LITHIUM-ION BATTERY THERMAL RUNAWAY PREVENTION USING WATER SPRAY COOLING

by

Eric Jordan Huhn

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Approved by:

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Dr. Jeff Kimble (Chair)

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Dr. Michael Benjamin

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Dr. Jake Smithwick

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Dr. Nicole Braxtan

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Dr. Shen-En Chen

ABSTRACT

ERIC HUHN. Lithium-Ion Battery Thermal Runaway Prevention Using Water Spray Cooling
(Under the direction of DR. JEFFREY KIMBLE)

Lithium-ion (li-ion) batteries are still a very new form of energy storage; only finding wide-spread commercial use since the 1970's. Ever since, li-ion batteries continue to make their way into more aspects of everyday life. Their high energy density compared to other forms of batteries have made them an attractive energy source for everything from hearing aids, to emergency backup power sources for entire cities. Although the knowledge of the risk of thermal runaway in these batteries hasn't been a secret, it has only been since the dawn of the new millennium that the scale of LIB usage has presented risks to the general public. The risk of LIB thermal runaway-fueled fires has resulted in tremendous amounts of ongoing research that include: 1) Figuring out the cause of battery thermal runaway and 2) how to detect and prevent LIB thermal runaway and fires. A key take way from several observations of real-life battery fires from firefighting professionals is that little can be done once a LIB-fueled fire starts. To that end, more emphasis must be placed on researching methods of containing, or preventing thermal runaway in LIBs, which is the root cause of these fires, regardless of external factors. An experiment was developed to determine if thermal runaway of a LIB can be stopped while the battery is being subjected to an external heat source. A water spray method was devised to reduce the battery temperature during the tests. The batteries used in current study are pouch-type batteries. The test results indicated that, without water spray cooling, the heat source would cause a thermal runaway-induced fire every time. Additionally, the batteries used in the experiment were placed at an extremely high state of charge (SOC), which exacerbates thermal runaway reactions. The experiment clearly showed that it is possible to prevent thermal runaway with an external cooling source.

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LIST OF ABBREVIATIONS

ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
BESS	Battery Energy Storage System
BMS	Battery Management System
CO_2	Carbon Dioxide
EV	Electric Vehicle
FDNY	Fire Department of New York [city]
FSRI	Fire Safety Research Institute
GWh	Gigawatt-Hour
IFC	International Fire Code
ISC	Internal Short Circuit
LFP	Lithium Iron Phosphate
LIB	Lithium Ion Battery
$Li\text{-}MnO_2$	Lithium Manganese Oxide
$Li\text{-}SO_2$	Lithium Sulfur Dioxide

Li-TiS_2	Lithium Titanium Disulfide
LMO	Lithium Metal Oxide
LMP	Lithium Metal Polymer
Mg	Magnesium
MgO	Magnesium Oxide
MWh	Megawatt Hour
NFPA	National Fire Protection Association
NMC	Lithium Nickel Manganese Cobalt
NCA	Lithium Nickel Cobalt Aluminum
SOC	State of Charge
UL	Underwriters Laboratory
UN	United Nations
V	Volt

CHAPTER 1: INTRODUCTION

1.1 Introduction

In recent history lithium-ion batteries (LIBs) have become a significant source of life safety and environmental hazards; fires on airplanes, fatal structure fires, explosions of personal electronic devices resulting in burn injuries, ship fires, etc. In response, many different industries are trying to find a solution for the problem of "LIB fires". At best, some solutions may provide temporary intervention against fire and superheated gasses. At worst, some of these "solutions" are dangerous to deploy and create additional hazards. However, the intended audience for these products do not know enough to distinguish between good, bad, and worthless. It is necessary to evaluate scientific advancements in understanding LIB fire hazards through thermal runaway against how the public understands li-ion batteries and fires. Before public education can be improved, the knowledge gaps must be identified.

Meanwhile, the global fire service continues to struggle with fires fueled by LIB thermal runaway. Key complications to traditional firefighting techniques are that 1) batteries are installed deep within a device, far from the effects of whatever water may be used to extinguish a fire, and 2) although thermal runaway can cause a fire, thermal runaway itself is not a fire and cannot be extinguished as other types of fuels, like woods or plastics, can be extinguished. LIBs create everything they need for a self-sustaining runaway electrochemical reaction within the confines of each individual cell. Practically speaking, relying on traditional methods of notification that a fire is occurring – smoke detector activation, heat detector activation, visible smoke or fire – sets up any response to a thermal runaway for failure. Using these methods of notification, the thermal runaway has already taken place and any effort to stop the propagation of the failure is an uphill battle against rapid heat generation from cascading thermal runaway.

1.2 Problem Statement

Is there a better way to address LIB fires than relying on smoke detectors and other devices that alert and activate only when the products of combustion are detected? Intervening in a thermal runaway fueled fire is a race against the laws of thermodynamics. To investigate this question, a need to reliably put li-ion batteries into thermal runaway, and also deliver a measured flow of water was needed. The object of this research was to evaluate whether a leading indicator of failure in a LIB could be identified, and then applying cooling to the battery when that indicator revealed itself. The volume of water required to keep a battery cool to avoid thermal runaway should be much less than the water required to extinguish a fire caused by thermal runaway. The data collected through research could be used to develop technologies and methods for early intervention against LIB thermal runaway.

1.3 Research Methodology

A literature review was conducted to determine where the scientific community was at in their understanding of thermal runaway, and how much of that understanding has made its way into the fire service. Google Scholar was searched extensively to review scientific papers. To understand the perspective of the fire service firefighting textbooks were reviewed, along with industry websites.

To determine if thermal runaway could be prevented when it would otherwise be imminent, a reliable and highly repeatable experiment was developed. Multiple streams of data collection were employed simultaneously throughout testing including thermal imaging, visible light imaging, and thermocouples. Multiple, identical battery specimens were prepared to minimize variations in testing outcomes. Safety was a paramount consideration in the development of the experiment. The test apparatus and testing control station were designed to be safely separated from each other so researchers would not be exposed to unstable batteries, or fire and explosions. Material handling only occurred when batteries were confirmed to be stable through temperature monitoring over prolonged periods of time.

1.4 Scope of Work

To ensure the experimental apparatus was functioning as intended, several “dry runs” and “dress rehearsals” were performed. The dry runs followed the test procedure script, only without batteries. Dress rehearsals added batteries but were intended to find and correct any unexpected side-effects of heating a LIB to failure. Three batteries were used for the dress rehearsals. Another batch of three batteries were tested to failure in “part 1” of the experiment. These batteries were specifically evaluated for leading indicators of failure via video camera, thermal imaging camera, and direct temperature measurement. A final batch of three batteries were tested in an identical method to “part 1”, but with the addition of water cooling. “Part 2” focused on identifying the leading indicator of failure and using that indicator as an initiation point for introducing water spray to see if failure could be prevented.

Successful prevention of thermal runaway would serve as a “proof of concept” that an early-intervention cooling system may be plausible for prevention of thermal runaway, or keeping the extent of a propagating thermal runaway to a manageable scale.

1.5 Organization of the Report

This report is broken up into four chapters. Chapter 1 provides background and context to the journey of creating this experiment. Chapter 2 is the literature review conducted to establish a baseline for the understanding of thermal runaway research and knowledge gaps in the fire service and fire protection industries. Chapter 3 is a detailed report of the experiment design and execution. Data is presented in section 3.5 to validate the proof of concept. Conclusions drawn from Chapters 2 and 3 are presented in the final chapter: Chapter 4. This chapter also discusses opportunities for further research.

CHAPTER 2: LITERATURE REVIEW

2.1 Abstract

Since the second decade of the 21st century many industries are coming together to “solve” the problem of lithium-ion battery “fires”. However, there is a pervasive lack of agreement about what a LIB “fire” actually is, and if and how it can be stopped. The global fire service has the most practical knowledge because they have had many years to learn about the problem first-hand. As a result of their experience professional firefighters have learned to handle LIB thermal runaway-fueled fires either by letting it burn itself out, or allocating a tremendous amount of resources at the problem in hopes of extinguishing the fire. Firefighters are still searching for a third tactic. However, questionable information abounds on “effective” LIB fire solutions. Products are in the market that claim to be “the solution” to LIB “fires”. Yet, instances of injuries and property loss from fires caused by LIB thermal runaway continue to increase. A review of available literature is warranted to merge scientific discovery and practical fire service knowledge. Without knowing the gaps, educational improvements cannot be made. At the very least, a distinction must be made between “thermal runaway” and “fire”. These two words are not interchangeable in the context of li-ion batteries because the two phenomena have completely different mechanisms. Unfortunately, professional firefighting will continue to have an uphill battle as the nature of LIB powered products will make it difficult for fire suppression interventions to be effective. There is currently no practical and safe way to direct cooling efforts at the li-ion cells in thermal runaway that are fueling fires. More effort must be directed at advocation for early warning strategies that may allow intervention to prevent catastrophic LIB failure, thermal runaway, and fires.

2.2 Introduction

Even though li-ion technology has been in use since the 1970s, why are the hazards just now becoming a hot topic? Or have they been known earlier? Either way, there is a huge range of knowledge between people who know very little about li-ion technology, and those so familiar with it that they are moving beyond li-ion technology and looking for the next best thing. So, where does society's understanding of the hazard lie? Is the knowledge lacking, or is it the communication? Table 2-1 is a timeline of select lithium-ion battery safety milestones.

Table 2-1 notable LIB safety milestones

Year	Event
1817	Lithium metal discovered (Reddy et al., 2020)
1901	Swedish engineer Waldmar Jungner invents rechargeable nickel-cadmium battery (Scrosati, 2011)
1969	W.F. Myers and J.W. Simmons patent Li-SO_2 battery (Reddy et al., 2020)
1975	Sanyo CS-8176L solar-rechargeable calculator powered by Li-MnO_2 battery (Reddy et al., 2020)
1977	Exxon exhibits rechargeable Li-TiS_2 battery at Chicago Electric Vehicle Show (Whittingham, 2012)
2006	Dell and HP recall laptops due to fire risk caused by li-ion batteries (CPSC, 2006a, 2006b)
2008	AT&T begins replacing 17,000 LMP batteries made by Avestor (who went bankrupt and ceased operations in 2006) after several fires (Green Car Congress, 2006; Searcey, 2008; Shepard, 2008)
2008	The Tesla Roadster is the first production electric vehicle to use Lithium-Ion battery technology (Shahan, 2015)
2010	Lithium-Ion batteries begin to be considered for grid-scale energy storage (Qian et al., 2011)
2011	NHTSA begins investigation into li-ion batteries in Chevrolet Volt after numerous fires (NHTSA, 2012)
2012	First recorded Li-Ion BESS fire in Flagstaff, AZ (Electric Power Research Institute; Ferguson, 2013)
2014	Tesla breaks ground on the first Gigafactory outside of Sparks, NV, USA (Wilson, 2021)
2016	Global Lithium-Ion battery production tops 100 GWh (IEA, 2022)
2016	Samsung Note 7 cell phones recalled due to fires (Hollister, 2016)
2016	NFPA publishes LIB hazard assessment (Blum & Long, 2016)
2017	"Drone Nerds" brand recalls "hoverboards" because of fires (Strobel, 2021)
2017	Rail car carrying Li-Ion batteries explodes outside of Houston, TX (KHOU, 2017)
2017	Automotive journalist Richard Hamond crashes a Rimac Concept One electric hypercar. The vehicle caught fire on-scene and spontaneously reignited for several days afterward. (Branquinho, 2017)
2017	The "first draft committee" for the future NFPA 855 standard (Standard for the Installation of Stationary Energy Storage Systems) meets for the first time. (NFPA, 2023)
2019	2 MWh BESS explodes in Surprise, AZ, USA seriously injuring five firefighters (Hill, 2020)
2020	NFPA 855 is published (NFPA, 2023)
2023	New York City, NY enacts legislation prohibiting the use of li-ion powered e-mobility devices without a UL registration (Charalambous, 2023)

2.3 Mechanisms of Lithium-Ion Battery Fires

The intent of this paper is not to describe in detail how LIBs work, or describe all the failure mechanisms of LIBs. However, some basic information must be presented to understand the discussions that follow. LIBs are made up of six primary components as shown in Figure 2-1 (Geisige, 2022; Ohneseit et al., 2023; Orendorff, 2012).

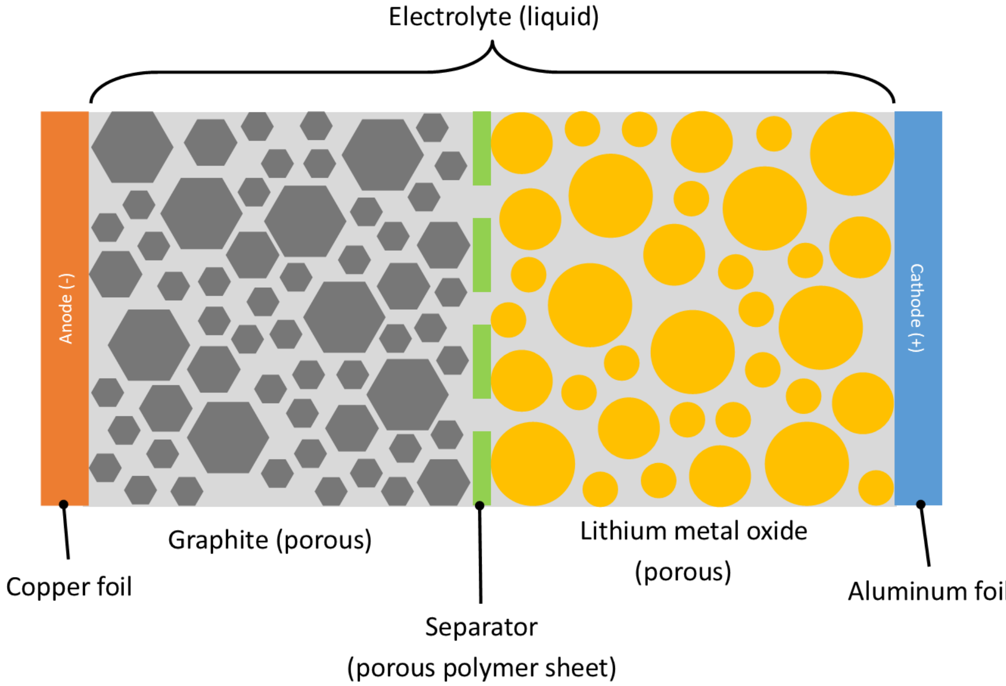


Figure 2-1 simplified diagram of the materials of a LIB

The positive and negative current collecting materials are most commonly aluminum and copper foil respectively. The Aluminum foil positive current collector (cathode) is coated in a Lithium metal oxide (LMO) material. This LMO material is where the chemistry of the LIB comes from. Lithium-Nickel-Manganese-Cobalt (NMC), Lithium-Iron-Phosphate (LFP), and Lithium-Nickel-Cobalt-Aluminum (NCA) are common LMO compounds. The copper foil negative current collector (anode) is commonly coated in graphite. Separating the LMO from the graphite is a thin, porous polymer separator. This separator physically prevents the positive side from coming in contact with the negative side and creating a short circuit. The graphite, LMO, and separator are flooded with an electrolyte solution which contains dissolved lithium salts. It should be noted that the above description is simplified. There are other materials that are generated as LIBs undergo their charge/discharge cycles (Chombo & Laoonual, 2020; Geisige, 2022). But the six components listed above make up the physical construction of LIBs.

LIBs have become the preeminent electrochemical energy storage technology because of their high energy density and long lifespan (Ghiji et al., 2021; Ouyang et al., 2019). These qualities are due to the complex electrochemical construction as described above. The combination of high energy density, and complex construction also means that when LIBs fail the results can be quite extreme (Lamb et al., 2021). LIBs have become famous for failing by seemingly exploding or otherwise creating a fireball or intense heat. We have all come to understand this phenomenon as “thermal runaway”. Thermal runaway can be triggered by a number of causes, but the end result is the same (Börger et al., 2019). Figure 2-2 illustrates the four basic causes of thermal runaway.

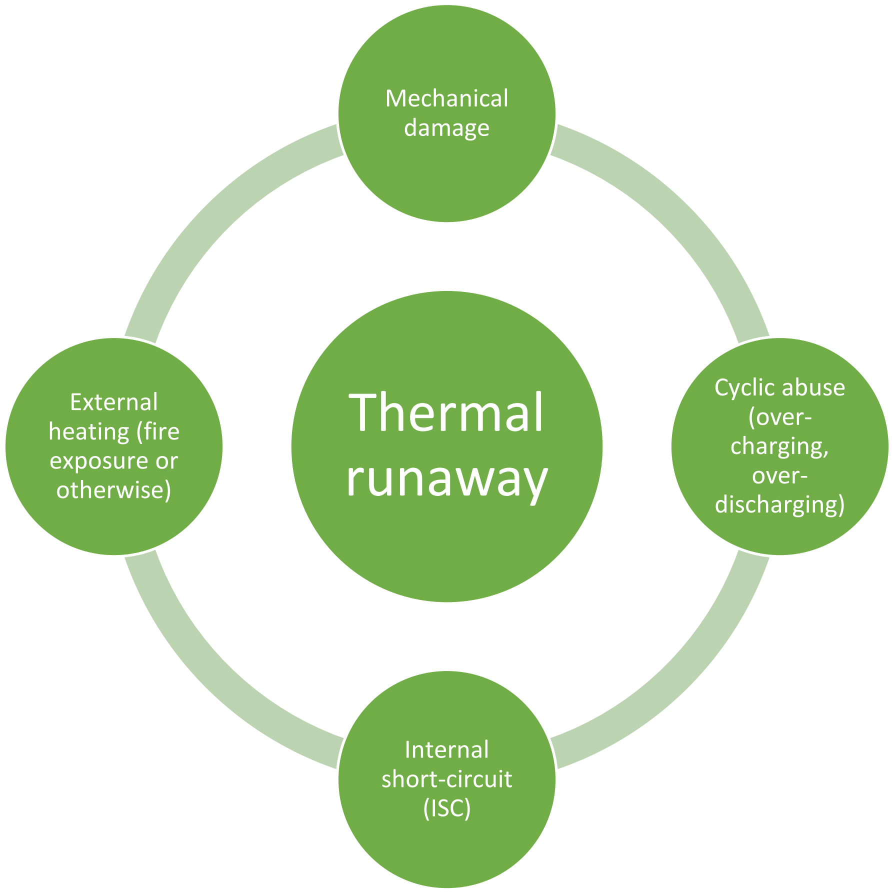


Figure 2-2 thermal runaway infographic

Thermal runaway is a problem of heat management (Börger et al., 2019). If a LIB begins to generate more heat than it can dissipate then the battery materials begin to break down and react with each other. This situation can arise as a result of overheating, either by internal cyclic abuse or external overheating, or from internal short circuits (ISC) (Ouyang et al., 2019).

Overheating can occur if the internal temperature becomes high enough, either by internal heat generation, or external heat exposure. The chemical reaction that makes LIBs so potent is naturally exothermic (Selman et al., 2001). If LIBs are charged or discharged beyond their design limits, cyclic abuse can occur; which can lead to thermal runaway. Over-charging can occur when a LIB is forced to a voltage above its rated capacity. When this occurs, the electrochemical reaction become irreversible and the internal cell temperature begins to rise as voltage continues to try and liberate lithium ions from the cathode even though the ions have been completely deposited to the anode (Ohsaki et al., 2005). Over-discharging, though less likely to initiate a thermal runaway event, is not impossible in larger battery packs. Irreversible damage to the electrolyte within a cell begins to occur when it is discharged below 0V (zero volt) (Guo et al., 2016). This will eventually open the door for internal short circuits to form, leading to thermal runaway.

Internal short circuits cause rapid, uncontrolled current transfer within the battery cell itself. These transfers can generate a tremendous amount of heat in a localized area in a short period of time (Santhanagopalan et al., 2009). ISC can be a result of internal faults like manufacturing defects (Feng, Ouyang, et al., 2018) or external damage which forces internal materials to come into contact with each other. Mechanical damage can initiate thermal runaway by deforming, or otherwise physically breaking down the layered structure of the battery, causing internal short circuits (Binghe Liu et al., 2018).

Regardless of how the internal temperature of a LIB increases thermal runaway can begin at relatively low temperatures. The first stage of thermal runaway occurs between the anode and electrolyte (Mikolajczak et al., 2011; Wang et al., 2012). This breakdown can begin at temperatures as low as 60°C (140°F). Once this temperature is reached, that is the when "thermal runaway" begins. As the runaway is taking place, the temperature and pressure inside the battery cell continues to increase due to the breakdown of materials. The electrolyte will begin to break down and react with the intercalated lithium atoms around 100°C (212°F). Once the temperature reaches around 130°C (266°F) the polymer separator begins to melt leading to the cathode and anode shorting out and further increasing the temperature of the cell (Mikolajczak et al., 2011; Wang et al., 2012). As the temperature continues to rise, eventually the breakdown and reactions of the various materials inside the cell will begin to release small amounts of oxygen. Wang et al (2012) suggests that the generation of oxygen inside the cell, coupled with the very high temperatures, and presence of flammable materials inside the cell, will begin to burn inside the cell. However, Mikolajczak et al (2011) suggests that the amount of oxygen created is so small, that it is insufficient to initiate an internal fire; further pointing out that no significant amount of oxygen is found in LIB cell vent gasses. It is worth nothing, however, that in any fire there is very little oxygen in the fire gasses [smoke] because the oxygen is consumed during combustion.

Many variables can affect the temperatures at which thermal runaway occurs. State of charge and LIB chemistry both influence LIB thermal stability (Lee et al., 2019; Ohneseit et al., 2023). Less energy dense chemistries, such as LFP, remain stable to higher temperatures than chemistries with higher energy density, such as NMC (Ohneseit et al., 2023). SOC is also an important factor in determining thermal stability because there is a direct correlation between electrical potential (voltage) and overall stored energy potential for a thermal runaway (Doose et al., 2023). Higher SOC will generally create a more energetic thermal runaway event.

2.4 Overview of Fire Classifications and Typical Fire Suppression

In order to correctly evaluate fire suppression methods against LIB thermal runaway, it is important to understand how thermal runaway is different from "fire". The Merriam-Webster dictionary defines "fire" as, "the phenomenon of combustion manifested in light, flame, and heat" ("fire," 2024). Thermal runaway certainly produces a lot of heat. But, is "combustion" occurring? In the Fire Protection Handbook, "combustion" is described as, "…an exothermic, or heat-producing, chemical reaction between some substance and oxygen." (NFPA, 2003). This chemical reaction seeks to take a fuel and oxidize it to a more stable material, such as carbon dioxide and water.

Let us look at a simplified example of a combustion reaction of wood (Papathanasiou, 2018):

$$6C_{10}H_{15}O_7 + HEAT = C_{50}H_{10}O + 10CH_2O \rightarrow 6CH_2O + 3O_2 = 6H_2O + 2CO_2 + 2CO + 2C + HEAT$$

The above chemical equation takes a simplified wood compound ($6C_{10}H_{15}O_7$) and adds heat. At approximately 150°C the wood begins to decompose and release gasses in a process called pyrolysis. One of the principal gasses that is released is formaldehyde ($C_{50}H_{10}O$). If heating is allowed to continue, at approximately 260°C the formaldehyde will react with the oxygen in the air ($3O_2$) and begin a self-sustaining, exothermic reaction (Papathanasiou, 2018).

Likewise, if we consider a combustion reaction of a flammable liquid such as ethanol we see a similar pattern (CK-12 Foundation, n.d.-a):

$$C_2H_5OH + 3O_2 + \text{IGNITION} = 2CO_2 + 3H_2O + \text{HEAT}$$

At elevated temperatures, or in the presence of an ignition source, the ethanol (C_2H_5OH) reacts with oxygen from the air ($3O_2$) and creates carbon dioxide ($2CO_2$) and water vapor ($3H_2O$) in an exothermic process.

Both of the above are classic examples of combustion via a rapid oxidation reaction with the air. Firefighting techniques are built around the understanding of combustion in this way. Firefighters and the public alike are taught to understand the ingredients of fire exist through the infographic of the "fire tetrahedron". Figure 2-3 is a common visualization of the fire tetrahedron.

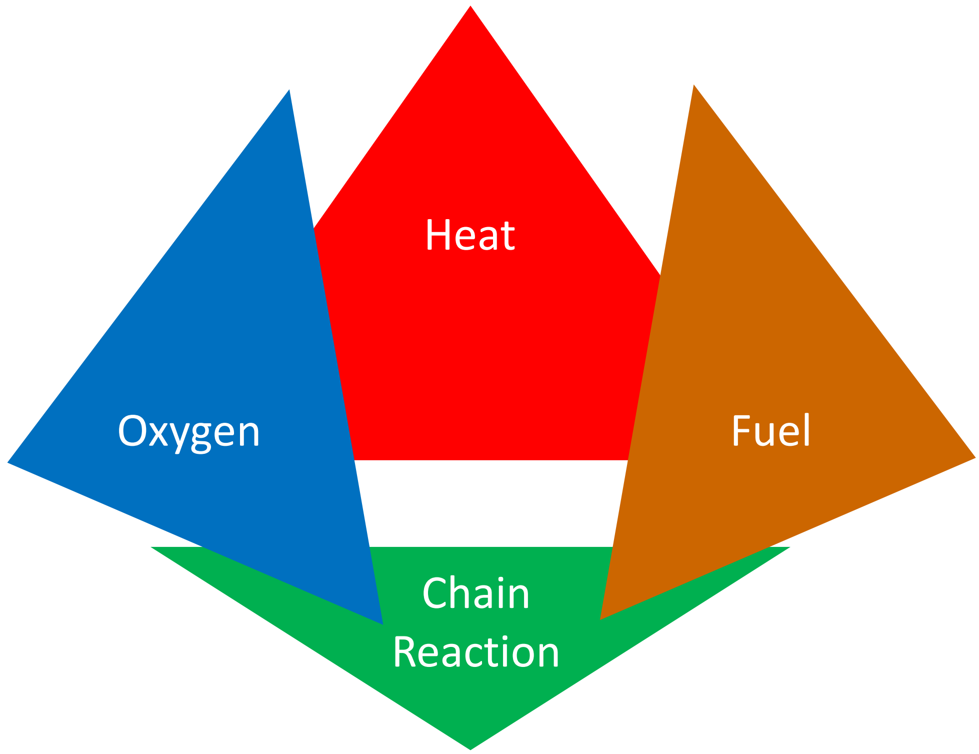


Figure 2-3 visualization of the fire tetrahedron

Oxygen, heat, fuel, and a chemical chain reaction are all required to exist simultaneously to start or sustain combustion. It is important to understand that “chemical reaction” in this context is specifically referring to a rapid oxidation reaction as has been described previously. To extinguish a fire this tetrahedron must be broken apart and the combustion process must be interrupted. The easiest way to prevent or stop a fire is to physically separate the fuel, oxygen, and heat or ignition source. The chemical chain reaction (combustion) will not begin if those three elements do not exist together. If physical separation is not possible, there are two primary mechanisms by which fires can be extinguished: cooling, and interrupting the chemical reaction.

Cooling can affect a fire in two ways. Cooling the fuel reduces the rate of pyrolysis of the fuel, and therefore reduce the rate of flammable vapor generation (Grant & Drysdale, 1997). Alternatively, the flame may be cooled by modifying the air that is supplying oxygen to feed the combustion (NFPA, 2003). If the oxygen concertation of the air is lowered, either by smothering or use of a gaseous extinguishing agent, then the heat begins to be absorbed rather than generated.

Interrupting the chemical chain reaction (combustion) involves introducing a new chemical to the combustion process. This new chemical also breaks down in the high heat of a fire, but instead of adding to the reaction, these new chemicals bind to oxygen molecules as they are in the middle of the oxidation reaction (NFPA, 2008). Once the oxygen molecules have been captured, a new, inert, compound is formed. The combustion process will stop, and the fire will be extinguished when there are not enough free oxygen molecules left to sustain the exothermic oxidation reaction (NFPA, 2008).

In contrast, the chemical reactions that are occurring during thermal runaway have less to do with taking oxygen from the air, and more to do with the reactions of the battery materials with each other. Wang et. al (2012). is a frequently cited paper that did an excellent job at explaining the reactions occurring between LIB materials during a thermal runaway. The first stage of thermal runaway can begin at temperatures as low as 70°C and involves the breakdown of the Solid-Electrolyte-Interface (SEI) as follows:

$$(CH_2OCO_2Li)_2 + HEAT \rightarrow Li_2CO_3 + C_2H_4 + CO + 1/2O_2 + HEAT$$

In the example from Wang et. al when the temperature inside the LIB reached 100°C the intercalated lithium begins to react with the organic solvent (ethylene carbonate in our example) used as the electrolyte. This reaction generates flammable hydrocarbon gasses.

$$2Li + C_3H_4O_3 \rightarrow Li_2CO_3 + C_2H_4 + HEAT$$

As exothermic process continues, the polymer separator melts around 130°C which allows the electrodes to short circuit. The added heat from the short circuiting allows the metallic oxide coating on the cathode to decompose. This reaction will release oxygen from the oxide layer which might then react with the hydrocarbon gasses that were generated during the reaction between the lithium and solvent.

Li_xCoO_2 + HEAT → $xLiCoO_2 + 1/3(1\text{-}x)Co_3O_4 + 1/3(1\text{-}x)O_2$

Co_3O_4 + HEAT → $3CoO = 1/2O_2CoO$ → $Co + 1/2O_2$ + HEAT

(Bombik, 2023; Wang et al., 2012)

2.5 Oxidation and its Role in Combustion and Electrochemistry.

Although, practically speaking, LIB thermal runaway and traditional fires, such as a camp fire, occur for very different reasons as discussed above. However, we must be careful when we talk about oxidation in its role during fires and thermal runaway. If we accept that fires are a byproduct of combustion ("fire," 2024), and combustion is a rapid oxidation reaction (NFPA, 2003) we must also acknowledge that oxidation itself is an electrochemical reaction that creates a change in electrical potential of two materials (CK-12 Foundation, n.d.-b). As any battery undergoes a charge/discharge cycle, oxidation (and the inverse, reduction) is occurring. This is because as a base metal is oxidized, it gives up an electron to the oxygen molecule, therefore becoming electronegative. Or, as the website LibreText Chemistry states,

Because the metals have lost electrons to oxygen, they have been oxidized; oxidation is therefore the loss of electrons. (CK-12 Foundation, n.d.-b)

So, is oxidation occurring during thermal runaway? From an electrochemistry standpoint, yes. If oxidation is occurring during a thermal runaway, is thermal runaway a combustion reaction? Again, if we strictly consider the definitions, yes, thermal runaway is a combustion reaction. However, we are probably safe to stop short of equating thermal runaway to fire. Going back to the illustration of the fire tetrahedron, we assume that those four elements (heat/ignition, oxygen, fuel, and a chemical chain reaction) must come together to create and sustain fire; and conversely those elements can be separated to extinguish a fire, or prevent it from occurring in the first place. This is where there is a clear difference between LIB thermal runaway and fire. LIBs contain everything they need to sustain a runaway reaction. Unlike isolating one of the parts of the fire tetrahedron to interrupt combustion and extinguish a fire, the parts of a LIB that are interacting with each other to fuel thermal runaway cannot be separated. Figure 2-4 illustrates how, although fire and thermal runaway share certain elements, they act in different ways.

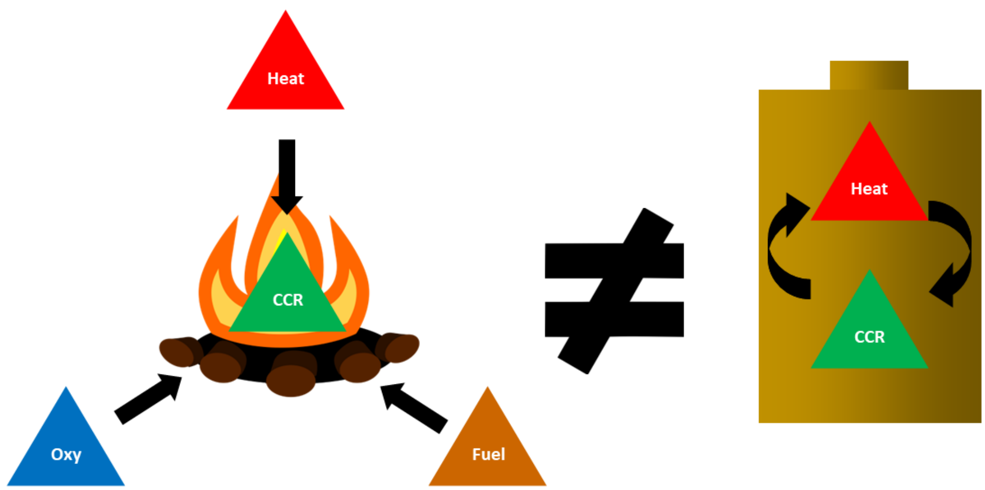


Figure 2-4 elements of the fire tetrahedron compared to the elements of thermal runaway.

2.6 Industry Perspectives

At the time of writing, a basic internet search for “lithium-ion battery fire protection” produces companies offering fire protection solutions based on the understanding of LIB thermal runaway-fueled fires as Class A, Class B, and/or Class D as defined by NFPA 10 (NFPA, 2022). Additionally, we see companies using the term “lithium battery” interchangeably with “lithium-ion battery”. We know that LIB thermal runaway-fueled fires don’t really fit into any of the existing NFPA 10 fire categories. So, it’s short-sighted to approach LIB thermal runaway-fueled fires as any specific class of fire. Also, the misunderstanding of lithium metal existing in a lithium-ion battery is wide-spread as terms such as “lithium battery” are used when referring to lithium-ion batteries. Lithium batteries, or “lithium metal batteries”, are a separate technology that utilize a different electrochemical reaction (Bin Liu et al., 2018).

Meanwhile, in professional firefighting, leaders are scrambling to keep up with the latest information. Most firefighting knowledge is derived from first-hand experience. The fire service is generally unaware of scientific research. The late Bobby Halton was widely regarded as one of the most influential leaders in the US fire service. In an opinion piece for Fire Engineering magazine, he mused

> *…as best I can tell after spending time with the best firefighters, folks in the industry, and serious researchers, the tactics for extinguishing these batteries are still under development. At this point, we don't have "experts" on extinguishing these batteries when they go into what is called "thermal runaway" … The best advice I have on lithium-ion battery issues is to contact the Fire Department of New York (FDNY) Hazardous Materials Division, which has embraced being a clearinghouse for the fire service on this issue.* (Halton, 2022)

In September of 2022, the FDNY hosted a symposium on LIB fire information and tactics. This symposium was put on in conjunction with the NFPA and the Underwriter's Laboratory Fire Safety Research Institute (UL FSRI). Presentations were given by the Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF), FDNY, and UL on their first-hand experience with LIB thermal runaway-fueled fires and fire investigations. Topics covered included E-mobility devices, personal electronics, vape pens, BESS, electric vehicles, and charging infrastructure. After the symposium, the FDNY made publicly available several internal white papers, training bulletins, and research published by the NFPA and UL (Ambrose, 2022).

Manufacturers such as Tesla, General Motors, and Rivian have published emergency response guides for firefighters responding to emergencies involving their products. These guides cover both high voltage shutdown, and fire protection. All three of the above manufactures suggest to use copious amounts of water, to the order of thousands of gallons per vehicle, to extinguish a fire and cool the battery pack (GM; Tesla). Rivian goes as far to say

…electric vehicle fires are best addressed with defensive firefighting and management of the environment to minimize risk. Only attempt to extinguish a fire if you have a specific need to do so." (Rivian, 2022)

In other words, "if a burning vehicle isn't posing a risk to anything else, consider just letting it burn."

Another aspect of LIB thermal runaway-fueled fire is how battery packs (or modules) are assembled. It is very difficult to affect the temperature of cells that may be undergoing thermal runaway because individual battery cells are typically within several layers of packaging. Cells may be bundled together with plastic wrap or metal casings to form modules. These modules may be further grouped together inside larger plastic or metal housings. Those larger housings could be within a cabinet, in the case of fixed energy storage, or within the chassis of an electric vehicle. Figure 2-5 illustrates how batteries may be incorporated into larger assemblies.

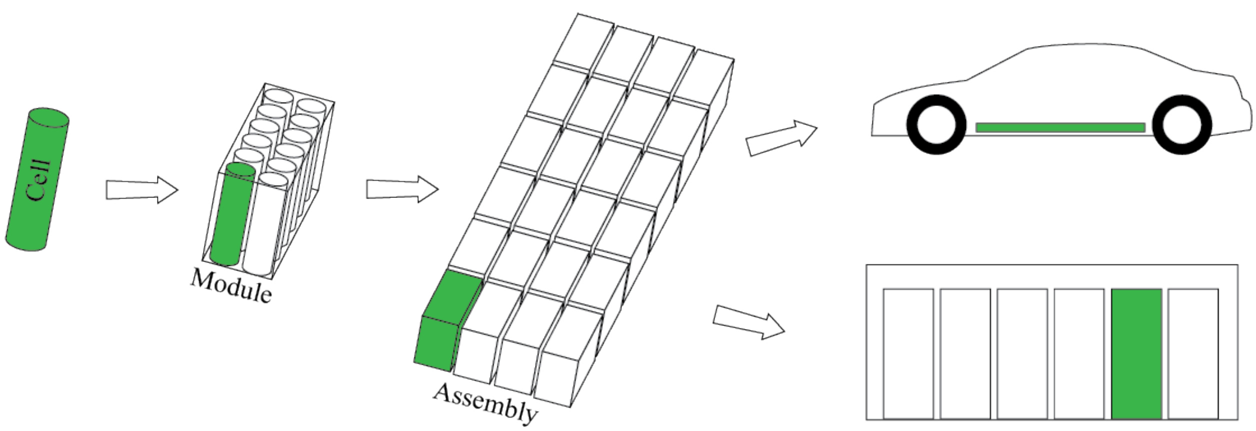


Figure 2-5 example of how battery cells may be incorporated into larger assemblies.

This creates challenges for fire protection and suppression as the driving force for fires that result from thermal runaway is not easily accessible by external intervention methods. As previously discussed, cooling may be a viable method of limiting the spread of thermal runaway. However, that assumes that the cooling medium (water) can actually affect the materials that are generating the heat. Without access to the

LIB cells, any cooling intervention will be ineffective as the cells in thermal runaway will need to expend their energy to the surrounding layers before being influenced by cooling. This is why the fire service frequently reports requiring tens of thousands of gallons (hundreds of thousands of liters) of water to "extinguish" an electric vehicle fire (CTIF, 2022). The source of the heat generation is protected from the cooling effects of water applied by the fire department as illustrated in Figure 2-6.

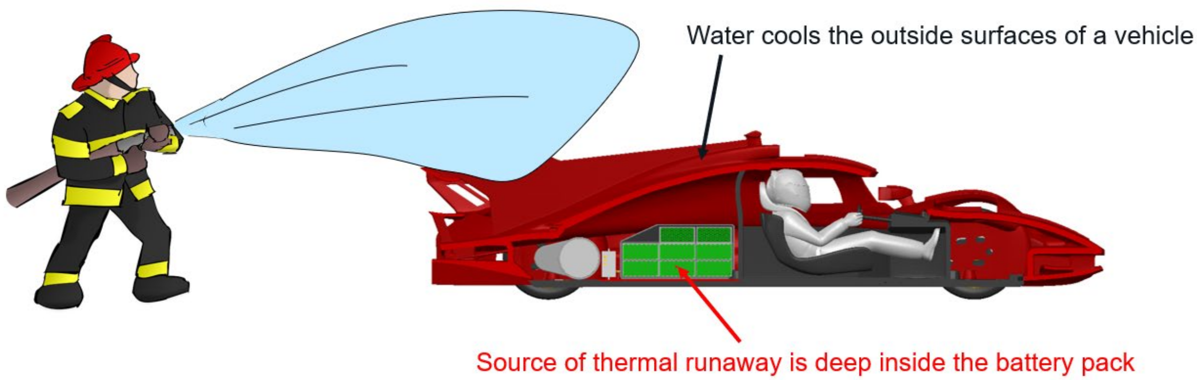


Figure 2-6 illustration of typical fire suppression methods on thermal runaway

2.7 Current Codes and Standards

NFPA 855 is the Standard for the Installation of Stationary Energy Storage Systems. If a battery is used for any purpose that is not designed to be moved around, then it falls under the scope of NFPA 855. This standard covers many different styles of energy storage, from mechanical to electrochemical. On the electrochemical (battery) front it covers many styles and chemistries of batteries. The goal of this standard, like any other NFPA standard, is to provide guidance on how to install the technology with the best interest of public safety (NFPA, 2023).

UL 9540 is the Standard for Safety of Energy Storage Systems and Equipment. Like NFPA 855, this UL standard provides guidance for many different types of energy storage, not just electrochemical, and not just lithium-ion chemistry. The UL standard goes into much greater detail regarding device safety by addressing how ESS are built, and the performance requirements of certain ESS components. UL 9540 also requires any ESS that wishes to meet the standard have a failure modes and effects analysis (FMEA) performed (UL, 2020a).

As a companion to UL 9540, the Underwriter's Laboratory also has standard 9450A which is the Test Method for Evaluating Thermal Runaway Fire Propagation. This test method is intended for ESS manufacturers to demonstrate the resistance of their energy storage product, that utilizes lithium-ion batteries, to thermal runaway events (UL, 2019).

UL 1642 is the Standard for Safety for Lithium Batteries. It is important to note that a "lithium battery" is different from a "lithium-ion battery". However, the batteries that fall under the scope of this standard, "…contain metallic lithium, or a lithium alloy, or a lithium ion…" (UL, 2020b) This standard provides manufacturers physical and electrochemical requirements to ensure the intrinsic safety of battery cells. Under most abuse cases, batteries that meet UL 1642 shall not explode or catch fire.

International Fire Code (IFC) began to include a section on Electrical Energy Storage Systems in the 2018 edition of the code (Section 1206). This section of the IFC contains similar information as NFPA 855, but is not the same as NFPA 855 (ICC, 2018).

In 2018 a Global Technical Regulation was published by the United Nations regarding Electric Vehicle Safety. This regulation…

> *…address potential safety risks of EVs while in use and after a crash event, including electrical shocks associated with the high voltage circuits of EVs and potential hazards associated with lithium-ion batteries and/or other Rechargeable Electrical Energy Storage Systems (REESS).* (UN, 2018)

The UN recognized that there is not a standard for evaluating thermal propagation during a runaway event in an EV. They echo the importance of understanding, and being able to quantify the thermal stability of EV batteries, but state that “further research is needed” and that “Several stakeholders have expressed their commitment to the task of developing the thermal propagation method…” (UN, 2018)

2.8 Conclusions

We’ve had a good understanding of how LIB thermal runaway occurs since the mid 2010’s. But, the fire service and fire protection industries are still trying to figure out how to extinguish thermal runaway-fueled fires. The process of communicating research findings to the people that would benefit most from the research is a practice known as “translational forensics” (Braxtan et al., 2023).

> *…translational forensics for structures in fire emphasizes on the acceleration of adaptation of research findings to the practices of fire investigation, prevention and protective designs.*

The fire service and fire protection industries best understand fires as based on which class they fall into according to NFPA 10. However, when we look at how those classes are defined, thermal runaway does not fit into any of those categories. Given what we know about LIB thermal runaway, it could be suggested that extinguishing a LIB that has undergone thermal runaway to the point of deflagration and fire is as likely as extinguishing a model rocket engine once it has been ignited. Additionally, the way in which li-ion batteries are incorporated into devices makes it difficult for fire protection efforts to be directly applied to the cells. More emphasis must be placed on identifying the early warning signs of a thermal runaway, and providing cooling measures so runaway doesn’t begin. At the very least, methods should be investigated to actively isolate LIB thermal events at the cell level so they do not propagate and involve much larger volumes of batteries.

The automotive industry was the first to publish specific information on LIB fire protection. Unfortunately, much of this information was a result of first-hand experience with fires and the lessons learned from firefighters. Stationary energy storage and BESS has been quickly following. Both fortunately and unfortunately, BESS fires have been far less frequent than EV fires, therefore the first-hand experience and lessons learned aren't as plentiful. NFPA 855 is relatively new, and energy storage has only been addressed in the IFC since 2018. The effectiveness of these standards may have yet to be proven.

Current practice dictates that EV fires could require thousands of gallons of water to cool and extinguish. If the amount of energy storage is scaled up from an EV to grid-level BESS unit, the amount of water that would be required to cool and extinguish a fire could be tens of thousands, if not hundreds of thousands of gallons of water; which even the best fire departments in the world would struggle to supply.

CHAPTER 3: EXPERIMENTAL STUDY (Paper 2)

3.1 Abstract

Lithium-ion (li-ion) batteries continue to make their way into more aspects of everyday life. Their high energy density compared to other forms of batteries have made them an attractive energy source for everything from hearing aids, to emergency backup power sources for entire cities. The risk of LIB thermal runaway-fueled fires resulted in tremendous amounts of ongoing research that include: 1) Figuring out the cause of LIB thermal runaway and 2) how to detect and prevent LIB thermal runaway and fires. A key take way from several observations of real-life battery fires from firefighting professionals is that little can be done once a LIB-fueled fire starts. To that end, more emphasis must be placed on researching methods of containing, or preventing thermal runaway in LIBs, which is the root cause of these fires, regardless of external factors. An experiment was developed to determine if thermal runaway of a LIB can be stopped while the battery is being subjected to an external heat source. A water spray method was devised to reduce the battery temperature during the tests. The batteries used in current study are pouch-type batteries. The test results indicated that, without water spray cooling, the heat source would generate a battery fire every time. Additionally, the batteries used in the experiment were placed at an extremely high state of charge (SOC), which exacerbates thermal runaway reactions. The experiment clearly showed that it is possible to prevent thermal runaway with an external cooling source.

3.2 Introduction

While it is unclear how often LIB fueled fires occur, they still pose a tremendous challenge for the global fire service (Durham, 2023). Reckless use and handling of these materials have created serious risks to public safety (Rubin, 2022). Due to the unique thermal runaway characteristics of LIBs, conventional fire protection and fire suppression technologies are not sufficient to address battery fires (Luo et al. 2018). The Arizona ES fire (DNV GL, 2020) and several EV fire cases demonstrated the challenges in fire protection technologies. The critical issue lies in the fact that it is hard to pinpoint electric faulting and fire initiation stages within a battery pack (Kim et al., 2018).

It has become apparent that LIB fires do not behave like fires as the fire service understands them (NTSB, 2020). In fact, what society generally calls a battery "fire" is not a fire at all due to the complicated electrochemical reaction that drives the rapid heating during a LIB thermal runaway (Ouyang et al., 2019; Wang et al., 2012). LIB thermal runaway is not something that can be "extinguished" once it begins.

As the fire service has been faced with LIB fueled fires, their approach to managing these fires has fallen into one of two categories: flow copious amounts of water for a prolonged period of time, or let it burn itself out (Rivian, 2022). However, there are use cases that preclude either one of those tactics. The aviation industry would like to look at LIBs as a potential energy source for aircraft engines. But, the fire risk is a concern that cannot be ignored (Tariq et al., 2017). The maritime industry would be another beneficiary of large-scale LIB use. But, in addition to the life safety risk, the environmental risks from LIB thermal runaway-fueled fires need to be addressed (Rao et al., 2015).

Therefore, in cases where LIB thermal runaway poses an unacceptable risk, more emphasis must be placed on prevention of thermal runaway, or limiting thermal runaway propagation.

At the most basic level, thermal runaway is a problem of energy balance. The battery is generating heat faster than that heat can be dissipated, which leads to a breakdown of materials and a self-sustaining electrochemical reaction which creates tremendous amounts of heat and pressure. So, what if, rather than trying to address thermal runaway when it presents as a fire or explosion, it is addressed as an energy balance problem by helping the battery dissipate heat before a runaway reaction can take place?

3.3 Thermal Runaway and Firefighting Challenges

As we talk about methods of fire protection we must return to our introduction to the "fire tetrahedron" from the previous chapter. According to the fire tetrahedron any fire requires four elements to progress: oxygen, fuel, heat/ignition source, and chemical chain reaction. Without all four of these elements existing at the same time, a fire will either not start, or be extinguished.

Fire suppression requires the ability to remove one of these elements from the other three. LIB thermal runaway therefore creates a challenge because all four of those elements occur within the cell during thermal runaway; they cannot be separated. Thermal runaway cannot be treated as a fire. Once thermal runaway begins within a cell, no external intervention can stop it.

3.4 Testing Methodology

An experiment was designed to test this theory; if additional cooling measures can be introduced to a lithium-ion battery when thermal runaway is immanent, the reaction can be stopped, or at least the severity of the failure can be reduced. Successful validation of this theory would make it possible to design new means of protection of the public and the environment from LIB thermal runaway.

The experiment was developed by determining what the desired output would look like, then selecting the appropriate hardware that would be able to generate such an output. Individual sensors were calibrated to ensure they provided a reliable output prior to being integrated with the other systems. Once all the hardware was procured all components were assembled in-situ. Hardware and software were joined in a series of “dress rehearsals” prior to introduction of testing specimens. Several specimens were tested early to allow for evaluation of data streams, and provide an opportunity to adjust hardware or software prior to final testing. Figure 3-1 is a process flow diagram of the workflow used to develop this experiment.

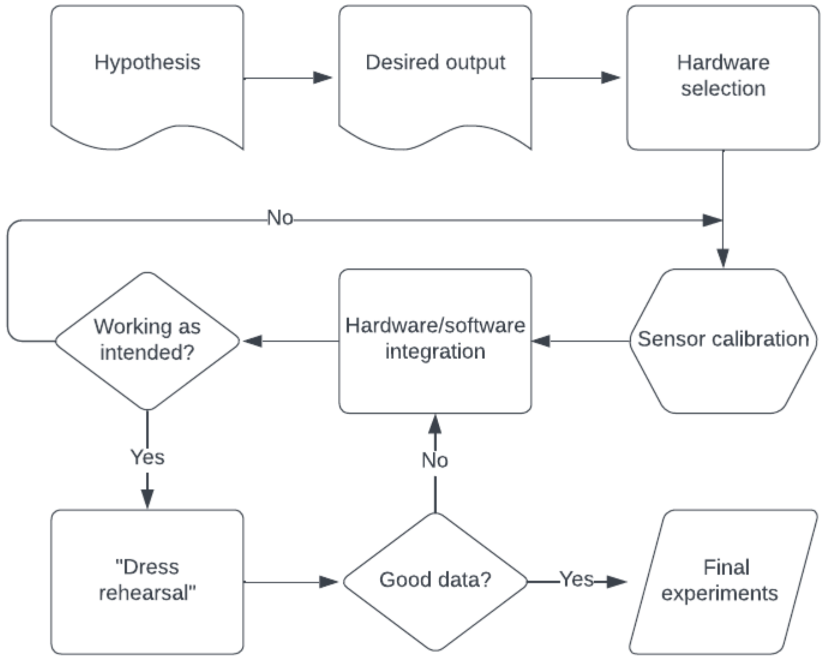


Figure 3-1 experimental process flow diagram

The experiment was comprised of two parts. Part one was a characterization of the batteries. They would be tested to failure in order to understand the failure mechanisms of the specific batteries used in the test. Part two was a repeat of part one, but with the additional external water cooling which would be initiated at a point in time as determined by part one. A schematic of the experimental apparatus is given in Figure 3-2.

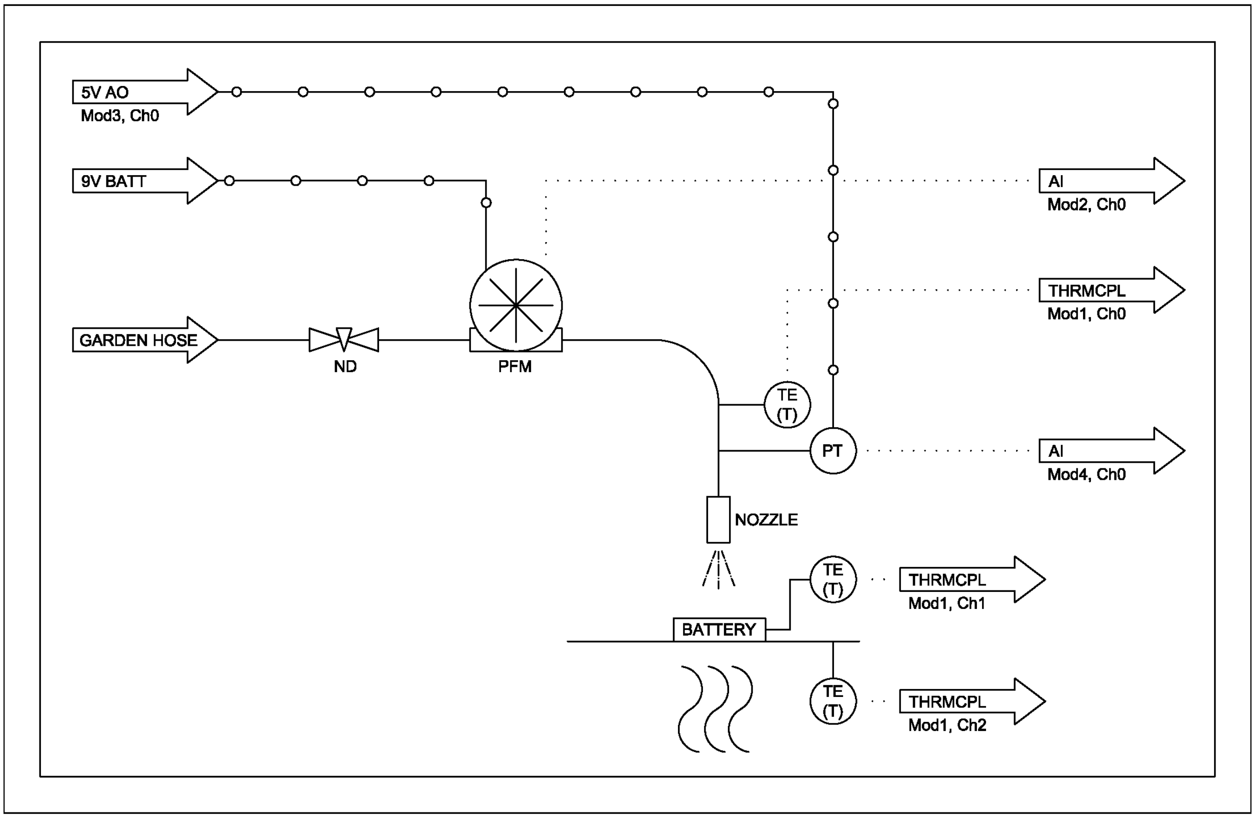


Figure 3-2 experimental apparatus schematic

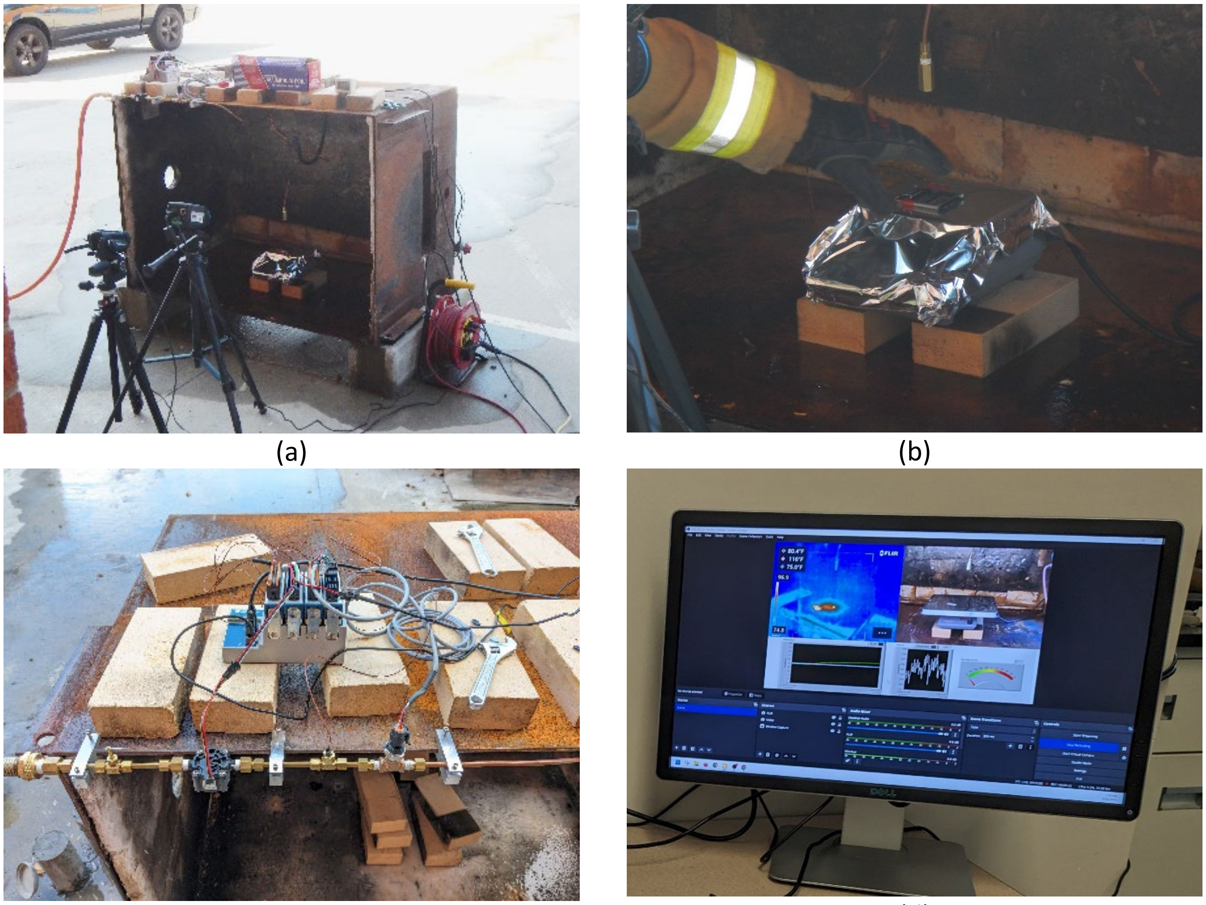
Unlike other LIB thermal runaway experiments this experiment is less interested in studying the mechanisms of how thermal runaway happens. Rather, it assumes that a thermal runaway has happened, or is immanent. Therefore, it was desired to construct the experiment is such a way that thermal runaway could be induced quickly, and reliably. The test apparatus is comprised of a hot plate, which is preset to 500°C, placed inside a 5-sided steel box. The inspiration for the apparatus comes from previous hotplate tests for battery thermal runaway (Coe, 2022). Other prominent LIB tests have used a nail penetration method for initiating thermal runaway (Doose et al., 2023; Ohneseit et al., 2023). However, for this test it was desired to induce thermal runaway without physically damaging the batteries. Modifications for this apparatus focus mainly on protection of testing hardware and improved test repeatability. The hot plate is covered with aluminum foil to protect the hot plate from battery shrapnel and water. A video camera and a thermal imaging camera are setup outside the box looking through the open side. The data acquisition system is placed on top of the box, with wires for the hot plate surface thermocouple and battery thermocouple running through a small hole to the hot plate area. Water tubing is attached to the box, which is used during part two of the experiment. This tubing allows for a garden hose to be connected, along with fittings for an in-line flow meter, pressure transducer, and thermocouple. The test monitoring station was placed inside an adjacent laboratory, away from the testing apparatus, to protect researchers from exposure to LIB catastrophic failure.

Signals from the thermocouples, flow meter, and pressure transducer were processed through a National Instruments CompactDAQ and recorded with LabVIEW. Video and thermal imaging feeds were composited together with a screen capture of LabVIEW through Open Broadcaster Software. A detailed equipment list is provided in Table 3-1.

Table 3-1 experimental equipment list

Description	Manufacturer	Model
Hot plate	Corning	PC-4000
Flow meter	Advanced Thermal Solutions	ATS-FM-34
Pressure transducer	Honeywell	480-MIPAN2XX500PSAXX-ND
Thermocouples	Nanmac	A4A-T-2-2-PK
Video camera	Canon	Aixia HF S200
Thermal imaging camera	FLIR	A600
Data acquisition system	National Instruments	cDAQ-9174 (with modules 9213, 9205, 9264, and 9219) running through LabVIEW 21.0
Live image feed management	Open Broadcaster Software	OBS Studio 30.0.0
Water flow control valve	McMaster-Carr	455K13
Water spray nozzle	McMaster-Carr	32885K144

Pictures of the completed apparatus are given in Figure 3-3(a)-(d).



(a) (b) (c) (d)

Figure 3-3 experimental setup photos

The specifications of the batteries used in the test are in Table 3-2.

Table 3-2 battery specifications

Manufacturer	Samsung
Model	EB-B220AC
Capacity	2600mAh/9.88Wh
Voltage (nominal/maximum)	3.8V/4.35V
Manufacture date	Sept. 2020

It was desired to have the batteries at a high state-of-charge (SOC). It has been shown that LIBs at higher SOC have more severe thermal runaway events (Ghiji et al., 2021; Lee et al., 2019). The batteries were charged to approximately 90% SOC using a Neware battery testing system, Model No: CT-4008Tn-5V6A-S1-U. In all, 15 identical batteries were prepared for testing.

Part one of the experiment, the characterization phase, involved heating batteries until they failed. To do this, a battery was prepared by taping the thermocouple to the long edge of the battery, and placing that battery on the hot plate with the long edge facing the cameras. This style of battery will fail along the edge where the connection terminals are (short edge), so it is important to have one of the long edges facing the open side of the box so battery components are not ejected from the box during failure. Once the battery was in place, data logging was initiated on the data acquisition system, thermal imaging system, and video capture system. With all data being recorded, power was supplied to the hot plate which then began to heat to its 500°C setpoint. The test was allowed to run until battery failure. After battery failure, all data logging was discontinued. This test was conducted a total of three times to confirm consistency of results.

The experimental procedure for part two is identical to part one up until a predetermined temperature before battery failure. That temperature would be the point at which thermal runaway would be immanent without immediate intervention. At that temperature a water spray was introduced to the top of the battery. The hot plate remained on, while the water spray was on, until the total test duration reached ten minutes. At the ten-minute mark the hot plate was turned off while water continued to flow. After an additional five minutes the water spray was turned off. The battery continued to be observed, and data continued to be collected for an additional fifteen minutes with the intention of looking for any signs of battery heating after the discontinuation of the cooling water. This test was also conducted a total of three times to confirm consistency of results.

3.5 Results and Discussion

3.5.1 Part 1

Notable findings from the tests of part one were the stability of the battery until failure, and an obvious physical deformity prior to failure. There was no recorded rise in temperature prior to battery failure; no “advanced warning”. The temperature rate-of-rise followed that of the hot plate until the battery failed. Figure 3-4 is a plot of battery temperature during the part one test.

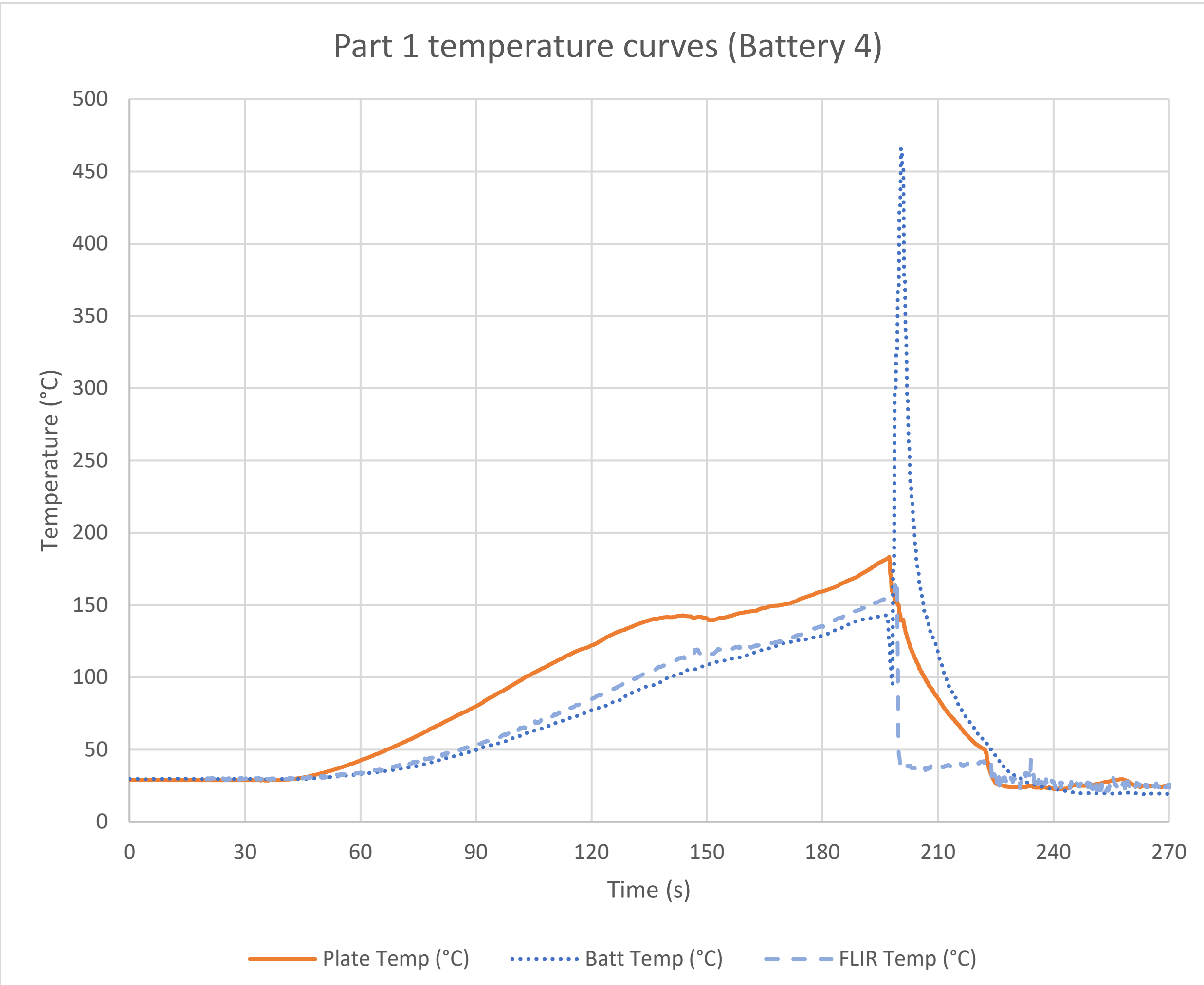


Figure 3-4 temperature curves from part 1

The other notable finding was that upon review of the video footage of the tests, the batteries swelled over the span of roughly 15 seconds beginning at 94°C as indicated by the battery thermocouple or 85°C as indicated by thermal imagery. Figure 3-5(a)-(d) are still frames captured by the thermal imaging camera with the outline of the battery highlighted.

Figure 3-5 battery images from part one showing swelling

Swelling of a LIB is an indication that pressure inside the battery is increasing from material decomposition (Feng, He, et al., 2018). Data collected during the part one tests indicated that about 1 minute after the battery temperature reached 100°C failure occurred.

As a result of the deformity observation of part one, it was decided that the temperature threshold for initiating cooling measures in part two would be 100°C. Figure 3-6(a)-(c) are images of the three LIB specimens that were tested in Part 1.

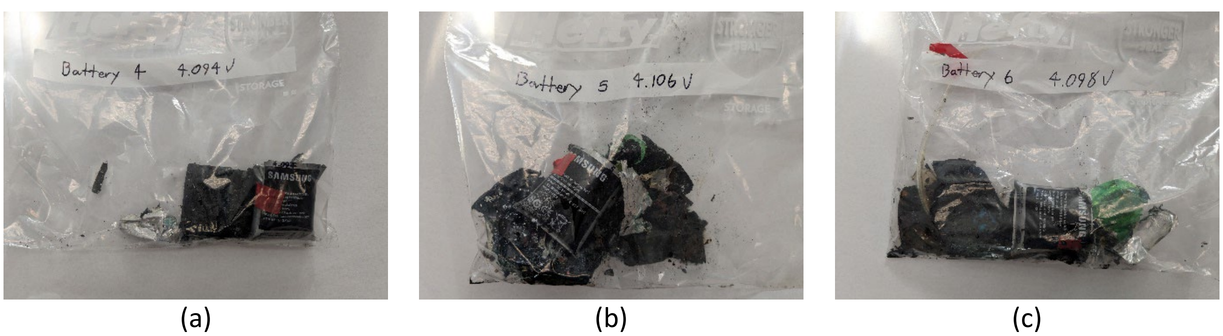


Figure 3-6 LIB specimens at the conclusion of Part 1 tests

3.5.2 Part 2

The initial conditions for Part 2 of the test were the same as Part 1. As noted in Part 1, a battery deformity was noticed at 100°C so this temperature was used as the signal to initiate the water spray. Figure 3-7 is a plot of battery temperature, and water mass flow during the part two test.

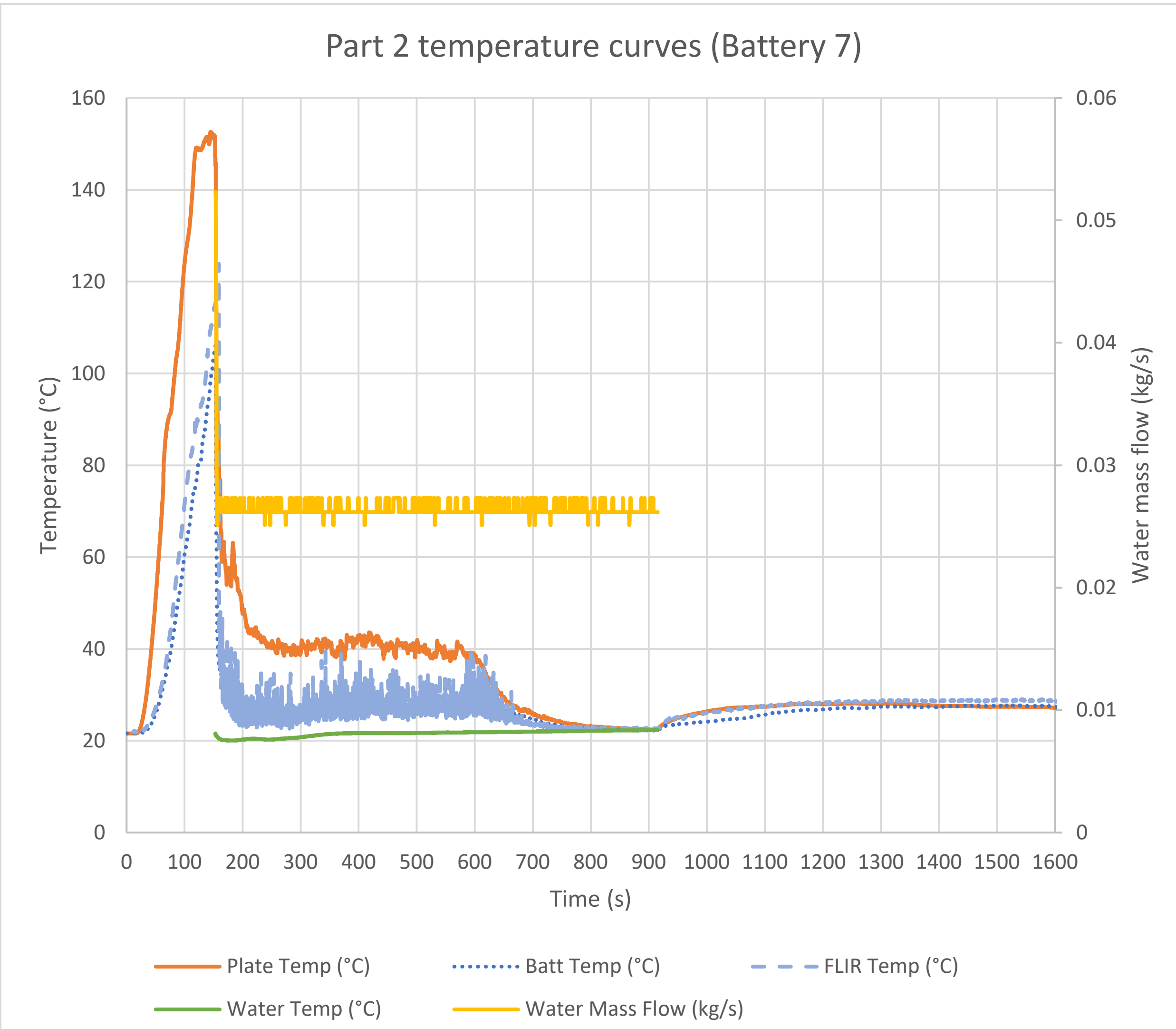
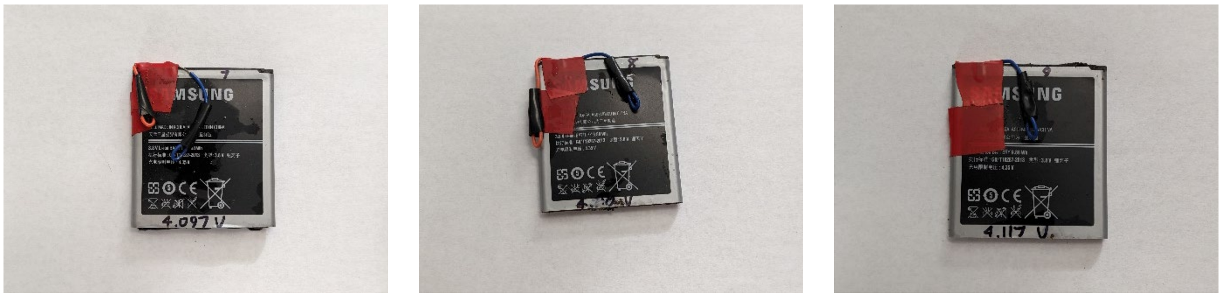


Figure 3-7 temperature curves from part 2 along with water mass flow

LIB temperature briefly exceeded 100°C prior to introduction of the water spray. Then the temperature quickly dropped. During the next 7 minutes the temperature fluctuates but neither trends up nor down. This may be attributed to the hot plate remaining on, trying to put heat into the battery, while the water spray tries to cool the battery. Once the water spray is discontinued the temperature fluctuations smooth out and reach an equilibrium temperature a few degrees above the beginning-of-test temperature. Figures 3-8(a)-(c) show the conditions of the Part 2 specimens after testing.



(a) (b) (c)

Figure 3-8 condition of test specimens after Part 2 tests

3.5.3 Findings

Figure 3-9 is the plots of part one and two together.

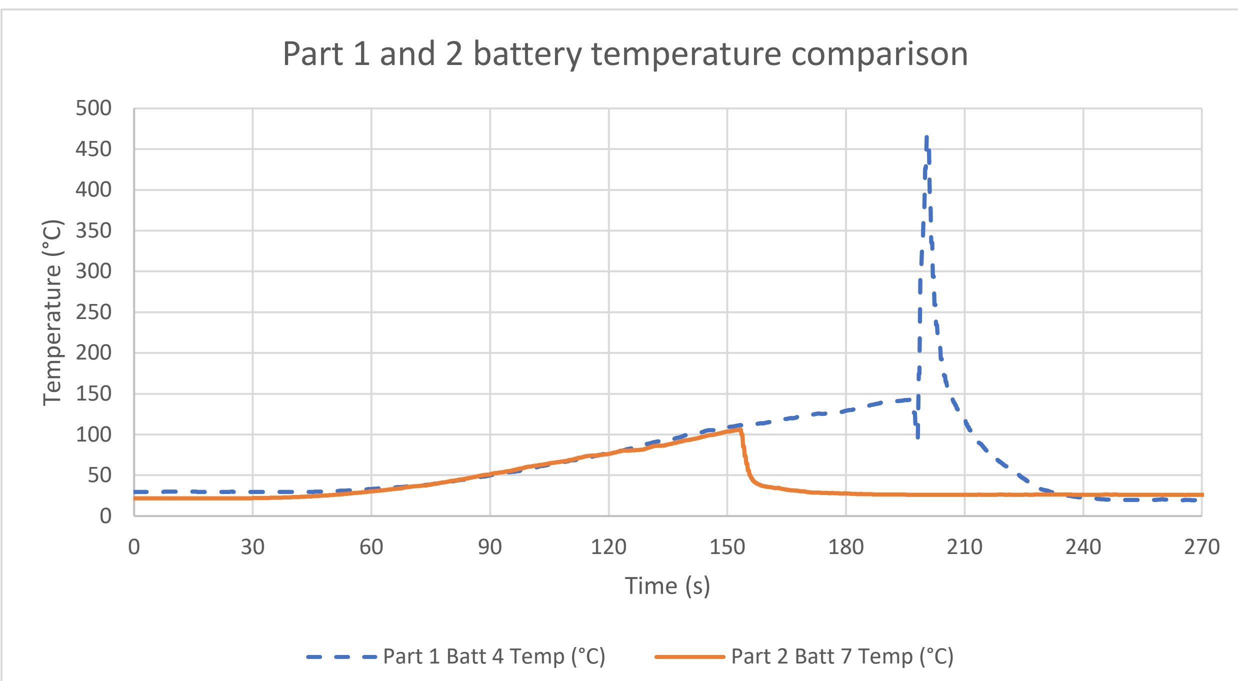


Figure 3-9 overlay of part1 and 2 curves

Figure 3-10, along with physical evidence that the battery did not fail during the part two test suggests that early cooling may be a viable option for thermal runaway prevention. Additionally, the batteries tested in part two were checked for voltage after the conclusion of the tests. Before and after voltages are given in Table 3-3. Seeing that the batteries were still very close to their initial voltage indicates that the specimens did not experience a catastrophic internal failure.

Table 3-3 battery voltages before and after testing

Battery #	Used in	Pre-test voltage	Post-test voltage/SOC
4	Part 1	4.094V	*destroyed*
5	Part 1	4.106V	*destroyed*
6	Part 1	4.098V	*destroyed*
7	Part 2	4.097V	4.095V
8	Part 2	4.110V	4.105V
9	Part 2	4.117V	4.114V

The test apparatus provided highly repeatable qualitative data. However, one instance of residual water from a previous test caused an erratic temperature profile of the hot plate during a Part 1 test, and during the final two tests of Part 2 the flow meter failed. The results of all three tests of both Parts 1 and 2 were similar to each other. However, the raw data is difficult to compare apples-to-apples. Therefore, in the above descriptions, only the most complete data set from each part of the experiment is presented. The data sets from the other tests are presented in Appendix II and III.

3.6 Conclusion

This experiment demonstrates that thermal runaway may be prevented by introducing cooling measures. Additional research in the area of advanced cooling as a means to prevent thermal runaway is warranted. As the results of this experiment illustrate, catastrophic battery failure was prevented with advanced cooling 60 seconds before which such a failure would have occurred. Also, the battery integrity appears to have been maintained as battery voltage before and after the part two test was unchanged.

The results of this experiment suggest that with the availability of battery telemetry, and direct access to the cells of a battery energy storage system, a fire protection system may be designed that could limit thermal runaway propagation through advanced cooling, or possibly prevent thermal runaway altogether using only a small fraction of cooling medium than would otherwise be required for a fully-developed thermal runaway-fueled fire.

Further research should incorporate established test methods from an organization such as UL, ASTM, ANSI, or FM Global for heating batteries and data collection. Additionally, the heat release rate of the battery should be measured to further evaluate the energy balance between a battery in thermal runaway (Chen et al., 2020) and the necessary flow of a cooling medium to control such a runaway. The experiment should also be repeated using different styles of battery (calendrical, prismatic, etc), and different chemistries (LFP, NMC, etc), to see if the results are the same.

Practically speaking, given the different form factors of LIB powered products, how an advanced cooling system could be integrated into new and existing products would need to be evaluated.

CHAPTER 4: CONCLUSION

LIB research is advancing at an amazing rate. New technologies that promise to bring safer batteries are undoubtedly on the horizon. In the meantime, there is an incredible amount of LIB energy storage that will be constructed before the tides change. Thermal runaway and the resulting fires will continue to be a challenge for many years to come. The fire service shouldn't need to flow tens of thousands of gallons of water (hundreds of thousands of liters) to control thermal runaway. It is possible that if LIB energy storage construction includes a means to directly cool the cells thermal runaway propagation can be halted using a fraction of the resources in a fraction of the time.

The experimental work depicted in the current study successfully demonstrated that if direct access to the LIB cells is available cooling intervention can be introduced that prevents thermal runaway from occurring. This intervention would require significantly less water than what has been used by professional firefighters when fighting li-ion thermal runaway-fueled fires. The testing apparatus that was developed to perform this test had a high degree of repeatability which will certainly lend itself to future testing.

The following summarizes the outcomes of the current study:

1) The fire service and fire protection industries see thermal runaway as "fires" and are approaching the problem as they would with any other fire.
2) Current approaches for incorporating LIBs into devices make it difficult for fire protection efforts to be directly applied to the cells. Hence, emphasis must be placed on identifying the early warning signs of a thermal runaway, and providing cooling measures so runaway does not begin.
3) The automotive industry was the first to publish specific information on LIB fire protection. Most of the understandings are the results of first-hand experience with fires and the lessons learned by the fire service.

4) Stationary energy storage and BESS fires have been far less frequent that EV fires, therefore the first-hand experience and lessons learned are not as plentiful.
5) NFPA 855 is relatively new, and energy storage has only been addressed in the IFC since 2018. The effectiveness of these standards may have yet to be proven.
6) The experiment conducted in this study demonstrated that thermal runaway may be prevented by introducing cooling measures. The results of this experiment illustrated that battery failure can be prevented with advanced cooling 60 seconds before which a catastrophic failure would have occurred. Also, the battery integrity appears to have been maintained as battery voltage before and after the Part 2 test was unchanged.
7) The results of the experiment suggest that with the availability of battery telemetry, and direct access to the cells of a BESS, a fire protection system may be designed that could limit thermal runaway propagation through advanced cooling, or possibly prevent thermal runaway altogether using only a small fraction of the cooling medium than would otherwise be required for a fully-developed thermal runaway-fueled fire.

CHAPTER 5: RECOMMENDATIONS FOR FUTURE STUDIES

The testing that was performed had a high degree of repeatability. However, several of the data streams needed to be manually synchronized after the fact. This resulted in a large post-test effort to index the data streams. An integrated system should be developed to either put all data into a single stream, or somehow provide a common time stamp to all unique data streams. Also, a better method of heating the LIBs should be investigated. Although the aluminum foil protected the hot plate and allowed for a quick reset the aluminum may have affected heat transfer to the LIB from the hot plate.

To further develop the system for advanced cooling of a thermal runaway, the tests outlined in this experiment should be repeated with different batteries at different initial conditions; different form factors (pouch, prismatic, cylindrical, etc), different chemistries (LFP, NMC, etc), and different SOC (30%, 50%, 75%). Multi-cell battery packs should also be assembled and tested. Multi-cell tests could have an additional component where an “initiating cell” is allowed to go into thermal runaway, but direct cooling is applied to protect the neighboring cells. Another consideration to investigate is the electrical effect of flowing water, which is electrically conductive, through a charged battery pack. Does this create a new risk? Would advanced cooling be as effective with a non-conductive fluid cooling medium?

Another area for research would be how to make advanced cooling an automatic process. Can a fire protection system be integrated with a BMS? Given how quickly thermal runaway can occur, what other ways could a stand-alone system monitor battery cells that would allow for early intervention?

With enough data to support early intervention, can a correlation be made between battery capacity and the amount of water that would be required to prevent thermal runaway, or runaway propagation? Certainly, some sort of full-scale test would be warranted to confirm that the results of small-scale tests can be effectively implemented in a commercial-scale application.

REFERENCES

Ambrose, P. (2022). *FDNY Shares Fire, Hazmat Lessons on Lithium-Ion Batteries*. HazmatNation. https://www.hazmatnation.com/news/fdny-shares-fire-hazmat-lessons-on-lithium-ion-batteries/

Blum, A. F., & Long, R. T. J. (2016). *Hazard Assessment of Lithium Ion Battery Energy Storage Systems*. F. P. R. Foundation.

Bombik, A. (2023). *Thermal Runaway: Why it can't be stopped* [Presentation]. EVRSafe, Charlotte, NC.

Börger, A., Mertens, J., & Wenzl, H. (2019). Thermal runaway and thermal runaway propagation in batteries: What do we talk about? *Journal of Energy Storage*, *24*, 100649. https://doi.org/https://doi.org/10.1016/j.est.2019.01.012

Branquinho, L. (2017). *Richard Hammond's crash: Why did his EV catch fire?* News24. https://www.news24.com/life/motoring/cardoctor/fuel_focus/richard-hammonds-crash-why-did-his-ev-catch-fire-20170614

Braxtan, N., Chen, S.-E., Kimble, J., Zhao, T., & Huhn, E. (2023). Translational Forensics in Li-Ion Battery Forensics to Building Fire Studies. *Journal of Performance of Constructed Facilities*, *37*(2), 02523001. https://doi.org/doi:10.1061/JPCFEV.CFENG-4313

Charalambous, P. (2023). *Amid a rise in fires and deaths, New York City enacts new e-bike rules*. ABC News. https://abcnews.go.com/US/amid-rise-fires-deaths-new-york-city-enacts-e-bike-law/story?id=97984159

Chen, H., Buston, J. E. H., Gill, J., Howard, D., Williams, R. C. E., Rao Vendra, C. M., Shelke, A., & Wen, J. X. (2020). An experimental study on thermal runaway characteristics of lithium-ion batteries with high specific energy and prediction of heat release rate. *Journal of Power Sources*, *472*, 228585. https://doi.org/https://doi.org/10.1016/j.jpowsour.2020.228585

Chombo, P. V., & Laoonual, Y. (2020). A review of safety strategies of a Li-ion battery. *Journal of Power Sources*, *478*, 228649. https://doi.org/https://doi.org/10.1016/j.jpowsour.2020.228649

CK-12 Foundation. (n.d.-a). *Combustion Reactions*. LibreTexts Chemistry. Retrieved 2024/01/25 from https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introductory_Chemistry_(CK-12)/11%3A_Chemical_Reactions/11.06%3A_Combustion_Reactions

CK-12 Foundation. (n.d.-b). *Oxidation-Reduction Reactions*. LibreTexts Chemistry. Retrieved 2024/03/31 from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/04%3A_Reactions_in_Aqueous_Solution/4.04%3A_Oxidation-Reduction_Reactions

Coe, C. S. (2022). *Experimental Study for Detection of Thermal Runaway, Explosion, and Fire in Li-Ion Batteries Initiated by Hot Plate Method* (Publication Number 29326182) [M.S., The University of North Carolina at Charlotte]. Dissertations & Theses @ University of North Carolina Charlotte; ProQuest Dissertations & Theses Global. United States -- North Carolina.

CPSC. (2006a). *Dell Announces Recall of Notebook Computer Batteries Due To Fire Hazard*. Consumer Product Safety Comission. Retrieved 02/05/2024 from https://www.cpsc.gov/Recalls/2006/dell-announces-recall-of-notebook-computer-batteries-due-to-fire-hazard

CPSC. (2006b). *HP Recalls Notebook Computer Batteries Due to Fire Hazard*. Consumer Product Safety Comission. Retrieved 02/05/2024 from https://www.cpsc.gov/Recalls/2006/hp-recalls-notebook-computer-batteries-due-to-fire-hazard

CTIF. (2022). *Up to 150 000 liters of water needed to put out a fire in an electric car*. International Association of Fire and Rescue Services. https://ctif.org/news/150-000-liters-water-needed-put-out-fire-electric-car#:~:text=...Teslas%20may%20take%20up,a%20parking%20lot%20car%20fire.

DNV GL. (2020). *McMicken battery energy storage system event technical analysis and recommendations. Report no 10209302-HOU-R-01*. Arizona Public Service.

Doose, S., Hahn, A., Fischer, S., Müller, J., Haselrieder, W., & Kwade, A. (2023). Comparison of the consequences of state of charge and state of health on the thermal runaway behavior of lithium ion batteries. *Journal of Energy Storage*, *62*, 106837. https://doi.org/https://doi.org/10.1016/j.est.2023.106837

Durham, P. (2023). *Lithium-ion battery fires: The missing data*. Retrieved 11/16/2023 from https://www.firerescue1.com/lithium-ion-battery-fires/articles/lithium-ion-battery-fires-the-missing-data-vuR8fCKUZgq55Vpm/

Electric Power Research Institute. *BESS Failure Event Database* https://storagewiki.epri.com/index.php/BESS_Failure_Event_Database

Feng, X., He, X., Ouyang, M., Wang, L., Lu, L., Ren, D., & Santhanagopalan, S. (2018). A Coupled Electrochemical-Thermal Failure Model for Predicting the Thermal Runaway Behavior of Lithium-Ion Batteries. *Journal of The Electrochemical Society*, *165*(16), A3748. https://doi.org/10.1149/2.0311816jes

Feng, X., Ouyang, M., Liu, X., Lu, L., Xia, Y., & He, X. (2018). Thermal runaway mechanism of lithium ion battery for electric vehicles: A review. *Energy Storage Materials*, *10*, 246-267. https://doi.org/https://doi.org/10.1016/j.ensm.2017.05.013

Ferguson, J. (2013). *APS fire probed*. Arizona Daily Sun. https://azdailysun.com/news/local/aps-fire-probed/article_1de2e924-ab0a-5e71-9a3a-6942c2d1c9bb.html

fire. In. (2024). *Merriam-Webster Dictionary*. Retrieved 2024/01/24, from https://www.merriam-webster.com/dictionary/fire

Geisige, J. (2022). *How a Lithium Ion Battery Actually Works // Photorealistic // 16 Month Project* [YouTube video]. https://www.youtube.com/watch?v=4-1psMHSpKs

Ghiji, M., Edmonds, S., & Moinuddin, K. (2021). A Review of Experimental and Numerical Studies of Lithium Ion Battery Fires. *Applied Sciences*, *11*(3). https://doi.org/10.3390/app11031247

GM. *First Responders Guides, Rescue Sheets, and Quick Reference Sheets*. General Motors. Retrieved 02/10/2023 from https://www.gmstc.com/index.php/first-responders/

Grant, G. B., & Drysdale, D. D. (1997). *The Suppression and Extinction of Class 'A' Fires Using Water Sprays*. Home Office Fire Research and Development Group.

Green Car Congress. (2006, 11/02/2006). *Avestor Shuts Down*. Green Car Congress. https://www.greencarcongress.com/2006/11/avestor_shuts_d.html

Guo, R., Ouyang, M., Lu, L., & Feng, X. (2016). Mechanism of the entire overdischarge process and overdischarge-induced internal short circuit in lithium-ion batteries. *Scientific Reports*, *6*, 30248. https://doi.org/10.1038/srep30248

Halton, B. (2022). *It's What We Do*. Fire Engineering. https://www.fireengineering.com/leadership/its-what-we-do/

Hill, D. (2020). *McMicken Battery Energy Storage System Event Technical Analysis and Recommendations*.

Hollister, S. (2016). *Here's why Samsung Note 7 phones are catching fire*. CNET. https://www.cnet.com/tech/mobile/why-is-samsung-galaxy-note-7-exploding-overheating/

ICC. (2018). International Fire Code. In: International Code Council.

IEA. (2022). *Commissioned EV and energy storage lithium-ion battery cell production capacity by region, and associated annual investment* https://www.iea.org/data-and-statistics/charts/commissioned-ev-and-energy-storage-lithium-ion-battery-cell-production-capacity-by-region-and-associated-annual-investment-2010-2022

KHOU. (2017). *Train car carrying Lithium batteries explodes near downtown Houston*. KHOU. https://www.khou.com/article/news/local/train-car-carrying-lithium-batteries-explodes-near-downtown-houston/285-433576556

Kim, T., Makwana, D., Adhikaree, A., Vagdoda, J. S., & Lee, Y. (2018). Cloud-Based Battery Condition Monitoring and Fault Diagnosis Platform for Large-Scale Lithium-Ion Battery Energy Storage Systems. *Energies*, *11*(1).

Lamb, J., Torres-Castro, L., Hewson, J. C., Shurtz, R. C., & Preger, Y. (2021). Investigating the Role of Energy Density in Thermal Runaway of Lithium-Ion Batteries with Accelerating Rate Calorimetry. *Journal of The Electrochemical Society*, *168*(060516). https://doi.org/10.1149/1945-7111/ac0699

Lee, C., Said, A. O., & Stoliarov, S. I. (2019). Impact of State of Charge and Cell Arrangement on Thermal Runaway Propagation in Lithium Ion Battery Cell Arrays. *Transportation Research Record*, *2673*(8), 408-417. https://doi.org/10.1177/0361198119845654

Liu, B., Jia, Y., Juan, L., Sha, Y., Chunhao, Y., Zihan, H., Wang, L., Yangxing, L., & Jun, X. (2018). Safety issues caused by internal short circuits in lithium-ion batteries. *Journal of Materials Chemistry A*, *6*. https://doi.org/10.1039/C8TA08997C

Liu, B., Zhang, J.-G., & Xu, W. (2018). Advancing Lithium Metal Batteries. *Joule*, *2*(5), 833-845. https://doi.org/https://doi.org/10.1016/j.joule.2018.03.008

Mikolajczak, C., Kahn, M., White, K., & Long, R. T. (2011). *Lithium-Ion Batteries Hazard and Use Assessment*. Springer. https://doi.org/10.1007/978-1-4614-3486-3

NFPA. (2003). *Fire Protection Handbook* (19 ed., Vol. 1). National Fire Protection Association.

NFPA. (2008). *Fire Protection Handbook* (20 ed., Vol. 2). National Fire Protection Association.

NFPA. (2022). Standard for Portable Fire Extinguishers. In (Vol. NFPA 10). Quincy, MA: National Fire Protection Association.

NFPA. (2023). Standard for the Installation of Stationary Energy Storage Systems. In (Vol. NFPA 855). Quincy, MA: National Fire Protection Association.

NHTSA. (2012). *Chevrolet Volt Battery Incident Overview Report*. National Highway Transportation Safety Board. https://static.nhtsa.gov/odi/inv/2011/INRP-PE11037-49880.pdf

NTSB. (2020). *Safety Risks to Emergency Responders from Lithium-Ion battery Fires in Electric Vehicles. Safety Report NTSB/SR-20/01*. National Highway Transportation Safety Board.

Ohneseit, S., Finster, P., Floras, C., Lubenau, N., Uhlmann, N., Seifert, H. J., & Ziebert, C. (2023). Thermal and Mechanical Safety Assessment of Type 21700 Lithium-Ion Batteries with NMC, NCA and LFP Cathodes–Investigation of Cell Abuse by Means of Accelerating Rate Calorimetry (ARC). *Batteries*, *9*(5), 237. https://www.mdpi.com/2313-0105/9/5/237

Ohsaki, T., Kishi, T., Kuboki, T., Takami, N., Shimura, N., Sato, Y., Sekino, M., & Satoh, A. (2005). Overcharge reaction of lithium-ion batteries. *Journal of Power Sources*, *146*(1), 97-100. https://doi.org/https://doi.org/10.1016/j.jpowsour.2005.03.105

Orendorff, C. J. (2012). The role of separators in lithium-ion cell safety. *The Electrochemical society interface*, *21*(2), 61.

Ouyang, D., Chen, M., Huang, Q., Weng, J., Wang, Z., & Wang, J. (2019). A Review on the Thermal Hazards of the Lithium-Ion Battery and the Corresponding Countermeasures. *Applied Sciences*, *9*(12). https://doi.org/10.3390/app9122483

Papathanasiou, S. (2018). *Wood Fire & Chemical Reactions*. See The Air. Retrieved 2024/01/24 from https://seetheair.org/2018/08/03/wood-fire-chemical-reactions/

Qian, H., Zhang, J., Lai, J. S., & Yu, W. (2011). A high-efficiency grid-tie battery energy storage system. *IEEE Transactions on Power Electronics*, *26*(3), 886-896. https://doi.org/10.1109/TPEL.2010.2096562

Rao, H., Huang, Z., Zhang, H., & Xiao, S. (2015, 25-28 June 2015). Study of fire tests and fire safety measures on lithiumion battery used on ships. 2015 International Conference on Transportation Information and Safety (ICTIS), Reddy, M. V., Mauger, A., Julien, C. M., Paolella, A., & Zaghib, K. (2020). Brief History of Early Lithium-Battery Development. *Materials (Basel)*, *13*(8). https://doi.org/10.3390/ma13081884

Rivian. (2022). *R1T Emergencty Response*. https://rivian.com/emergency-response

Rubin, A. (2022). *Lithium-Ion Batteries in E-Bikes and Other Devices Pose Fire Risks*. nytimes.com. Retrieved 11/16/2023 from https://www.nytimes.com/2022/11/14/us/lithium-ion-ebike-battery-fires.html

Santhanagopalan, S., Ramadass, P., & Zhang, J. (2009). Analysis of internal short-circuit in a lithium ion cell. *Journal of Power Sources*, *194*(1), 550-557. https://doi.org/https://doi.org/10.1016/j.jpowsour.2009.05.002

Scrosati, B. (2011). History of lithium batteries. *Journal of Solid State Electrochemistry*, *15*(7), 1623-1630. https://doi.org/10.1007/s10008-011-1386-8

Searcey, D. (2008, 01/16/2008). *Batteries Hamper AT&T TV Effort*. The Wall Street Journal. https://www.wsj.com/articles/SB120045143379793329

Selman, J. R., Al Hallaj, S., Uchida, I., & Hirano, Y. (2001). Cooperative research on safety fundamentals of lithium batteries. *Journal of Power Sources*, *97-98*, 726-732. https://doi.org/https://doi.org/10.1016/S0378-7753(01)00732-7

Shahan, Z. (2015). *Electric Car Evolution*. CleanTechnica. https://cleantechnica.com/2015/04/26/electric-car-history/

Shepard, J. (2008, 01/20/2008). *AT&T Begins Battery Replacement Program After Reports of Fires*. EE Power. https://eepower.com/news/att-begins-battery-replacement-program-after-reports-of-fires/#

Strobel, P. (2021). *Hoverboard Recalls List: Are They Safe In 2021?* ERideHero. https://eridehero.com/

Tariq, M., Maswood, A. I., Gajanayake, C. J., & Gupta, A. K. (2017). Aircraft batteries: current trend towards more electric aircraft. *IET Electrical Systems in Transportation*, *7*(2), 93-103. https://doi.org/https://doi.org/10.1049/iet-est.2016.0019

Tesla. *Fire Responders Information*. Retrieved 02/10/2023 from https://www.tesla.com/firstresponders

UL. (2019). Standard for Test Method for Evaluating Thermal Runaway Fire Propogation in Battery Energy Storage Systems. In (Vol. UL 9540A): Underwriters Laboratory.

UL. (2020a). Standard for Energy Storage Systems and Equipment. In (Vol. UL 9540): Underwriters Laboratory.

UL. (2020b). Standard for Lithium Batteries. In (Vol. UL 1642): Underwriters Laboratory.

UN. (2018). Global Technical Regulation on the Electric Vehicle Safety. In (Vol. GTR 20): United Nations.

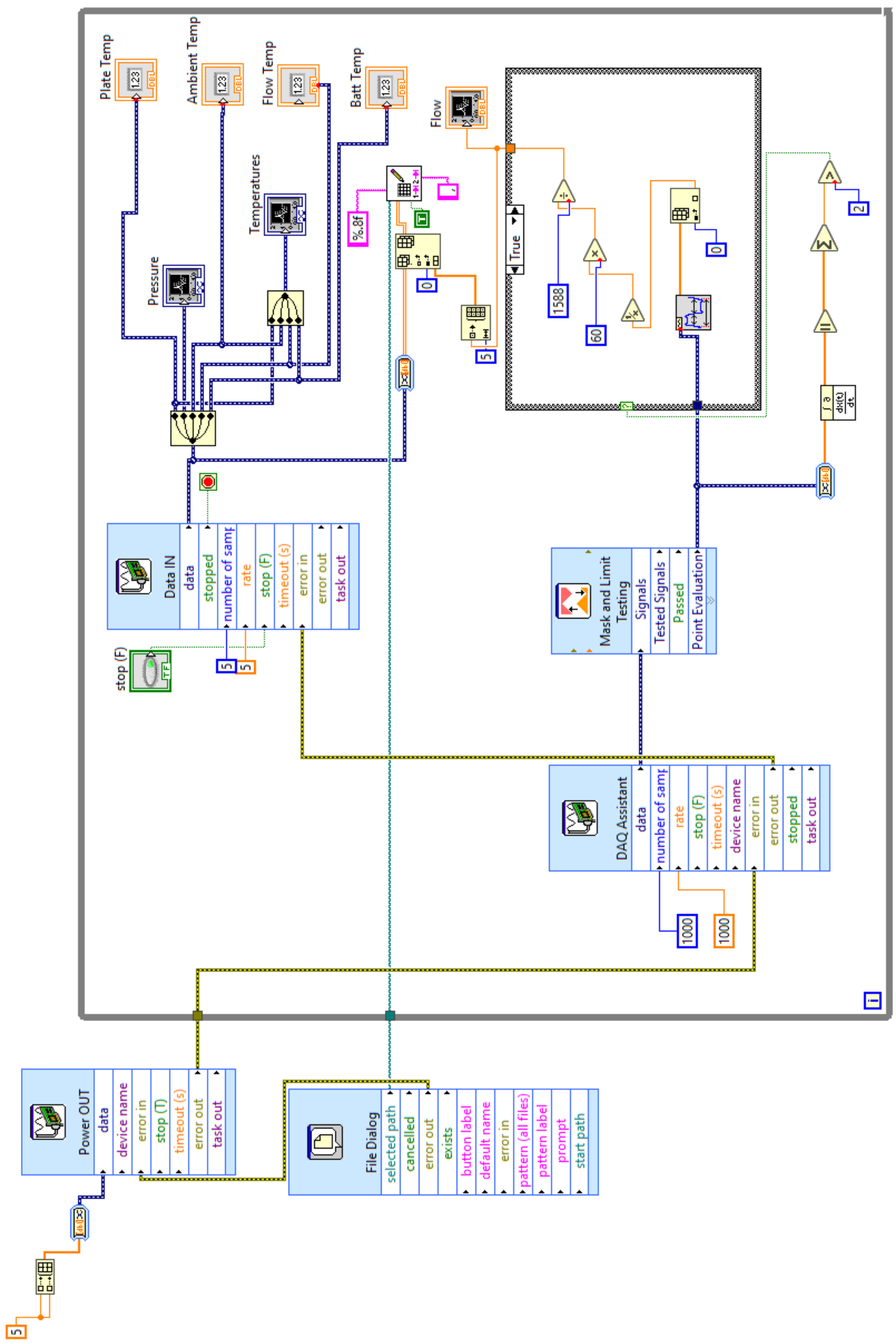
Wang, Q., Ping, P., Zhao, X., Chu, G., Sun, J., & Chen, C. (2012). Thermal runaway caused fire and explosion of lithium ion battery. *Journal of Power Sources*, *208*, 210-224. https://doi.org/https://doi.org/10.1016/j.jpowsour.2012.02.038

Whittingham, M. S. (2012). History, Evolution, and Future Status of Energy Storage. *Proceedings of the IEEE*, *100*(Special Centennial Issue), 1518-1534. https://doi.org/10.1109/JPROC.2012.2190170

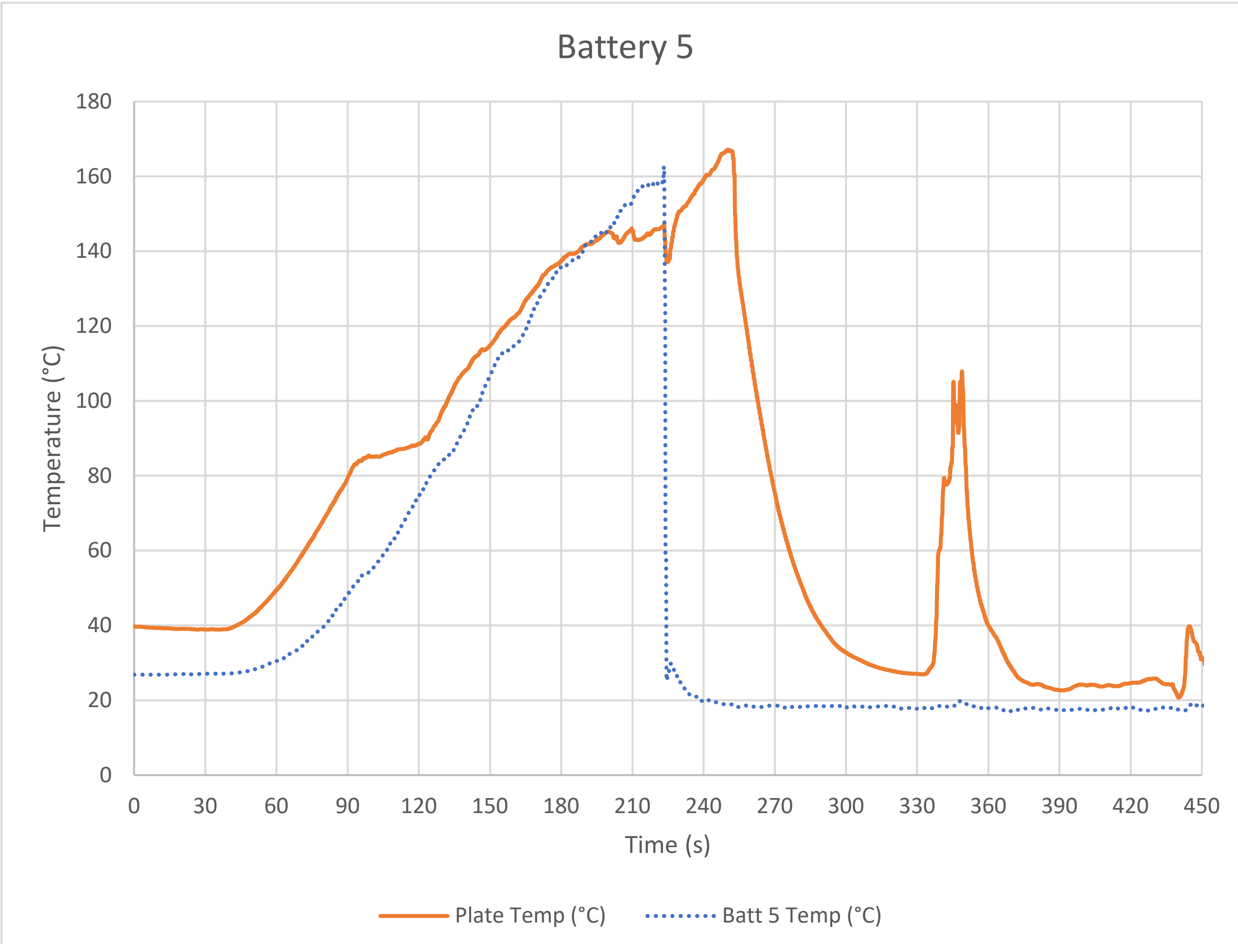
Wilson, G. (2021). *Timeline: Tesla's Construction of Gigafactories*. Manufacturing Digital Magazine. https://manufacturingdigital.com/digital-factory/timeline-teslas-construction-gigafactories

CHAPTER 6: APPENDICIES

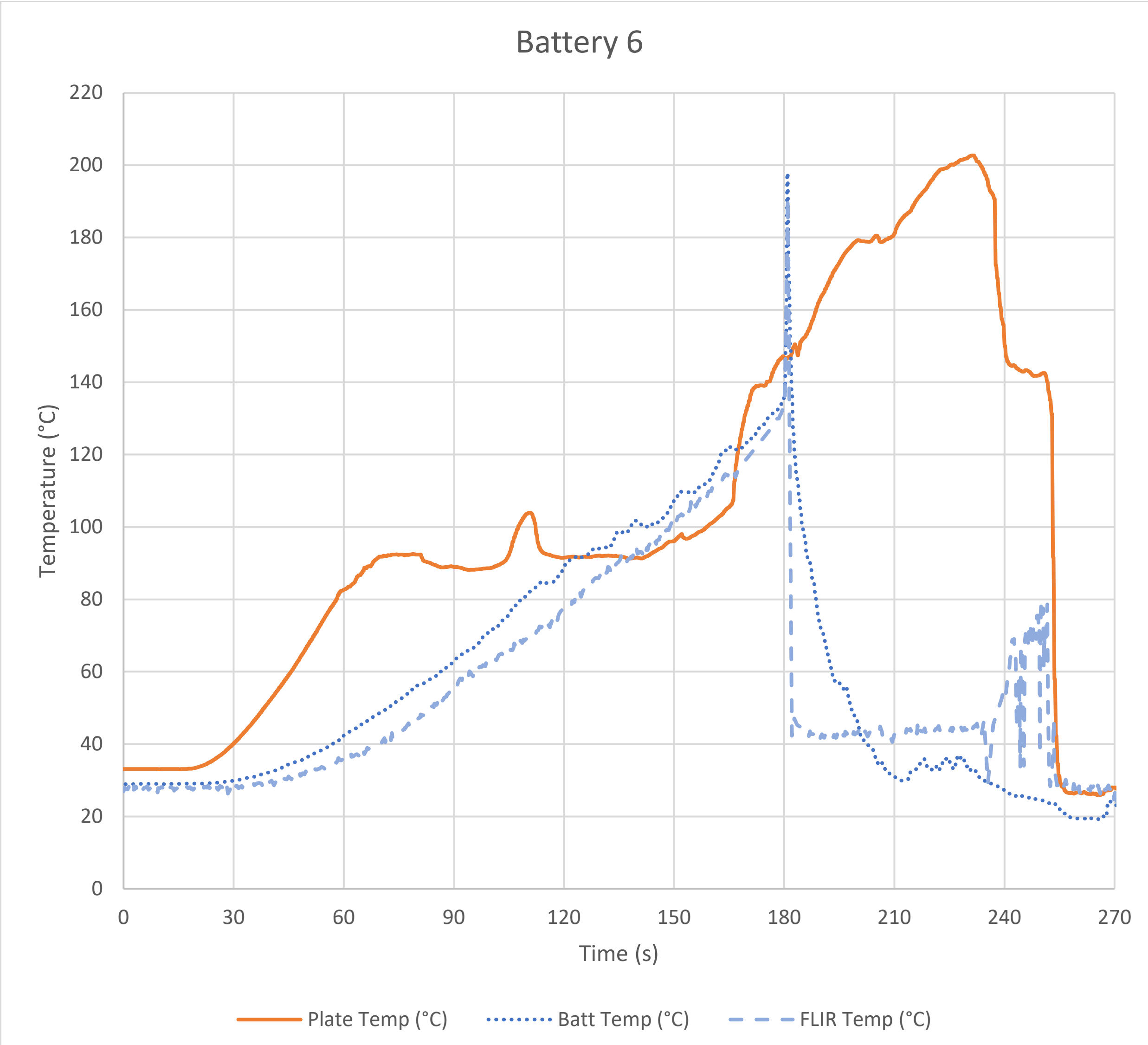
Appendix I: LabVIEW block diagram



Appendix II: Data sets from other Part 1 tests

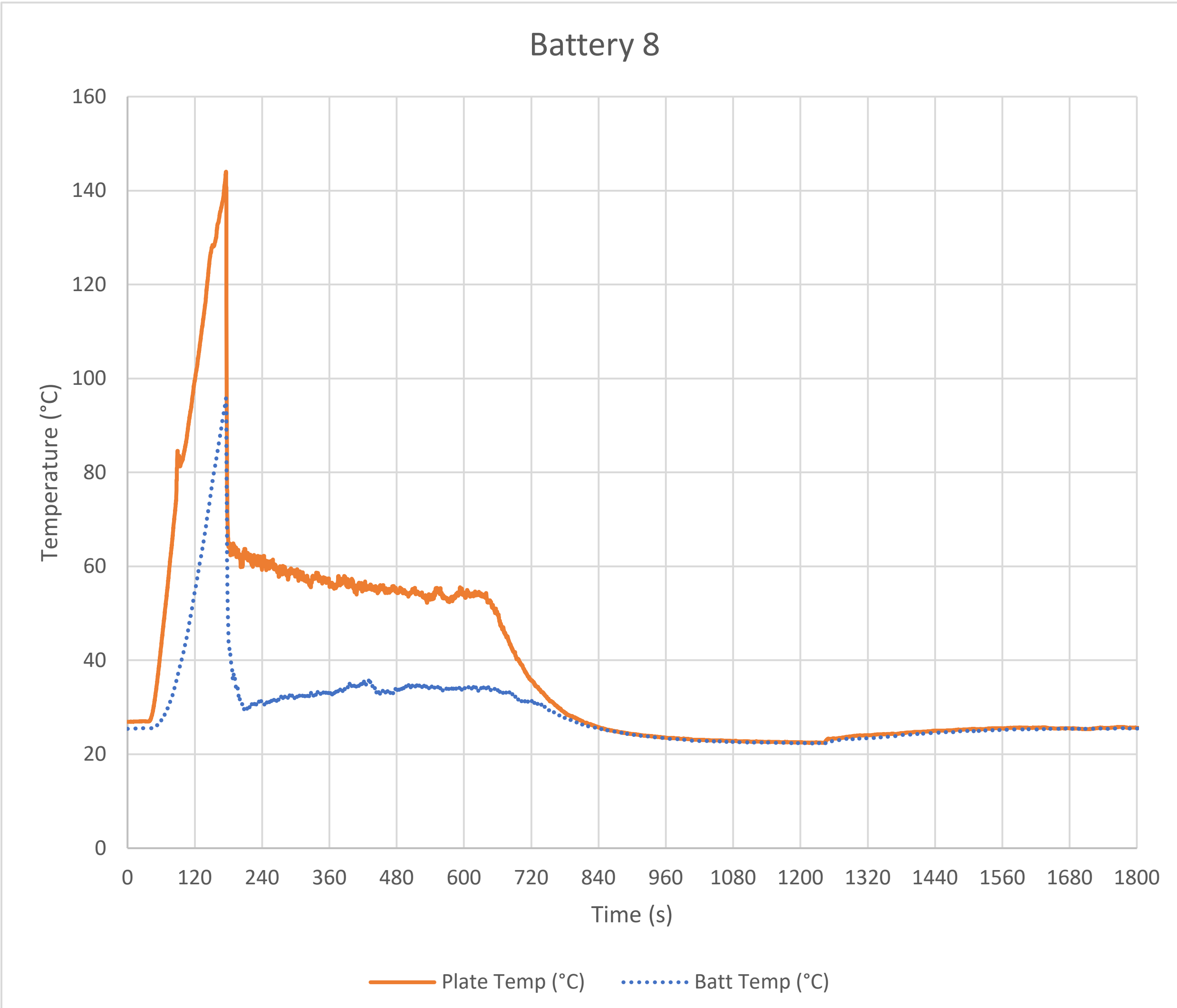


Battery thermocouple was attached to the outer casing which was blown off when the battery failed.

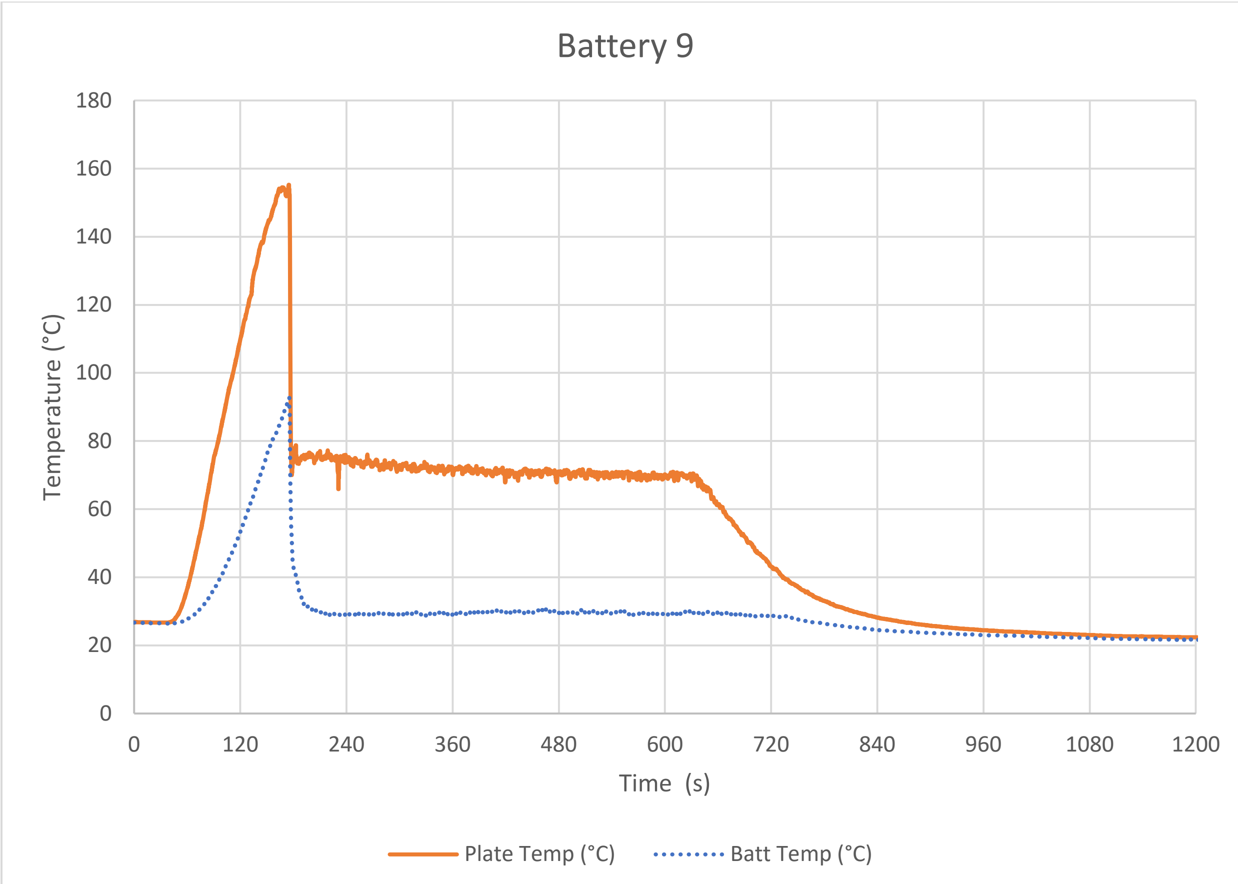


Water from a previous test got between the hot plate and aluminum foil. This caused erratic hot plate temperature readings during the heat-up phase of this test as that water boiled off.

Appendix III: Data sets from other Part 2 tests



Flow meter failed to collect data.



After attempting to diagnose the flow meter, the test of battery 9 also did not provide flow data. Data collection was terminated when the water flow was discontinued at the 20min mark.

Appendix IV: Early hand calculations to determine viability of early cooling

E. Huhn 10/14/22

Battery Fire Suppression Energy Balance

1st law of thermodynamics : $Q_{in} = Q_{out}$

Q_{in} = hot plate power

Q_{out} = cooling medium

$Q_{out} = \dot{m}(c_p \Delta T + \Delta H_{vap})$

	water	liquid CO_2	liquid N_2
c_p	$4.19 \frac{kJ}{kg \cdot K}$	$0.849 \frac{kJ}{kg \cdot K}$	$1.04 \frac{kJ}{kg \cdot K}$
ΔT	70K	100 K	300K
ΔH_{vap}	$2256 \frac{kJ}{kg}$	$574 \frac{kJ}{kg}$	$199 \frac{kJ}{kg}$

$Q_{out\_H_2O} = \dot{m}\left(2549.3 \frac{kJ}{kg}\right)$

$Q_{out\_CO_2} = \dot{m}\left(658.9 \frac{kJ}{kg}\right)$

$Q_{out\_N_2} = \dot{m}\left(511 \frac{kJ}{kg}\right)$

Since a Watt is a Joule per second, we can determine the mass flow of a fluid needed to absorb all the heat.

We're going to make some assumptions for our back-of-the-napkin calculations:

- the initial temperature of the water is 30°C (1 atm)
- the initial temperature of the CO_2 is 0°C (40 atm)
- the initial temperature of the N_2 is −200°C (1 atm)

the hot plate is 900W (0.9kW)

E: Huhn 10/14/22

$0.9kW = Q_{out\_H_2O} = \dot{m}(2549.3\frac{kJ}{kg})$

$\dot{m} = \frac{0.9\frac{kJ}{s}}{2549.3\frac{kJ}{kg}} = 0.000353\,kg/s$ of water

$\frac{0.000353\,kg/s}{995.67\,kg/m^3} = 3.55\times10^{-7}\,m^3/s$

$= 0.0056\,GPM$

$0.9kW = Q_{out\_CO_2} = \dot{m}(658.9\frac{kJ}{kg})$

$\dot{m} = \frac{0.9\frac{kJ}{s}}{658.9\frac{kJ}{kg}} = 0.001366\,kg/s$ of CO_2

$\frac{0.001366\,kg/s}{927\,kg/m^3} = 1.47\times10^{-6}\,m^3/s$

$= 0.0233\,GPM$

$0.9\,kW = Q_{out\_N_2} = \dot{m}(511\frac{kJ}{kg})$

$\dot{m} = \frac{0.9\frac{kJ}{s}}{511\frac{kJ}{kg}} = 0.001761\,kg/s$ of N_2

$\frac{0.001761\,kg/s}{808.4\,kg/m^3} = 2.18\times10^{-6}\,m^3/s$

$= 0.0346\,GPM$

100°C is too hot though. If we want to control the temperature to a safer 60°C the numbers look like this:

$\Delta T_{H_2O} = 30K$ $\quad \Delta T_{CO_2} = 60K$ $\quad \Delta T_{N_2} = 260K$

... and we lose the $\Delta H_{vap\_H_2O}$ because the water never flashes.

$\dot{m}_{H_2O\_60} = \frac{0.9}{4.19(30)} = 0.00716\,kg/s$

THE WATER REQUIREMENT TO MAINTAIN SUB-BOILING TEMPS IS 20X HIGHER!

$\dot{m}_{CO_2\_60} = \frac{0.9}{0.849(60)+574} = 0.00144\,kg/s$

$\dot{m}_{N_2\_60} = \frac{0.9}{1.04(260)+199} = 0.00191\,kg/s$