 20 mm above the top of the battery. On application of the water mist, extinguishment of the flame occurred within seconds. Video footage of the experiment shows the mist disrupting the connection between the fuel and the ignition source. If the water mist velocity at the burner is greater than the flame velocity, the flame and fuel are separated and extinguishment occurs. Similar to the extinguishing mechanism observed when a candle is extinguished by blowing it out.

Future Studies

To understand the interaction of water mist with a lithium-ion battery vent fire, further experiments will utilise a simplified battery comprising electrolyte as the only combustible material. Standard sized 18650 battery shells (65mm height x 18mm diameter) will be filled with a steel rod, to compensate volumetrically for the internal battery components, and electrolyte. These simplified batteries will be heated to determine electrolyte burning characteristics and the water mist parameters to produce extinguishment. Extinguishing experiments may extend to commercial 18650 batteries.

Future experiments involving the heating of an array of the simplified batteries will be used to investigate the onset of thermal runaway in adjoining batteries and the ability of water mist to provide cooling to prevent electrolyte venting, the subsequent fire and possibly thermal runaway. This research will incorporate larger scale batteries to assess scaling effects.

Additional experiments are planned to measure changes in battery mass and cell temperature to further understand progression to thermal runaway. This investigation will guide sensor usage to trigger the release of water mist.

Additional work will include ongoing development of Computational Fluid Dynamics models to predict the fire extinguishing capabilities of water mist on lithium-ion battery fires.

CONCLUSION

Lithium-ion main storage batteries have the capability to improve the endurance of submarines through superior energy storage. A review of the literature has shown that lithium-ion batteries pose a fire hazard; however the development of fire extinguishment systems for large banks of lithium-ion batteries in a marine environment is not yet sufficiently established to provide a satisfactory level of fire security.

Water mist could be a suitable method to extinguish lithium-ion battery fires on submarines because it offers suppression and cooling with a low water volume requirement. This collaborative research project is examining the ability and efficacy of water mist in protecting against lithium-ion battery fires. Initial extinguishing results, on gas flames and simplified batteries, using both vertical and horizontal nozzle orientations shows the potential of water mist as an extinguishing method.

The data gathered by this research will be used to further develop and validate CFD models and investigate design parameters of a water mist suppression system. Numerical modelling of the lithium-ion battery fire and water mist extinguishing will allow the design of a water mist system for any compartment configuration without the requirement of testing.

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