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Lithium Battery Fire Tests and Mitigation

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14. ABSTRACT

More than 100 lithium battery casualty tests were conducted to characterize the conditions produced during a range of both unmitigated and mitigated casualties. Both primary and secondary batteries were tested. This report summarizes the data and findings from these tests, including methods of mitigating thermal runaway of these cells under casualty conditions.

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ACRONYMS

Ah	Ampere Hours
BCS	Battery Charging Station
BCCT	Battery Casualty Characterization Tests
BLEVE	Boiling Liquid Expanding Vapor Explosion
BSC	Battery Stowage Compartment
BSL	Battery Storage Locker
C	Celsius
CAS	Chemical Abstract Service
CBD	Chesapeake Bay Detachment
COTS	Commercial Off The Shelf
F	Fahrenheit
ft	Feet
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS/IR	Gas Chromatography–Mass Spectroscopy/Infrared
HMS	Hazard Mitigation Suite
HMT	Hazard Mitigation Test
HRR	Heat Release Rate
HSD	Heat Sensing Device
kW	Kilowatts
kWh	Kilowatt Hours
LBCMS	Lithium Battery Casualty Mitigation System for Lithium Battery Fires
LEL	Lower Explosive Limit
MCE	Maximum Credible Event
MW	Megawatts
NRL	Naval Research Laboratory
PHA	Preliminary Hazard Analysis
PHRR	Peak Heat Release Rate
SHA	System Hazard Analysis
SOC	State of Charge
VOC	Volatile Organic Compound

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EXECUTIVE SUMMARY

Lithium batteries can pose a significant hazard during an acute casualty. Potential causes of such casualties include an electrical or mechanical short, overcharging the battery, exposure to excess heat, physical abuse, or spontaneous failure due to a latent defect. During this reaction, the battery may violently vent or rupture, releasing combustible, toxic, and/or acidic vapors and aerosols, and/or incandescent metal particles or carbon. These may result in a major fire or explosion and release of large quantities of toxic and acidic gases. More than 100 battery casualty and mitigation tests were conducted from 2009 to 2012 by the Naval Research Laboratory (NRL) aboard the research test ship ex-USS *Shadwell*. This report summarizes the results of these tests based on specific battery chemistries.

Primary and secondary lithium batteries with a range of chemistries, form factors, and capacities were tested. Lithium batteries may be made up of layers of anode (copper foil coated with a specialty carbon) and cathode (typically aluminum foil coated with a lithiated metal oxide or phosphate) separated by a microporous polyolefin film referred to as a separator. An electrolyte composed of an organic solvent and dissolved lithium salt provides the medium for lithium ion transport. A cell is constructed by stacking alternating layers of electrodes (typical for high-rate capability prismatic cells), or by winding long strips of electrodes into a "jelly roll" configuration (typical for cylindrical cells).

The lithium battery chemistries currently used throughout the industry produce cell voltages ranging from 3.2 to 4.2 V. The capacity of the cell (measured in ampere-hours) varies widely and is a function of the number of layers of electrodes in a prismatic cell or the length of the strip in a cylindrical cell. The commercial industry combines a large number of cells wired together in series and in parallel to produce battery packs and modules with a desired voltage and capacity. These packs can contain hundreds of cells.

NRL battery casualty tests were conducted on individual cells and on a variety of battery packs. The cell chemistries studied are $Li/LiCoO_2$, $Li/Li_{0.5}CoO_2$, $Li/SOCl_2$, $Li/LiFePO_4$, Li/CF_x, Li/MnO_2, Li/SO_2Cl_2-$SOCl_2$, and $Li/NiCoAlO_4$. All tests reported here were conducted on commercially available battery cells.

Based on the tests conducted, single cell reactions can be described using six terms: vent, smoker, flare, burner, explosive, and fireball. Smaller, lower capacity solid cathode cells typically vent and/or smoke and medium to higher capacity cells (specifically the oxyhalides) either ignite and burn or explode. Intuitively, one expects the type of reaction to be a function of the amount of energy contained in the cell at the time of the event. Therefore, the type of reaction should be a function of both the battery capacity and the state of charge (SOC) at the time of the event. Based on a very limited data set (not statistically valid), it appears that the threshold between a venting and a flaming reaction lies in the 10 to 20 watt-hour range. Battery pack configurations can significantly alter these single cell results.

The reaction products measured when a cell vents (without ignition) are electrolyte constituents, such as carbonates or oxyhalides. These are organic solvent gases and aerosols with flammable constituents and the potential to ignite. In some instances, the carbonates break down upon release to produce high levels of CO_2, CO, and a range of hydrocarbons. When a cell burns in a casualty, the electrolyte burns fairly efficiently, producing primarily CO_2 as the by-product. Acid gas can also be produced and is directly related to cell chemistry (and appears to be related to cell capacity): cells that

contain sulfur (e.g., Li/SOCl$_2$) produce sulfuric acid, cells that contain fluorine (e.g., LiPF$_6$) produce hydrofluoric acid, and cells that contain chlorine (e.g., Li/SOCl$_2$) produce hydrochloric acid. There is not enough data to develop a quantitative relationship between cell energy and acid gas production, but for a given cell chemistry, the amount of acid gas produced is expected to be directly proportional to the cell energy.

The mean heat release rate (HRR) for the small commercial cells (such as the AA size) is typically on the order of 10 kW. The larger commercial cells can produce mean heat release rates approaching 100 kW. The more reactive cell chemistries (i.e., Li/SOCl$_2$ and Li/SO$_2$Cl$_2$-SOCl$_2$) produce violent/explosive type reactions approaching 500 kW.

Tests conducted with multiple-cell packs demonstrate that single cell data for a specific cell type may not be indicative of the reactions of battery packs made up of those same cells: single cell tests and battery pack tests yielded different types of reactions. Specifically, except for the iron phosphate cells, all the packs/modules produced burning reactions, while many of the single cells only vented and never caught fire. This difference was attributed to the greater amount of electrical energy contained in a pack that could contribute to the severity of the reaction and provide an ignition source. In addition, during almost every unmitigated pack/module test, all the cells reacted and the casing materials were completely consumed.

The heat release rate of the multicell packs was a function of the propagation rate from cell to cell within the battery pack and the contribution of the battery pack casing material. The propagation rate from cell to cell ranged from seconds to minutes depending of the type of cell and the battery pack configuration. Some of the smaller packs were consumed in a few minutes while some of the larger packs reacted/burned for over an hour.

Combustion energy of a battery pack was shown to be proportional to the electrical energy contained in the pack after adjusting for the contribution of the packaging material. Some battery packs have metal casings that provide little if any contribution to the fire, whereas some packs have thick hard plastic casings that provide a significant contribution to the fire. After adjusting the combustion energies to account for the case material, the combustion energy is typically about six times the electrical energy potential of the battery.

With respect to suppression, the results from these tests demonstrate that it is virtually impossible to stop a reaction within a lithium cell once it has begun. Consequently, the objective of a fire suppression system should be to thermally manage the conditions in the space and try to cool adjacent cells in an attempt to slow or prevent cell-to-cell propagation. Suppression of the packaging material is also desired. Water appears to be the best suppression agent.

The ability of a suppression system to prevent secondary cell reactions within a complex battery pack is, in part, a function of the openness of the battery pack housing. If the battery housing is fairly open, a fast acting suppression system may be able to reduce the exposures to the adjacent cells within the housing to below the critical temperature value (below the level at which adjacent cells react). The best way to achieve this objective is to rapidly submerse the battery pack in water. The severity of the initial reaction, the proximity of the adjacent cells, and the vulnerability of adjacent cells are variables associated with achieving this performance objective. If the cells are contained within a closed housing (air tight, water tight, or even just a fairly tight enclosure), the suppression system will not be able to contain the reaction to the initial cell, and in most scenarios, all the cells within the pack will react, even if submersed under water. Battery pack submersion does prevent the spread to other packs.

A water spray/sprinkler system (versus a flooding system) has the ability to thermally manage the conditions around the pack of origin, but is unlikely to be effective in preventing the complete consumption/reaction of that initial pack. In some instances, passive thermal barriers between battery packs combined with the thermal management provided by a water spray/sprinkler system is the best approach to mitigate the overall hazard/risk. Two such configurations of a mitigation suite, called the Lithium Battery Casualty Mitigation System, were developed and tested.

There are currently no established criteria for classifying the hazards associated with a lithium battery casualty. Although the data presented here and historical data show that lithium batteries have the potential to ignite and cause a fire, the primary hazard associated with a battery casualty appears to be the gases produced during the reaction. These gases have been determined to be toxic and/or flammable. The concentration of toxic and/or flammable gases produced is a function of the battery chemistry, the number of cells involved in the reaction, the type of reaction (i.e., burning or venting), and the size of the compartment in which the reaction occurs. Since copious amounts of gases are produced during the reaction of larger batteries and battery packs, it must be assumed that any battery casualty will render the storage compartment untenable for unprotected personnel (personnel not wearing a breathing apparatus). During a venting scenario, the resulting mixture could be in the flammable range. A delayed ignition of these gases could produce a large fireball and overpressures that could produce structural damage and additional battery casualties. The consequences from such a scenario could be catastrophic.

The results presented here provide a general understanding of the hazards associated with lithium batteries and approaches to minimize the risk. The reaction characteristics and lessons learned provide a starting point for the development of a database that can be used both to conduct analytical assessments of lithium battery hazards and to develop battery packs for future applications.

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LITHIUM BATTERY FIRE TESTS AND MITIGATION

1   INTRODUCTION

Lithium batteries can pose a significant hazard during an acute casualty. Potential causes for such casualties include an electrical or mechanical short, overcharging the battery, exposure to excess heat, physical abuse, or spontaneous failure due to latent defect. During this reaction, the battery may violently vent or rupture, releasing combustible, toxic, and/or acidic vapors and aerosols, and/or incandescent metal particles or carbon. These may result in a major fire or explosion and release of large quantities of toxic and acidic gases.

The Naval Research Laboratory (NRL) recently participated in several major research programs initiated to characterize and mitigate lithium battery fire hazards. The overall goal is to be able to safely handle, store, and charge this class of energy sources. More than 100 battery casualty tests were conducted between 2009 and 2012 to characterize the conditions produced during a range of both unmitigated and mitigated casualties, and to evaluate different containment and suppression systems. This report summarizes the results of these tests. The discussion is divided into data for single cells and data for groupings of cells that comprise what is termed a battery pack. Video clips of some of the tests are presented in the Appendix (on enclosed DVD).

2   DEFINITIONS

The following definitions apply to this report:

Battery: A power source designed to meet the specific needs of an application (voltage, current, power output/duration), containing one or more cells.

Battery pack: A group of cells permanently wired together.

Capacity: The quantity of electrical charge delivered by a battery under specific conditions. It is usually expressed in ampere-hours (Ah).

Casing: The outer shell of a cell or a battery.

Casualty: A scenario consisting of one or more cell reactions leading to a cell failure.

Cell: The smallest individual constituent energy storage unit of a battery.

Electrolyte: Any substance containing free ions that make the substance electrically (ionically) conductive. Most of the electrolytes assessed in this report are liquid and are mixtures of covalent organic and inorganic solvents containing dissolved ionic lithium salts. Where the electrolytes are not organic esters/carbonate mixtures, they are inorganic oxyhalides, usually with sulfur components.

Hazard: An existing or potential condition that can result in a mishap.

Housing: A structure that surrounds the battery pack that is an integral part of the battery. The battery casing and battery housing may be synonymous terms.

Large form cell: A single cell larger in form than two "D" size cells.

Lithium battery: For the purpose of this report, lithium batteries include all cells or batteries in which lithium metal, any lithium alloy, or any form of lithium in a supporting matrix serves as the active anodic component.

Lithium-ion battery: Lithium-ion batteries are comprised of cells that use lithium intercalation compounds as the positive and negative electrodes. As the battery is cycled, lithium ions (Li+) exchange between the positive and negative electrodes. Lithium-ion batteries are a subset of "lithium battery."

Primary battery: A battery designed to be discharged only once, i.e., not designed to be recharged; also called a nonrechargeable battery.

Reaction: A cell-level event resulting from one of the following: electrical abuse (shorting or overcharging), thermal abuse, or physical damage.

Secondary battery: A battery in which the electrochemical reaction is thermodynamically reversible and is designed to be recharged in use. Common secondary batteries include the lead-acid, nickel-cadmium, and lithium-ion batteries common to many consumer products. A secondary battery may also be referred to as a rechargeable battery.

Thermal runaway: An internal reaction within a cell or battery that generates enough heat to cause the cell to fail in one or more of the following modes: vent aerosols or smoke, jet incandescent particles, jet fire, explode, or ignite/catch fire. The intrinsic nature of thermal runaway is thermal acceleration of nearby cells to form a cascading event.

3   BATTERY TUTORIAL

3.1   General

Lithium batteries are a family of cells that consist of a lithium anode (negative terminal) and a variety of different types of cathodes (positive terminal) and electrolytes [1]. Lithium batteries are grouped into two general categories: primary and secondary batteries. Primary lithium batteries are comprised of single-use cells containing metallic lithium anodes and cannot be recharged. Secondary lithium-ion batteries are comprised of rechargeable cells containing an intercalated lithium compound for the anode and cathode. In this report, nonrechargeable (primary) lithium batteries are referred to as "lithium primary" batteries (often referred to as simply "lithium" batteries in the battery industry), and rechargeable (secondary) lithium batteries are "lithium-ion" or "Li-ion" batteries.

Lithium primary batteries can be classified into several categories based on the type of electrolyte (or solvent) and cathode material used. These classifications include soluble-cathode cells, solid-electrolyte cells, and solid-cathode cells.

Soluble-cathode cells use liquid or gaseous cathode materials, such as sulfur dioxide (SO_2) or thionyl chloride ($SOCl_2$), that dissolve in the electrolyte or are the electrolyte solvent. These soluble cathode lithium cells are used for low to high discharge rate applications. The high-rate designs, using large electrode surface areas, are noted for their high power density and are capable of delivering the highest current densities of any active primary cell.

Solid-electrolyte cells are noted for their extremely long storage life, in excess of 20 years, but are capable of only low-rate discharge in the microampere range. They are used in applications such as

memory backup, cardiac pacemakers, and similar equipment where current requirements are low but long life is critical. This battery type was not evaluated in the programs reported here.

Solid-cathode cells are the most commonly used type of lithium primary cell. They are designed, generally, for low- to medium-rate applications such as memory backup, security devices, portable electronic equipment, photographic equipment, watches, calculators, and small lights. Although a number of different solid-cathode lithium batteries have been developed, the lithium/manganese dioxide (Li/MnO_2) battery was one of the first to be used commercially and is still the most popular. It is relatively inexpensive, has excellent shelf life, has good high-rate and low-temperature performance, and is available in coin and cylindrical cells. The lithium/carbon monofluoride ($Li(CF)_n$) battery is another of the early solid-cathode batteries and is attractive because of its high theoretical capacity and flat discharge characteristics. It is also manufactured in coin, cylindrical, and prismatic configurations. The higher cost of polycarbon monofluoride has affected the commercial potential of this system but it is finding use in biomedical, military, and space applications. The construction of these primary cells is similar to that of the secondary (lithium-ion) cells described next.

Secondary/lithium-ion batteries are used across a range of portable applications ranging from consumer electronics to medical technology to military systems. They are characterized by medium to high energy density and are being developed in a variety of chemistries. In a lithium-ion cell, layers of anode (copper foil coated with a specialty carbon) and cathode (typically aluminum foil coated with a lithiated metal oxide or phosphate) are separated by a microporous polyolefin film referred to as a separator. An electrolyte composed of an organic solvent and dissolved lithium salt provides the medium for lithium ion transport. A cell can be constructed by stacking alternating layers of electrodes (typical for high-rate capability prismatic cells), or by winding long strips of electrodes into a "jelly roll" configuration (typical for cylindrical cells). Lithium ions move from the anode to the cathode during discharge and are intercalated into the cathode (i.e., inserted into voids in the crystallographic structure). The ions reverse direction during charging, as shown in Fig. 1.

3.2   Chemistries

The most common type of lithium-ion cell contains an intercalated lithium (lithium alloy) anode and lithiated cobalt dioxide as cathode. These batteries are inexpensive and have medium to high energy densities, but can self-discharge (begin a thermal runaway reaction) at temperatures in the 60 °C range. Since lithium ions are intercalated into host materials during charge or discharge, there is no free lithium metal within a lithium-ion cell. Consequently, if a cell ignites due to external flame impingement or due to an internal short, "metal fire" (e.g., lithium, sodium, or magnesium) suppression equipment and techniques are neither appropriate nor cost effective for controlling the fire.

Other chemistries, principally primary chemistries, that are being actively pursued/developed by the battery industry include thionyl chloride, sulfuryl chloride, sulfur dioxide, carbon monofluoride, and manganese dioxide. These cells have the highest energy densities (about twice that of Li-ion cells) but are more expensive based on total deliverable energy and useable life. The solid-electrode group of batteries is comprised of "specialty" type cells used primarily in the medical profession. These cells include silver, copper, iron, and lead (oxides and sulfides) chemistries. These cells are highly reliable, very expensive, and have limited current capacities. The automotive industry is aggressively pursuing higher energy density chemistries that may eventually be adopted for the commodity type usages.

Cathode   Anode

Positive Electrode   Negative Electrode

Co
O
Li

charge
Li+

discharge
Li+

Electrolyte
Carbonates
Lithium salts

LiCoO₂   Specialty Carbon

Al foil   poly film separator   Cu foil
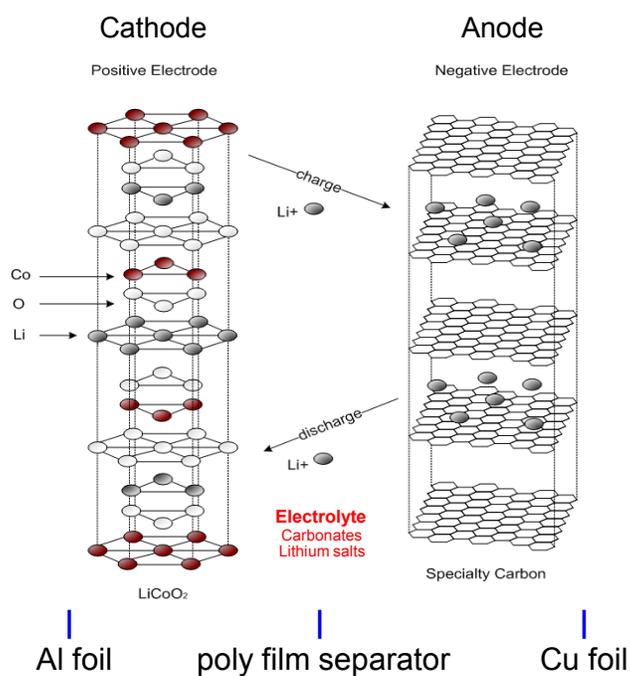
Fig. 1 — Generalized Li-ion cell components/configuration

The electrolyte in a lithium-ion cell is typically a mixture of a lithium salt dissolved in organic carbonates such as ethylene carbonate or diethyl carbonate. The compounds vary depending upon desired cell properties. For example, a cell designed for low-temperature applications will likely contain a lower viscosity electrolyte than one optimized for room temperature applications.

The flammability characteristics of common carbonates used in lithium cell electrolytes in a neat state are provided in Table 1. These characteristics apply only to liquefied carbonates. During a cell venting scenario, when the electrolyte may be released as an aerosol with partial decomposition to lower molecular weight species, both the flash point and the auto-ignition temperature may be lower.

The lithium-ion electrolyte solution contains solvated lithium ions, which are provided by lithium salts, most commonly lithium hexafluorophosphate ($LiPF_6$). At elevated temperatures, $LiPF_6$ decomposes to release hydrofluoric acid (HF) during a battery casualty if the resulting materials are exposed to moisture. The higher energy density primary cells also produce acid gases (sulfuric and hydrochloric) during high-temperature reaction processes if exposed to moisture in the air.

Table 1 — Flammability Characteristics of Typical Electrolyte Compounds

Compound	CAS Registry Number	Molecular Formula	Flash Point	Boiling Point	Auto-Ignition Temperature	Heat of Combustion
Diethyl Carbonate (DEC)	105-58-8	$C_5H_{10}O_3$	25°C 77°F	126°C 259°F	445°C 833°F	−20.9 kJ/ml −5.0 kcal/ml
Dimethyl Carbonate (DMC)	616-38-6	$C_3H_6O_3$	18°C 64°F	91°C 195°F	458°C 856°F	−15.9 kJ/ml −3.8 kcal/ml
Ethylene Carbonate (EC)	96-49-1	$C_3H_4O_3$	145°C 293°F	248°C 478°F	465°C 869°F	−17.2 kJ/ml −4.1 kcal/ml
Ethyl Methyl Carbonate (EMC)	623-53-0	$C_4H_8O_3$	25°C 77°F	107°C 225°F	440°C 824°F	−19.2 kJ/ml −4.6 kcal/ml
Propylene Carbonate (PC)	108-32-7	$C_4H_6O_3$	135°C 275°F	242°C 468°F	455°C 851°F	−20.1 kJ/ml −4.8 kcal/ml
Tetrahydrofuran (THF)	109-99-9	C_4H_8O	−14°C 6°F	65°C 149°F	321°C 610°F	−31.2 kJ/ml −7.5 kcal/ml
Dimethylether	115-10-6	C_2H_6O	−41°C −42°F	−23.7°C 11°F	350°C 662°F	−51.3 kJ/ml −12.3 kcal/ml
1,3-Dioxolane	646-06-0	$C_3H_6O_2$	2°C 35°F	75°C 167°F	?	−24.4 kJ/ml −5.8 kcal/ml
1,2-Dimethoxyethane (Ethylene Glycol)	110-11-4	$C_4H_{10}O_2$	104°C 232°F	83°C 197.5°F	400°C 752°F	−21.3 kJ/ml −5.1 kcal/ml
Acetonitrile (Methyl Cyanide)	75-05-8	CH_3CN	6°C 42°F	81.6°C 179°F	524°C 975°F	−23.9 kJ/ml −5.7 kcal/ml
Thionyl Chloride	7719-09-7	$SOCl_2$	?	78.8°C 174°F	?	?

Source: http:/webbook.nist.gov/chemistry/

3.3   Cell Construction/Configuration

There are three basic lithium battery cell designs: coin shaped, cylindrical, and prismatic (Fig. 2). Coin shaped cells (sometimes referred to as button cells) are low-current cells used in watches, calculators, and remote keyless entry systems for cars, to name a few examples. They are available in many sizes and capacities, with a common variety being the 3 V manganese variety. Cylindrical cells incorporate the same design parameters that have been the standard for alkaline cells for years (A, AA, AAA, C, and D cells) with the option of spiral or bobbin internal construction. Prismatic cells include standard 9 V battery designs. A prismatic variety referred to as "pouch" cells are typically used in laptop computers.

Cell construction is a major variable affecting the severity of a battery mishap. The severity of a reaction is in part related to the buildup and release of pressure from inside the cell. Some cells have pressure relief vents and these typically produce less severe reactions than unvented cells that contain the pressure.

Fig. 2 — Typical cell designs. Top row: prismatic, cylindrical. Middle row: pouch (prismatic). Bottom row: coin.

3.4   Battery Packs

A lithium battery pack is made from two or more individual cells packaged together. The cells are connected/wired together to achieve a desired voltage and capacity. Connecting cells in parallel increases pack ampere-hour and discharge capacity, while connecting cells in series increases pack voltage. The cylindrical cell form factor 18650 is the "workhorse" of the lithium-ion battery industry and is used in a majority of commercially available battery packs. The "18" refers to the diameter of the cell and the "65" refers to the length of the cell, both in millimeters. Examples of battery packs produced with cylindrical cells are shown in Fig. 3.

In large format battery packs, cells may be connected together in series and/or in parallel to form battery modules, which may then be connected in series and/or in parallel to make larger battery packs to meet desired voltage and capacity requirements. Modules are used to facilitate different configurations and easy replacement of faulty portions of large battery packs (a module is a Lowest Replaceable Unit, LRU). Large format battery pack architecture can be significantly more complex than small consumer electronics battery packs which typically contain series connected elements consisting of two or more parallel connected cells. Many larger battery packs have built-in circuitry used to monitor charging and control the discharge cycle of the battery (i.e., shut down the battery when the charge level drops below a specified value). These large battery packs are used in the automotive industry.

Fig. 3 — Example battery packs

4 BATTERY CASUALTY CHARACTERIZATION TESTS — OVERVIEW

For U.S. Navy applications, the Navy requires that all lithium batteries are reviewed and formally approved in the context of each application. The Navy has adopted requirements and protocols for certifying lithium batteries that include Preliminary Hazard Analysis (PHA), Battery Casualty Characterization Tests (BCCT), Hazard Mitigation Tests (HMT), and a final System Hazard Analysis (SHA).

The BCCTs are typically conducted in two phases: single cell tests and all-up battery pack tests. The rationale is to quantify the reaction on a smaller, manageable scale, then increase the size and severity once the magnitude of the reaction has been bounded. A summary of the types of tests and associated parameters that make up the BCCT is provided below.

Battery casualty initiation: A key parameter of the BCCT is the method used to initiate the battery casualty. The method(s) used during the BCCT is typically determined in the PHA. For example, the most likely and most severe scenario for a lithium-ion battery results from being overcharged. Other potential initiating events include an internal manufacturer's defect, physical damage, and an external heat source.

Reaction products analysis: Tests are conducted to characterize the products released during the cell/battery casualty. A comprehensive approach is required that includes an initial qualitative study to assess the nature of the expected chemical species and relative concentration ranges. Ultimately, the products are assessed in terms of acidity, corrosiveness, toxicity, and aerosol particle composition. Real-time analysis is done via electrochemical sensors and optical methods (in situ Fourier transform infrared spectroscopy, FTIR). Samples are also collected using gas sampling canisters, sorbent tubes, and impingers. These grab samples are analyzed using a gas chromatography–mass spectrometry/infrared (GC-MS/IR) technique.

Heat release rate (HRR): The heat release rate is determined for each type/model of cell and battery. The HRR may determine whether there will be a cascading effect in a casualty. A hood calorimeter is used to make these measurements through an assessment of combustion products. This may also be done in an apparatus that allows the measurement of oxygen consumption during the casualty. When

measuring the HRR for a specific battery, in most cases there is an acceleration of the HRR, termed the peak heat release rate, PHRR.

Thermal exposures: The thermal exposure produced during the casualty (near field) is measured using both radiometers and calorimeters. These measurements provide information on exposures to items intimate with the casualty and provide an indication of the likelihood of a cascading event (reactions of adjacent batteries). "Mock collateral casualty exposure items" may be used in addition to radiometers and calorimeters to determine significant heating of local items to a casualty event.

Smoke generation: The amount of smoke/aerosols produced during the casualty is determined using an optical density meter. The measurement is typically made in the stack (hood exhaust ductwork) just below the gas sampling probe and in the test compartment.

Pressure transients: Pressure transients are recorded during these tests (both near field and far field). The pressure release may be a moderate and sustained pressure rise from low-order combustion to deflagration of battery components internal to the cell(s). The pressure release may also be sudden and abrupt stemming from a sudden failure of pressure containment of battery cell cases or battery pressure containment vessels.

Fragmentation of the cell and/or battery casing: Debris may be ejected from the article under test at high velocities. The location of flying debris (a debris map) is documented after each test. This debris may include small to large portions of the cell and/or battery casings, battery enclosures, or pressure vessel housings. Video recorded during each test is analyzed (frame by frame) to assess whether the debris is burning/flaming while it is ejected. Alternate measurement techniques include witness plates to capture the debris thrown or impact sensors. Burning incandescent debris provides a secondary ignition source that can result in fire spread and/or other battery casualties.

5　COMMERCIALLY AVAILABLE BATTERY/CELL DESCRIPTIONS

The battery cells that were tested during these programs are described in Tables 2 through 5. All are commercially available cells. A number of these cells were assessed for heat release rate only in a battery pack configuration, not individually.

Table 2 — A/AA and Pouch-size Commercially Available Cells Tested

Cell Manufacturer	A	B-1	B-2	C-1	D-1	E
Type	Secondary	Secondary	Primary	Secondary	Secondary	Secondary
Form Factor	Pouch cell	AA Cell	AA Cell	18650	18650	18650
Chemistry	$Li/LiCoO_2$	$Li/Li_{0.5}CoO_2$	$Li/SOCl_2$	$Li/LiFePO_4$	$Li/LiFePO_4$	$Li/Li_{0.5}CoO_2$
Voltage	3.7 V	3.7 V	3.6 V	3.3 V	3.2 V	3.7 V
Capacity	3.3 Ah	0.16 Ah	2.0 Ah	1.1 Ah	1.5 Ah	2.2 Ah
Energy	12.2 Wh	0.6 Wh	7.2 Wh	3.6 Wh	4.8 Wh	8.1 Wh
Mass	95 g	19 g	18 g	39 g	46 g	48 g

Table 3 — C-size Commercially Available Cells Tested

Cell Manufacturer	F	H-1	D-2	C-2
Type	Secondary	Primary	Secondary	Secondary
Form Factor	C Cell	5/4 C Cell	5/4 C Cell	5/4 C Cell
Chemistry	Li/CF$_x$	Li/MnO$_2$	Li/LiFePO$_4$	Li/LiFePO$_4$
Voltage	3.0 V	3.3 V	3.2 V	3.3 V
Capacity	5.0 Ah	6.1 Ah	3.2 Ah	1.1 Ah
Energy	15.0 Wh	20.1 Wh	10.3 Wh	3.6 Wh
Mass	42 g	71 g	82 g	70 g

Table 4 — D-size Commercially Available Cells Tested

Cell Manufacturer	K	G	H-2	B-3	B-4
Type	Primary	Primary	Primary	Primary	Primary
Form Factor	DD Cell	D Cell	D Cell	D Cell	D Cell
Chemistry	Li/CF$_x$	Li/SOCl$_2$	Li/MnO$_2$	Li/SOCl$_2$	Li/SO$_2$Cl$_2$ -SOCl$_2$
Voltage	3.6 V	3.6 V	3.3 V	3.6 V	3.9 V
Capacity	40.0 Ah	19.0 Ah	11.1 Ah	19.0 Ah	16.5 Ah
Energy	144.0 Wh	68.4 Wh	37.0 Wh	68.4 Wh	64.4 Wh
Mass	320 g	100 g	115 g	93 g	100 g

Table 5 — Large Form and Pouch Commercially Available Single Cells Tested

Cell Manufacturer	I-1	I-2	J	I-3
Type	Secondary	Secondary	Secondary	Secondary
Chemistry (Cathode)	Lithium Nickel Cobalt Aluminum Oxide	Lithium Nickel Cobalt Aluminum Oxide	Lithium Polymer Format Lithium Cobalt Oxide	Lithium Nickel Cobalt Aluminum Oxide
Voltage	3.6 V	3.6 V	4.2 V	3.6 V
Capacity	4.0 Ah	33.0 Ah	53.0 Ah	52.0 Ah
Energy	14.4 Wh	118.8 Wh	222.6 Wh	187.2 Wh
Mass	340 g	940 g	1200 g	1000 g

6   REACTION DESCRIPTIONS (SINGLE CELL)

6.1   Initiating Events

The primary failure mode of a lithium battery is associated with a flaw or damage to the thin porous electrical insulation layer that separates the anode and the cathode (the separator). This is typically a microporous polyolefin layer 15 to 40 micrometers in thickness for the Li-ion cells and a glass or ceramic paper for oxyhalide cells. A flaw/damage to the separator can result in an internal short circuit that produces enough heat to vaporize the electrolyte and result in a boiling liquid expanding vapor explosion (BLEVE) type reaction. The separator can fail due to internal defects (production issues), physical damage (handling issues), exposure to high temperature (fire), and in the case of secondary cells, overcharging resulting in bridging of the separators. Once an internal short develops, a sudden release of stored energy can occur that may result in thermal runaway. This event can cascade to adjacent cells and throughout an entire battery pack and destroy the device the battery is serving. Fires involving lithium batteries can initiate within the product, which means that in storage, a fire can initiate deep within a battery pack or piece of equipment, beyond the influence of conventional fire protection systems.

The potential for manufacturers' defects was emphasized during the 1st Battery Safety Conference conducted November 2011 in Boston. In the presentation "Advances in System Design, Integration and Testing for Safety and Reliability," keynote speaker Dr. Brian Barnett (of TIAX LLC, a technology advancement company) presented the conclusions of an extensive study that found the probability of a manufacturer's defect is 10^{-6}. This failure rate is not bad when compared to other baseline probabilities such as electrical equipment failure (10^{-4}) and human error (10^{-2} to 10^{-3}). However, 10^{-6} is large when considering the number of cells produced per year (10^{10}) and increasing each year through wider use of these popular energy sources. This translates into the possibility of thousands of defects/failures per year.

6.2   General Types of Casualties

The experimental data suggest that the severity of a casualty reaction is a function of a number of parameters including battery size, chemistry, construction, and the charge level of the battery. In almost every battery casualty test conducted to date, the same hazardous components have been observed: flammable by-products (aerosols, vapors, and liquids), toxic gases, and flying debris (some burning), and in some instances, sustained burning of the electrolyte and casing material. The following sections provide a general terminology for describing cell level reactions.

During a runaway reaction within a cell, a significant amount of gas is produced that causes an increase in pressure within the cell housing. The mechanism of release of this pressure is dependent on the rate of the reaction and the configuration of the cell housing. For example, at a low state of charge (SOC), the event may consist of a small amount of liquid/aerosol sprayed through the overpressure vents (if available) or through a seam in the battery housing. The vented products are typically flammable and can be ignited if exposed to a flame.

At a high SOC (fully charged batteries), the venting is much more forceful and typically involves a much larger volume of liquid/aerosol. The flammable electrolyte liquid/aerosol can be ignited, forming small torch-like flames at the vent locations. During some instances, the electrolyte and battery contents may ignite with sustained burning, producing a moderate size, nonviolent fire.

In some cases, there can be a stronger, sometimes substantial, pressure pulse associated with this electrolyte release. Depending on the battery construction, flaming debris can be expelled (sprayed or thrown from the battery). Occasionally, the pressure release ports fail to operate correctly (or the battery is not equipped with vent ports), causing a buildup of pressure inside the cell casing until the casing fails.

When this occurs, the cell explodes, expelling the contents throughout the test chamber, producing a measurable pressure pulse. These explosive type reactions can vary from firecracker type bangs to as loud as shotgun blasts or greater. As with the slower venting scenarios, if the contents are flammable, the aerosol emitted can be ignited. Since the entire electrolyte content of the battery is released at once in these explosive type reactions, a substantial fireball occurs if the products are ignited. The ejected burning or incandescent material may start nearby fires or ignite the vapors being vented from the cell/battery. In these studies, the lithium-ion and solid cathode lithium cells use a flammable electrolyte.

In summary, single cell reactions can be described using the following six terms: vent, smoker, flare, burner, explosive, and fireball. Figure 4 shows photographs of all these scenarios except venting. Video clips are presented in the Appendix.

Smoker	Flare	Burner	Explosive	Fireball

Fig. 4 — Single cell reaction classifications

6.3   Observed Cell Casualties

The reactions observed in the commercially available cells are described in Tables 6 through 9. In general, the smaller, lower capacity solid-cathode cells typically vented and/or smoked and the medium to higher capacity cells (specifically the oxyhalides) either ignited and burned or exploded.

Intuitively, one expects the type of reaction to be a function of the amount of energy contained in the cell at the time of the event. If this is the case, the type of reaction should be a function of both the battery capacity and the state of charge at the time of the event. Based on a very limited data set (i.e., not a statistically valid set of data), it appears that the threshold between a venting and a flaming reaction lies in the 10 to 20 Wh range. Battery pack configurations can significantly alter these single cell results.

Table 6 — A/AA/Pouch-size Commercially Available Cell Reaction Descriptions

Cell Manufacturer	A	B-1	C-1	E
Type	Secondary	Secondary	Secondary	Secondary
Form Factor	Pouch cell	AA Cell	18650	18650
Chemistry	Li/CoO_2	$Li/Li_{0.5}CoO_2$	$Li/FePO_4$	$Li/Li_{0.5}CoO_2$
Voltage Capacity Energy	3.7 V 3.3 Ah 12.2 Wh	3.7 V 0.16 Ah 0.6 Wh	3.3 V 1.1 Ah 3.6 Wh	3.7 V 2.2 Ah 8.1 Wh
SOC	100%	100%	100%	100%
Initiator	Calrod heater	Calrod heater	Calrod heater	Calrod heater
Reaction Type	Moderate venting	Moderate venting	Moderate venting	Venting/small flames
Reaction Description	Moderate venting for 1:12, no flames	Moderate venting for 0:22 followed by nonviolent rupture	Moderate venting for 0:48 followed by violent rupture, no flames	Moderate venting with small flames, short duration event (0:15)
Reaction Photograph				

Table 7 — C-size Commercially Available Cell Reaction Descriptions

Cell Manufacturer	F	H-1	D-2
Type	Secondary	Primary	Secondary
Form Factor	C Cell	5/4 C Cell	5/4 C Cell
Chemistry	Li/CF_x	Li/MnO_2	$Li/LiFePO_4$
Voltage Capacity Energy	3.0 V 5.0 Ah 15.0 Wh	3.3 V 6.1 Ah 20.1 Wh	3.2 V 3.2 Ah 10.3 Wh
SOC	100%	100%	100%
Initiator	Calrod heater	Calrod heater	Calrod heater
Reaction Type	Moderate flaming	Flare with sparks	Vent/Smoker
Reaction Description	3:45 venting, rupture with sparks, 1:30 burning	0:18 Roman candle, 0:57 moderate burning	Moderate venting of about one minute
Reaction Photograph			

Table 8 — D-size Commercially Available Cell Reaction Descriptions

Cell Manufacturer	H-2	B-3	B-4	K	G
Type	Primary	Primary	Primary	Primary	Primary
Form Factor	D Cell	D Cell	D Cell	DD Cell	D Cell
Chemistry	Li/MnO_2	$Li/SOCl_2$	Li/SO_2Cl_2	Li/CF_x	$Li/SOCl_2$
Voltage Capacity Energy	3.3 V 11.1 Ah 37.0 Wh	3.6 V 19.0 Ah 68.4 Wh	3.9 V 16.5 Ah 64.4 Wh	3.6 V 40.0 Ah 144.0 Wh	3.6 V 19.0 Ah 68.4 Wh
SOC	100%	100%	100%	100%	100%
Initiator	Calrod heater	Calrod heater	Calrod heater	Calrod heater	Propane flame
Reaction Type	Flare	Explosion	Explosion	Vigorous flaming	Rupture
Reaction Description	Fast venting with flaming combustion, long duration event (1:00)	Explosion, small fireball, no residual burning	Explosion, small fireball, no residual burning	Violent rupture with vigorous burning	Cell ruptured sometime during test (unnoticeable)
Reaction Photograph					
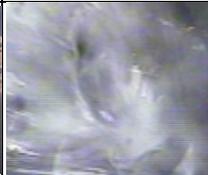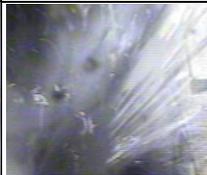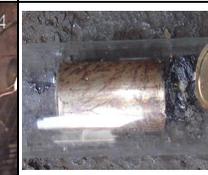
Table 9 — Large Form and Pouch Cell Reaction Descriptions

Manufacturer	I-1	I-2	J	I-3
Type	Secondary	Secondary	Secondary	Secondary
Chemistry	Lithium Nickel Cobalt Aluminum Oxide	Lithium Nickel Cobalt Aluminum Oxide	Lithium Polymer Format Lithium Cobalt Oxide	Lithium Nickel Cobalt Aluminum Oxide
Voltage Capacity Energy	~4 V ~5 Ah ~20 Wh	~4 V ~32 Ah ~128 Wh	~4 V ~53 Ah ~200 Wh	~4 V ~52 Ah ~208 Wh
SOC	100%	100%	100%	100%
Initiator	Calrod heater	Calrod heater	Calrod heater	Calrod heater
Reaction Type	Vent/Smoker	Smoker/flare	Fireball	Fireball
Reaction Description	Moderate venting for several minutes, no ignition/flames	Moderate venting that was ignited manually. Once ignited, flames jetted from end for several minutes.	Cell produced a 4–5 ft diameter fireball for about 30 seconds	Cell produced a 4–5 ft diameter fireball for about 30 seconds
Photograph				

6.4   SOC Effects on Reaction Types (Li-Ion Only)

A quasi-parametric assessment of the effects of SOC on cell level reactions was conducted on the large form and pouch cells. A detailed description of the reactions is provided in Table 10 and a summary in Table 11.

The lithium nickel cobalt aluminum oxide cells (~20 Wh, manufacturer I-1) produced significant amounts of smoke with very little flame and little if any HRR, regardless of SOC. These cells are classified as "vent/smokers." The same chemistry but larger capacity cells (~128 Wh, manufacturer I-2) vented/smoked at a low SOC (20%) but caught fire and readily burned at a higher SOC (100% and overcharged). These cells are considered "flares/burners." The lithium polymer format lithium cobalt oxide cells (~200 Wh, manufacturer J) burned slowly at a low SOC (20%) but produced fireballs at higher charge levels and are considered "burners" and "fireballs" depending on the SOC. The lithium nickel cobalt aluminum oxide cells (~200 Wh) exploded (hydraulic/pneumatic) at a low SOC (20%) but produced fireballs at higher charge levels and are considered "explosive" and "fireballs" depending on the SOC. All cells reacted more violently when initiated by deliberate overcharging.

As shown in Tables 10 and 11, the reaction severity tends to increase with the SOC of the battery. This is expected, since the higher the SOC, the more energy available in the cell to generate heat,

vaporize the electrolyte, and rupture the cell casing. As noted in Section 6.3, there appears to be a threshold between a venting and a flaming reaction in the 10 to 20 Wh range. Again, battery pack configurations can significantly alter these single cell results.

Although reaction severity increases with SOC, the HRR is not necessarily a function of the SOC. At lower SOC, there is less tendency for the cell to burn, thus less HRR; but if ignited at low SOC, the total HRR is about the same as at high SOC. This is shown in Section 8.2.

Table 10 — Large Form and Pouch Cell Reaction Descriptions for Various SOCs

Battery/ Cell Classification	20% SOC	100% SOC	Overcharged
I-1 **Vent/ Smokers** ~14.4 Wh 340 g	Battery vented (slow)/no fire PHRR <5 kW Avg. HRR <5 kW Fire duration – NA 	Battery vented (moderate)/ no fire (similar to previous test) PHRR <5 kW Avg. HRR <5 kW Fire duration – NA 	Battery jetted aerosol/smoke from one end for about 1 minute, no fire PHRR <5 kW Avg. HRR <5 kW Fire duration – NA
I-2 **Burners/ Fireballs** ~120 Wh 940 g	Battery vented prolonged dense aerosol/no fire PHRR <5 kW Avg. HRR <5 kW Fire duration – NA 	Battery vented gases that were ignited by sparker followed by prolonged sustained burning PHRR <5 kW Avg. HRR <5 kW Fire duration – NA 	Battery produced a fireball (4–5 ft diameter) followed by sustained burning from both ends of the battery PHRR 120 kW Avg. HRR 50 kW Fire duration 40 sec

Table 10 (cont.) — Large Form and Pouch Cell Reaction Descriptions for Various SOCs

Battery/ Cell Classification	20% SOC	100% SOC	Overcharged
J **Burners/ Fireballs** ~222 Wh 1200 g	Battery vented and burned slowly PHRR 55 kW Avg. HRR 27 kW Fire duration 80 sec	Battery reacted producing a fireball (4–5 ft diameter) followed by sustained burning (smaller size) PHRR 120 kW Avg. HRR 50 kW Fire duration 35 sec	Battery jetted aerosol then instantaneously ignited, producing fireball greater than 5 ft diameter PHRR 135 kW Avg. HRR 65 kW Fire duration 10 sec
I-3 **Explosive/ Fireballs** ~190 Wh 1000 g	Sudden violent rupture spreading debris throughout the chamber, no fire, limited smoke PHRR <5 kW Avg. HRR <5 kW Fire duration – NA	Battery violently ruptured into a fireball (4–5 ft diameter) followed by sustained burning (smaller size) PHRR 92 kW Avg. HRR 45 kW Fire duration 22 sec	End blew off of battery, flames jetted (~ 5 ft) from open end PHRR 98 kW Avg. HRR 50 kW Fire duration 25 sec
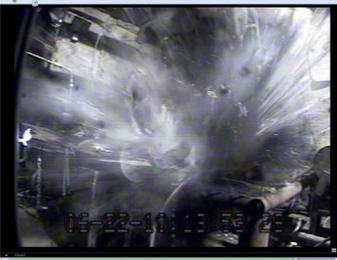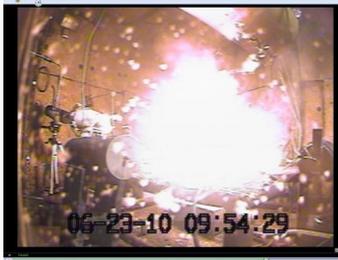
Table 11 — Summary of Large Form and Pouch Cell Reactions for Various SOCs

Cell	SOC	Reaction Description
I-1	20%	Minor off-gassing and contribution to heat release rate.
I-1	100%	Minor off-gassing and contribution to heat release rate.
I-2	20%	Minor off-gassing and contribution to heat release rate.
I-2	100%	Significant off-gassing and moderate contribution to heat release rate.
I-2	100%+	Major off-gassing and significant contribution to heat release rate, as cells jetted violently and exited the containment.
J	20%	Significant off-gassing and contribution to heat release rate. Surprisingly little damage to cell assemblies.
J	100%	Significant off-gassing and contribution to heat release rate. Surprisingly little damage to cell assemblies.
I-3	20%	Off-gassing and moderate contribution to heat release rate.
I-3	100%	Significant off-gassing and contribution to heat release rate. Battery left test table.
I-3	100%+	Major off-gassing and significant contribution to heat release rate, as cells jetted violently and exited the containment.

7   REACTION PRODUCTS TESTING AND RESULTS (SINGLE CELL)

7.1   Reaction Products Test Description

Reaction products were measured and documented using a range of standard analytical techniques. The reaction products tests were conducted in a 5 m^3 (177 ft^3) enclosure at the Naval Research Laboratory Chesapeake Bay Detachment test site located in Chesapeake Beach, Maryland. The casualty was typically initiated by heating the exterior of the cell using a cartridge heater (Calrod heater) fastened to the side of the cell. The products were assessed in terms of acidity, corrosiveness, and toxicity. Real-time analysis was done via electrochemical sensors and optical methods. Samples were also collected using gas sample canisters, sorbent tubes, and impingers. The collected samples were analyzed using gas chromatography–mass spectrometry/infrared (GC-MS/IR).

7.2   Reaction Products for Cells at 100% SOC

7.2.1   *Reaction Products of Commercially Available Cells*

The reaction products measured for the commercial cells are listed in Tables 12 through 14. When the cell vents (without ignition), the majority of the products released are aerosol electrolyte constituents (e.g., carbonates or oxyhalides). A significant amount of these organic solvent gases and aerosols have flammable constituents. This aerosol mixture was not further characterized in these tests, but a reaction products test chamber could be equipped with an oxygen analyzer and an explosive gas meter to measure the Lower Explosive Limit (LEL) of the gases within the chamber, and other equipment to measure aerosol concentrations (the flammability of aerosols are dependent on particle size and number density). In some venting scenarios, the carbonates break down upon release to produce high levels of carbon

dioxide (CO_2) and carbon monoxide (CO). When the cell burns during a casualty, the electrolyte burns fairly efficiently, producing primarily CO_2 as the by-product, as determined by in situ gas analyzers.

The production of acid gas is directly related to the cell chemistry (and appears to be related to cell capacity). Cells that contain sulfur produce sulfuric acid, cells that contain fluorine produce hydrofluoric acid, and cells that contain chlorine produce hydrochloric acid. There is not enough data to develop a quantitative relationship between cell energy and the amount of acid gas produced, but for a given cell chemistry, the amount of acid gas produced is expected to be directly proportional to the cell energy.

Table 12 — A/AA/Pouch-size Commercially Available Cell Reaction Products

Compounds	A Pouch cell 100% SOC	B-1 AA cell 100% SOC	C-1 18650 100% SOC	E 18650 100% SOC
	mg	mg	mg	mg
Butyrolacetone				
Tetrahydrofuran			50	
Propene	175	24	5	
Benzene				
Hexafluoropropene				
Isoprene			10	
Methyl Carbonate			350	7
1,3 Butadiene	20			
Chlorobenzene			50	
1,2 Dimethoxyethane			10	
Isobutene	90			
Ethanol		33		
CO_2	5500			3300
CO	825			675
SO_2				37
Hydrochloric Acid				
Hydrofluoric Acid				
Propylene Carbonate				
1,2 Methoxyethane				
Dimethyl Carbonate	2200	825	1210	156
Ethylene Carbonate	2000		660	238
1,2 Dimethoxyethane	110			
Total (g)	**10.9**	**0.9**	**2.3**	**4.4**
Initial Mass of Cell (g)	**95**	**19**	**39**	**48**
Percentage (%)	**12**	**5**	**6**	**9**

Table 13 — C-size Commercially Available Cell Reaction Products

Compounds	F C Cell 100% SOC	H-1 5/4 C Cell 100% SOC	D-2 5/4 C Cell 100% SOC
	mg	mg	mg
Butyrolacetone	305		
Tetrahydrofuran	10		
Propene	13		5
Benzene	11		
Hexafluoropropene	7		
Isoprene	11		31
Methyl Carbonate		12	305
1,3 Butadiene			
Chlorobenzene			
1,2 Dimethoxyethane			
Isobutene			
H_2SO_4			88
CO_2	20350	14301	12310
CO	1232	2695	1865
SO_2	77	105	
Hydrochloric Acid			280
Hydrofluoric Acid	92		140
Propylene Carbonate		220	
1,2 Methoxyethane		1513	
Dimethyl Carbonate			75
Ethylene Carbonate			
1,2 Dimethoxyethane			
Carbonyl Sulfide			269*
Dimethyl Sulfide			406*
Ethyl Methyl Sulfide			113*
Total (g)	**22.1**	**18.9**	**15.9**
Initial Mass of Cell (g)	**42**	**71**	**82**
Percentage (%)	**53**	**27**	**19**

* Reaction produced moderate amounts of sulfide compounds

Table 14 — D/DD-size Commercially Available Cell Reaction Products

Compounds	H-2 D Cell 100% SOC	B-3 D Cell 100% SOC	B-4 D Cell 100% SOC	K DD Cell 100% SOC
	mg	mg	mg	mg
Butyrolacetone				
Tetrahydrofuran	1752			
Propene	65			
Benzene	18	7	3	
Hexafluoropropene				
Isoprene				
Methyl Carbonate				15
1,3 Butadiene	13			
Chlorobenzene	27			
1,2 Dimethoxyethane	700			
Isobutene	27			
H_2SO_4		1050	390	600
CO_2	13750	26000	27500	
CO	2640	413	330	3465
SO_2	105	4455	4125	4950
Hydrochloric Acid		2200	1403	440
Hydrofluoric Acid				1193
Propylene Carbonate	633			
1,2 Methoxyethane				
Dimethyl Carbonate				
Ethylene Carbonate				
1,2 Dimethoxyethane	3080			
Carbon Tetrachloride		26	21	
Total (g)	**22.8**	**34.2**	**31.1**	**10.7**
Initial Mass of Cell (g)	**115**	**93**	**100**	**320**
Percentage (%)	**20**	**37**	**31**	**3**

7.2.2   Reaction Products of Large Form and Pouch Lithium-Ion Cells

The reaction products measured for the large form and pouch lithium-ion cells are listed in Table 15. When the cell vents (no ignition), the majority of the products released are electrolyte constituents (i.e., carbonates). Therefore, a significant amount of the gas has flammable constituents. In some instances, the carbonates break down upon release to produce high levels of CO and CO_2, especially under thermal runaway conditions at higher state of charge. When the cell burns, the electrolyte burns fairly efficiently, producing primarily CO_2 and water as the by-products.

Large form oxyhalide catholyte (primary) cells were not tested in these studies. The larger quantities of oxyhalide catholyte in these cells would likely produce higher levels of sulfur- and chloride-based compounds during venting and cell failures.

Table 15 — Large Form and Pouch Cell Reaction Products

Compound	I-1 100% SOC (mg)	I-2 100% SOC (mg)	J 100% SOC (mg)	I-3 100% SOC (mg)
1,3 Butadiene	7	95	125	
1,4 Dioxane	34		25	
Benzene		145	25	43
Bromomethane	50	90	125	
CO_2	1265	8800	11825	13780
Chloromethane			48	37
Dimethyl Carbonate	1870	4125	4675	5225
Ethylbenzene		25	15	
Ethylene	94	495	1100	1100
Ethylene Carbonate	1018	1870	4235	4540
Hydrobromic Acid		6		
Hydrochloric Acid			60	60
Hydrofluoric Acid	99	55	630	550
Methane	550	2750	1375	1515
Methyl Butyrate	5500	18370	16225	
Methyl Fluoride	17	61	66	66
Phosphoric Acid	46		75	85
Propene	255	1000	1500	55
Styrene	37	65	10	
SO_2			1100	
Tetrahydrofuran		34	10	
Toluene	36	65	10	
* Total (g)	**11**	**38**	**43**	**27**
Initial Mass of Cell (g)	**340**	**940**	**1200**	**1000**
Percentage (%)	**3**	**4**	**4**	**3**

* These totals do not include the CO_2 values above, which would dramatically increase these totals.

7.3   SOC Effects on Reaction Products

The SOC of the cell affects the type of reaction. Low SOC cells tend to vent pneumatically or hydraulically. At higher SOC, cells tend to ignite. When the cell vents (with no ignition), the majority of the products released are electrolyte constituents (e.g., carbonates) or partial thermal breakdown products, including hydrogen and methane. A significant amount of these reaction products are flammable. In some instances, the carbonates break down upon release to produce high levels of CO_2 and CO. When the cell burns, the electrolyte burns fairly efficiently, producing primarily CO_2 and water vapor as the by-products.

Acid gas production appears to be higher in the burning reactions, and consequently, tends to be higher for higher SOC lithium batteries. Higher SOC also results in greater energy dissipation and heating or potential for incandescent materials such as metal foils and carbonaceous compounds being ejected.

7.4   Reaction Products at Low Oxygen Levels

At lower oxygen concentration, cells are less likely to ignite; they tend to vent only, and the reaction products are as previously described for venting reactions. For example, the H-1 cell at 21% oxygen vented and burned. At 12% oxygen, the cell only vented and sparked but did not ignite.

7.5   Acid Gas Production

The acid gas production is directly related to the cell chemistry, as noted above. For lithium oxyhalide catholyte cells, the acid gas formation can overwhelm the available water in the local atmosphere, or the addition of water vapor will increase the acid formation under these conditions.

7.6   Gas Volume Production

The volume of gas produced by each cell was estimated using the ideal gas law and the steady-state pressure in the test chamber after each test. These chamber pressures and associated gas volumes are listed in Table 16. The term steady-state used in the table means that these were the conditions measured after the gas temperature in the chamber enclosure had cooled back to ambient conditions. In many cases, the chamber pressure spiked higher than the values listed in Table 16 due to expansion of the gases as the temperature increased in the chamber during the reaction. For some oxyhalide cell chemistries, the apparent gas volume expansion will not make sense until the reaction products that are gaseous at high temperature fall below their boiling point and liquefy or solidify. Examples are lithium sulfide, lithium chloride, and aluminum chloride.

Additional work is needed to use these characterizations and this characterization technique. The electrolyte percentage in lithium-ion cells, for instance, is typically within 3% of the cell mass. For cells that vary by an order of magnitude in mass (cell E versus cell I-1) in a fixed volume chamber at similar SOC, statistically the final pressure is the same.

Table 16 — Cell Level Gas Production Quantities

Cell		SOC	Steady-State Pressure (atm)	Steady-State Gas Volume (m^3)
A	Pouch Cell	100%	1.00	Neg.
B-1	AA Cell	100%	1.00	Neg.
C-1	18650	100%	1.00	Neg.
E	18650	100%	1.05	0.017
F	C Cell	100%	1.10	0.034
H-1	5/4 C Cell	100%	1.08	0.027
H-2	D Cell	100%	1.13	0.044
B-3	D Cell	100%	1.06	0.020
B-4	D Cell	100%	1.15	0.051
K	DD Cell	100%	1.25	0.085
I-1	Large Form	100%	1.00	Neg.
I-2	Large Form	100%	1.05	0.017
J	Pouch Cell	100%	ND	ND
I-3	Large Form	100%	1.5	0.170

ND = no data; Neg. = negligible effects

8   HEAT RELEASE RATE TESTS AND RESULTS (SINGLE CELL)

8.1   Heat Release Rate Test Description

Heat release rate and related parameters were characterized on the U.S. Navy test ship ex-USS *Shadwell* located in Mobile, Alabama [2]. The heat release rate of the cell casualty was determined using a hood calorimeter. Four other types of measurements were made during the HRR tests: unburned hydrocarbons, smoke production (obscuration), thermal exposures (radiant and total), and overpressures. The energy contained in the unburned hydrocarbons was added to the HRR measured by the hood. Smoke production was assessed using an optical density meter installed in the compartment. The thermal exposures were determined by mapping the radiant and total heat fluxes in close proximity to the cell. Infrared and radiometric imaging cameras were also used to quantify hot gas release that may impinge on nearby objects. The overpressures were measured both local to the cell and globally in the test compartment.

The tests were conducted under a 1 MW hood calorimeter. The hood calorimeter was instrumented for gas temperature, gas velocity (volumetric flow rate), and typical fire/combustion gas concentrations (CO, CO_2, and O_2). The water vapor constituent of the combustion process was removed with an ice-water cold trap. In addition, explosive gas concentrations (Lower Explosive Limit) and potentially toxic and flammable gases (e.g., SO_2 and volatile organic compounds, VOCs) were measured. The test compartment and area below the hood were instrumented for temperature (five thermocouple trees), pressure, and smoke obscuration (using three optical density meters). The area around the test specimen/battery was instrumented to measure any localized exposures produced by the battery casualty. A computerized data acquisition system was used to collect and record the measurements during the test at a rate of one scan per second (1 Hz).

8.2   Heat Release Rate Test Results

8.2.1   *HRRs of Commercially Available Cells*

In general, the heat release rates of the commercially available cells were too low to measure using the 1 MW hood calorimeter on the ex-USS *Shadwell*. In future assessments, the heat release rates of the small commercial cells will be measured using a recently installed smaller hood calorimeter with a range from 10 to 100 kW.

Although the HRRs of the smaller commercial cells could not be measured using the 1 MW hood calorimeter, an estimation of the heat energy content of these cells was made based on the temperatures measured in the test chamber during reaction products testing at CBD. Specifically, the energy released was estimated by multiplying the mass of the gas in the CBD test chamber, an average specific heat for the gas(es), and the increase in temperature that occurred in the chamber during reaction. The resulting energies are listed in Table 17. The mean HRRs were determined by dividing the total energy released, by the duration of the reaction (determined based on measurements and visual observations). These values are also shown in Table 17.

Table 17 — HRRs of Commercially Available Cells

Cell		SOC	Delta-T (°C)	Mean HRR (kW)	Duration (sec)	Energy Released (kJ)
A	Pouch Cell	100%	Neg.	Neg.	Neg.	Neg.
B-1	AA Cell	100%	Neg.	Neg.	Neg.	Neg.
C-1	18650	100%	Neg.	Neg.	Neg.	Neg.
E	18650	100%	5	0.4	70	27.5
F	C Cell	100%	50	3.0	90	275
K	DD Cell	100%	30	5.5	30	165
H-1	5/4 C Cell	100%	36	3.3	60	200
H-2	D Cell	100%	131	6	120	720
B-3	D Cell	100%	85	> 470	< 1	470
B-4	D Cell	100%	60	> 330	< 1	330

Neg. = negligible

8.2.2   HRRs of Large Form and Pouch Cells

The HRR data for large form and pouch cells are provided in Table 18. The cells were tested at three SOCs: 20%, 100%, and overcharged (listed in the table as 100%+). The cell/SOC combinations that show negligible HRRs produced venting reactions with little or no burning. These were measured using a special-purpose smaller hood and lower air flow interfaced to the 1 MW hood instrumentation. Special gas collection and air flow would be needed to achieve measureable HRRs and PHRRs for moderate size single cells of lithium primary (with organic) and lithium-ion cells.

Table 18 — HRRs of Large Form and Pouch Cells

Cell	SOC	Peak HRR (kW)	Mean HRR (kW)	Duration (sec)	Energy Released (MJ)
I-1	20%	Neg.	Neg.	-	-
I-1	100%	Neg.	Neg.	-	-
I-1	100%+	Neg.	Neg.	-	
I-2	20%	Neg.	Neg.	-	-
I-2	100%	Neg.	Neg.	-	-
I-2	100%+	50	~15	40	600
I-3	20%	Neg.	Neg.	-	-
I-3	100%	45	~10	22	220
I-3	100%+	50	~15	25	375
J	20%	27	~10	80	800
J	100%	50	~25	35	875
J	100%+	50	~50	25	1250

Neg. = negligible; **-** = Could not be accurately determined

9 HEAT RELEASE RATE TESTS AND RESULTS (GROUPS OF CELLS)

9.1 Burning Characteristics of Commercially Available Battery Packs/Modules

The commercially available battery packs/modules that were tested are described in Table 19 and the burning characteristics are summarized in Table 20. The first notable observation during testing was that the packs/modules reacted differently compared to the single cell tests. Specifically, except for the iron phosphate cells (discussed below), all the packs/modules produced burning reactions, while many of the single cells just vented and never caught fire. In addition, during almost every unmitigated pack/module test, all the cells in the module reacted and the casing materials were completely consumed.

Table 19 — Commercially Available Battery Packs Tested

No. of Cells	10	10	24	63	32
Cell Type	D Cell	D Cell	18650	18650	5/4 C Cell
Manufacturer	**H-2**	Li-SO$_2$ *	**E**	**E**	**H-1**
Type	Primary	Primary	Secondary	Secondary	Primary
Voltage	27 V	27 V	30 V	26 V	24 V
Capacity	11.1 Ah	15.0 Ah	7.2 Ah	21.0 Ah	24.4 Ah
Energy	300 Wh	405 Wh	207 Wh	540 Wh	586 Wh
No. of Cells	90	6	4	4	
Cell Type	Li/MnO$_2$ *	Pouch	18650	26650	
Manufacturer		**A**	**C-1**	**C-2**	
Type	Primary	Secondary	Secondary	Secondary	
Voltage	24 V	22.2 V	13.2 V	13.2 V	
Capacity	30.0 Ah	3.85 Ah	1.1 Ah	2.3 Ah	
Energy	720 Wh	85.5 Wh	14.5 Wh	30.4 Wh	

* These cells were not tested as single cells

Table 20 — Commercially Available Battery Pack HRRs

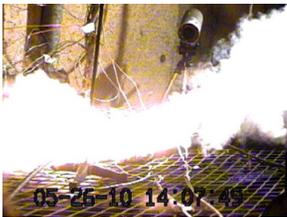| Pack/ Module Mfr. or Type	No. of Cells	Peak HRR (kW)	Mean HRR (kW)	Duration (sec)	Total Energy Released (MJ)	Fire Photograph
E	1 pack of 24	120	~35	60, 200	6.9	
	16 packs of 24	240	~150	560	85.0	
E	2 packs of 63	185	~60	100, 350	21.2	
H-1	1 pack of 32	135	~35	120, 320	11.4	
H-2	1 pack of 10	125	~50	250	13.2	
	2 packs of 10	115	~50	240, 540	25.5	
	3 packs of 10	165	~90	100, 350	32.5	
	10 packs of 10	inconclusive				
LiMnO$_2$	1 pack of 90	130	~60	120, 120	14.2	

Table 20 (cont.) — Commercially Available Battery Pack HRRs

Pack/ Module Mfr. or Type	No. of Cells	Peak HRR (kW)	Mean HRR (kW)	Duration (sec)	Total Energy Released (MJ)	Fire Photograph
Li-SO$_2$	1 pack of 10	35	20	300	6.0	
C-1	1 pack of 4 18650 cells	<5	Neg.	100, 350	Neg.	
C-2	1 pack of 4 26650 cells	<5	Neg.	100, 350	Neg.	
A	1 pack of 6 pouch cells	10	~5	175	0.9	

Neg. = negligible

The pack/module burning characteristics presented in Table 20 are the most severe measured during testing (for that specific set of conditions). There were many instances when the same test was conducted multiple times and produced significantly different results each time. Specifically, the heat release rate histories showed dramatic differences (i.e., lower intensity, longer duration burns sometimes); however, the total thermal energy released was typically in good agreement across the repeated tests.

An example of HRR variation is provided in Fig. 5, which shows the heat release rate histories of two tests conducted with two 63-cell 18650 (manufacturer E) Li/Li$_{0.5}$CoO$_2$ battery packs/modules at 100% SOC. The left graph shows a lower intensity (105 kW PHRR), longer duration event and the right graph shows a higher intensity (190 kW PHRR), shorter duration event. The two tests were conducted with identical conditions. The propagation from one pack to the receptor pack can be seen to initiate in

the slight double spike midway through the event. This transition (two distinct HRR contributions) is more clearly seen for the 20% SOC event in Fig. 9.

Two 63-cell E Packs/Modules (100% SOC)
~105 kW PHRR
~200 sec duration
~ 22.5 MJ energy released

Two 63-cell E Packs/Modules (100% SOC)
~190 kW PHRR
~ 100 sec duration
~ 22.5 MJ energy released

Figure 162 – Heat release rate

Figure 218 – Heat release rate
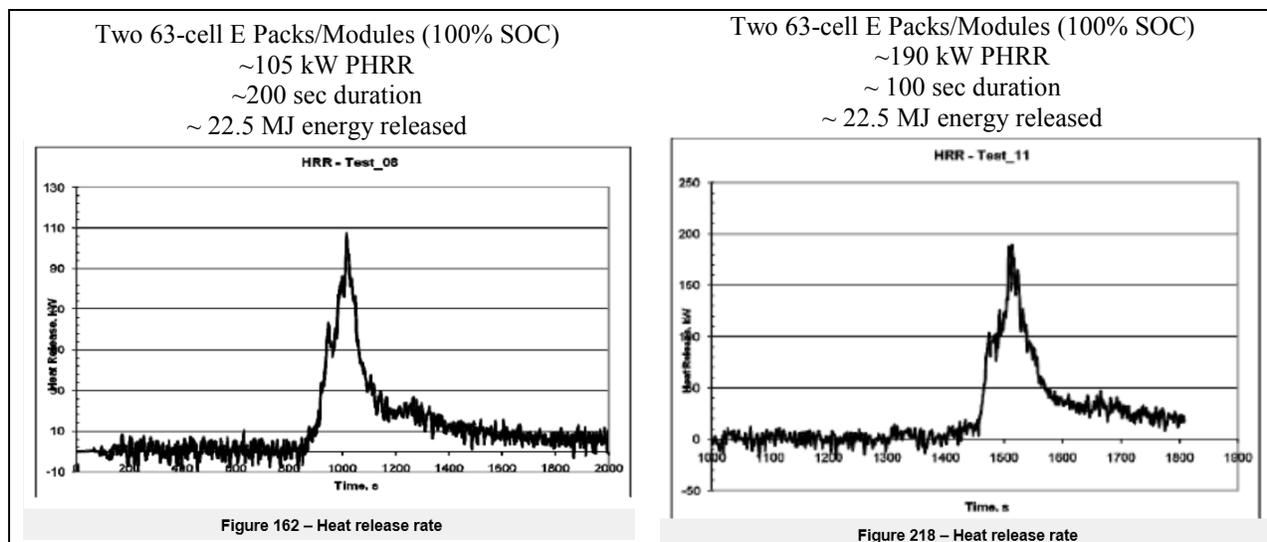
Fig. 5 — Example of variations in burning characteristics for identical tests

A typical single pack HHR plot is provided in Fig. 6. The plot shows a single spike representing the period during which all the cells within the pack vent and ignite. This period typically lasts 1 to 2 minutes, depending on the type and number of cells within the pack. After this rapid-growth-rate, high-intensity burning period, the reaction then decays to a small/steady fire that lasts 3 to 5 minutes as the combustible packaging, circuit boards, and wiring (insulation) is consumed.

Heat Release – Test 6

Fig. 6 — Typical HRR history for a single pack/module of lithium primary cells

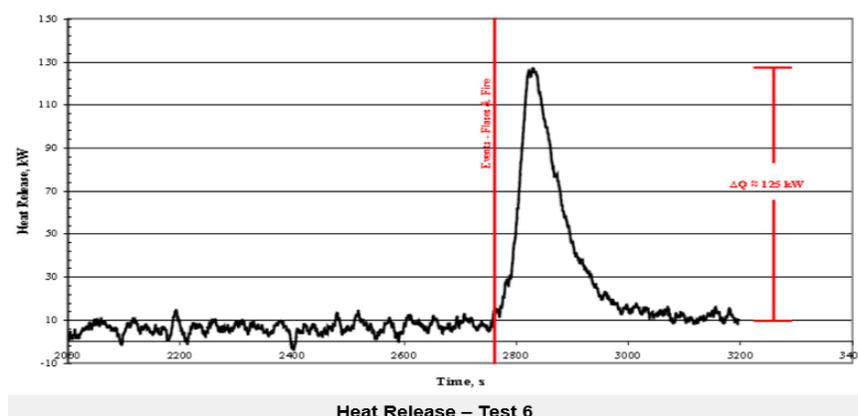For multiple packs/modules, the HRR history can have a single spike or multiple spikes, depending on how quickly the fire spreads to the adjacent pack (and the level of communication between packs). A typical multiple pack HHR plot with multiple spikes is shown in Fig. 7. The multiple spikes indicate the fire spreading to adjacent packs. The time between the spikes appears to be loosely related to the thermal inertia of the packaging. For example, the time between spikes is typically greater for the E and H-2 packs due to the thickness of the hard plastic battery case. Conversely, the time between spikes is shorter and typically less pronounced for thinner battery cases such as the shrink wrap used on the E battery packs/modules. In any case, after all the cells have reacted, the fire decays to a small/steady fire that lasts 3 to 5 minutes as the combustible packaging, circuit boards, and wiring (insulation) are consumed.
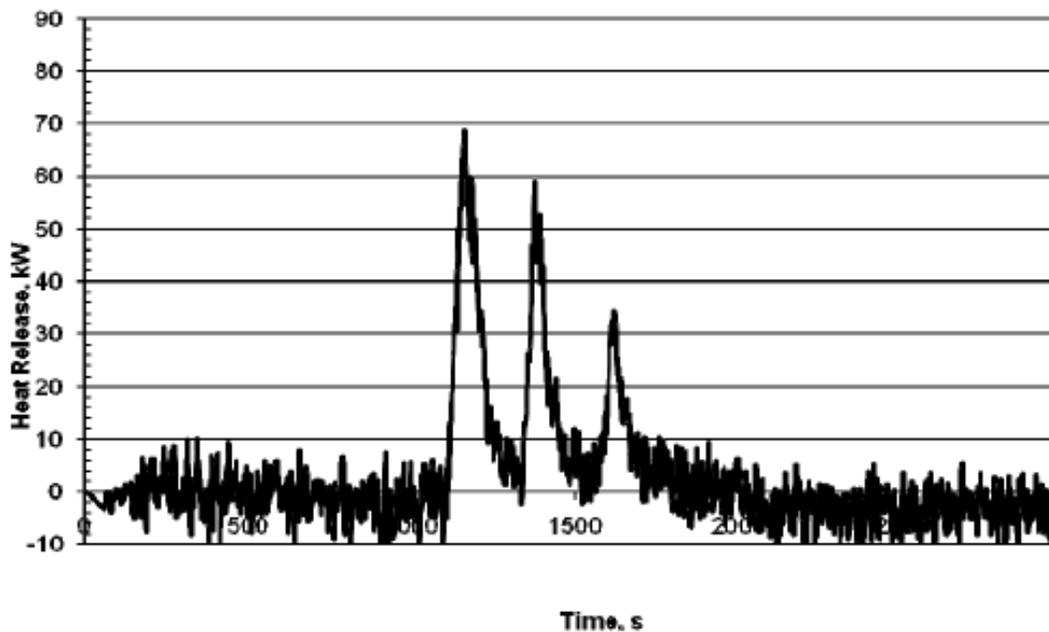
Fig. 7 — Typical HRR history for a group of packs/modules

As noted above, the phosphate-based lithium-ion packs/modules were the only ones tested that did not readily react to consume all the cells in the pack. Four tests were conducted with C-1 and C-2 battery packs (two 1100 mAh and two 2300 mAh). The results were similar for each of the four tests. In short, a single cell within each pack was heated until the cell achieved thermal runaway, but the reaction never spread to any of the adjacent cells. Figure 8 shows one of these packs being tested. Only one cell in the pack reacted.

Fig. 8 — Typical phosphate-based pack/module (C-1) under test

9.2   SOC Effects on Combustion Energy Released

Although the type of reaction, venting versus flaming, appears to be a function of SOC at the single cell level, the amount of combustion energy released during a burning reaction (the most common reaction at the pack/module level) appears to be constant regardless of SOC. An example of this is shown in Fig. 9. The left graph shows the HRR of two 63-cell E packs at 20% SOC and the right graph shows the HRR of two 63-cell E packs at 100% SOC. Although the peaks and the durations are different, the total combustion energy released during the two reactions is essentially identical (~22.5 MJ).
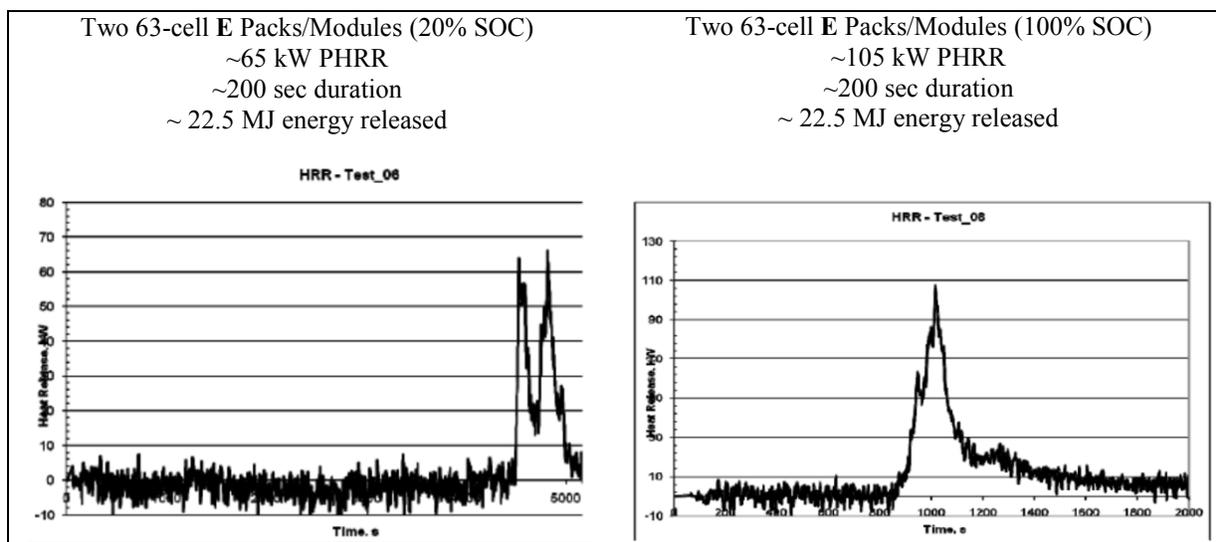

Fig. 9 — Example of two tests with equal amounts of energy released

9.3   Combustion Energy as a Function of Electrical Energy

Intuitively, one expects the combustion energy potential to be proportional to the electrical energy potential. The rationale is that the fuel load, i.e., the amount of combustibles (electrolyte and separator material), should be proportional to the electrical energy potential.

The published [1] electrical energy potential for each test configuration and the measured combustion energy released are shown in Table 21. The two right-hand columns show the ratio of the measured combustion energy to the published electrical energy.

At initial glance, there appears to be a fairly wide range in the ratios of combustion energy to electrical energy (5 to 12). However, the lithium-ion E battery packs have a hard plastic case with about 150 grams of plastic material. This plastic contributes about 30% of the total combustion energy for the pack. Similarly, the lithium manganese oxide H-2 battery packs have a hard plastic case with about 200 grams of plastic material. This plastic contributes about 40% of the total combustion energy for the pack.

After adjusting the combustion energies to account for the case material, there is fairly good agreement between the results of these tests, suggesting that the combustion energy is typically about six times the electrical energy potential of the battery.

Table 21 — Combustion Energy and Electrical Energy Comparison

Cell Type	No. of Cells	Combustion Energy Released (MJ)	Electrical Energy (Wh, MJ)	Ratio Comb./Elect.	Adjusted Ratio Comb./Elect.
E	1 pack of 24	6.9	207, 0.75	9.2	6.4
E	16 packs of 24 in a cardboard box	85.0	3312, 11.9	7.1	5.4
E	2 packs of 63	21.2	1080, 3.9	5.4	5.4
H-1	32	11.4	586, 2.1	5.4	5.4
H-2	1 pack of 10	13.2	300, 1.1	12	7.2
H-2	2 packs of 10	25.5	600, 2.2	11.6	6.9
H-2	3 packs of 10	32.5	900, 3.2	10.1	6.1
$LiMnO_2$	1 pack	14.2	720, 2.6	5.4	5.4

9.4   HRRs of Bulk Storage Configurations

Two HRR tests were conducted in bulk packing configurations such as might be encountered in shipping and storage. The first test consisted of 16 packs of 24 cells each of E type cells packed in a cardboard shipping box. The second test consisted of six 10-cell boxes of F cells. Pre-test photos and the HRR histories measured during the two tests are shown in Figs. 10 and 11. The 16 packs of E cells were triggered by exposure to a propane flame, and the six boxes of F cells were initiated by heat tape wrapped around the boxes.

A comparison between these results and the smaller scale tests suggests that for these two configurations, the cells tended to react sequentially rather than simultaneously. The peak HRRs were similar to the smaller battery configurations but the duration of burning was longer. These two tests provide only limited data; a rapidly growing reaction with numerous cells reacting simultaneously is easily conceivable.
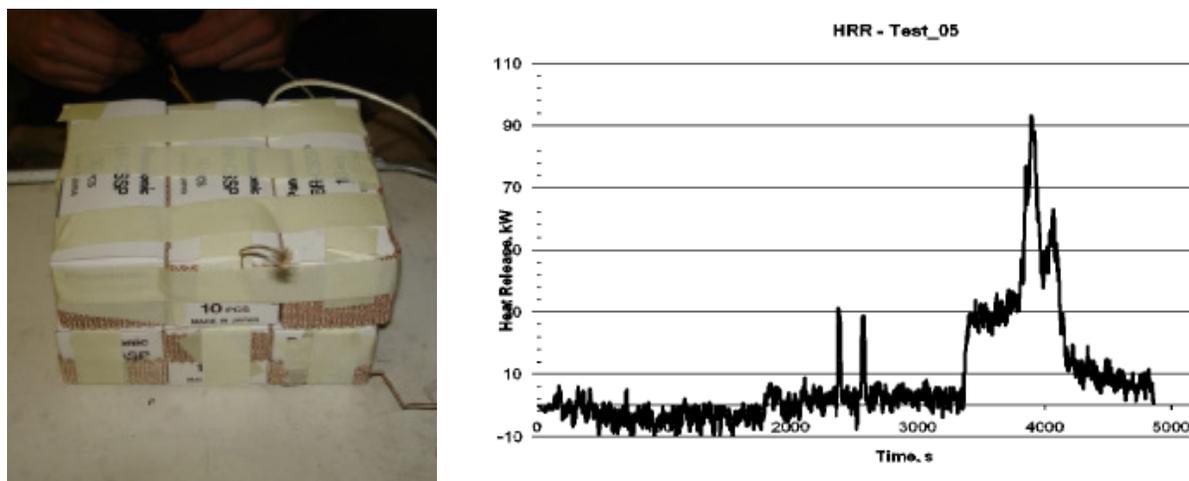

Fig. 10 — Bulk storage test, E type cells

Fig. 11 — Bulk storage test, F type cells

10   SAFE STORAGE AND CASUALTY MITIGATION OF MULTICELL LITHIUM BATTERIES

One objective of the battery casualty test programs was to develop a facility to contain large lithium batteries and prevent a cascading casualty during storage and charging. The containment/mitigation structure developed is termed a Battery Storage Locker (BSL). In general terms, the BSL was designed to limit a casualty to the initial battery and to contain, to the maximum extent possible, the exposures (both thermal and products) produced by the event. The final mitigation system includes a pressure vessel housing to contain the gaseous products released during a casualty, a smoke detection system to notify personnel of the event, and a self-contained, closed head sprinkling system designed to suppress and ultimately extinguish a fire. The entire package is referred to as the Lithium Battery Casualty Mitigation System (LBCMS).

10.1   Battery Storage Locker (BSL) Development History

The initial approach was to develop a BSL similar to a commercial off-the-shelf (COTS) flammable liquid storage cabinet. Two series of tests were conducted to quantify the conditions produced in a prototype rectangular BSL and to assess/refine the design for the overall LBCMS. These conditions became the basis for the performance requirements for the system and components. Later, a cylindrical BSL was developed and tested (see Section 10.4.2).

The rectangular BSL design was based on a box-in-a-box concept. The inner box is the battery compartment. The battery compartment provides a passive barrier to contain the initial battery casualty and prevent direct exposures to and from adjacent battery packs. The battery compartment is also designed to contain the extinguishing agent (i.e., water) so that the battery can be completely submerged to aid in extinguishment and minimize cell-to-cell propagation within the battery. The battery compartment is equipped with a hinged lid (held closed by gravity, not secured) that is designed to vent the pressure and products of the initial battery casualty into the outer box. The outer box is a sealed unit that serves as a plenum to contain the reaction products.

The prototype BSL (Fig. 12) was constructed of 0.64 cm (0.25 in.) steel plate with dimensions of 46 cm × 46 cm × 1860 cm (18 in. × 18 in. × 73 in.). It contained three battery compartments and a plenum area located above and in front of each compartment. Each battery compartment was roughly 30 cm deep × 30 cm tall × 60 cm long (12 in. × 12 in. × 24 in.). The top of the BSL was also equipped with a hinged lid to provide access to the battery compartments. This lid was held shut using two latches located at the front of the BSL.

Each battery compartment was equipped with a closed head sprinkler to suppress and extinguish a casualty within the compartment. During development, a variety of detection technologies were installed in the plenum to aid in the downselect of the final technology.

4X LIFTING LUGS

ODM HOLE WITH 1" COUPLING

FRONT ISOMETRIC VIEW

MCT

2X LATCH

3" TYP

4" X 3" LONG PIPE NIPPLE

3X 1/2" COUPLINGS

HINGES AR

3X 1/2" COUPLINGS

REAR ISOMETRIC VIEW

3X 1/2" COUPLINGS

ODM HOLE WITH 1" COUPLING

HINGES AR

3X INTERNAL COMPARTMENT LID

14"

12"

12"

24" TYP

FRONT ISOMETRIC VIEW INTERNAL BOXES

BATTERY TEST BOX 09/16/10
FABRICATED FROM 1/4" (6mm) PLATE
WEIGHT= 575 LBS

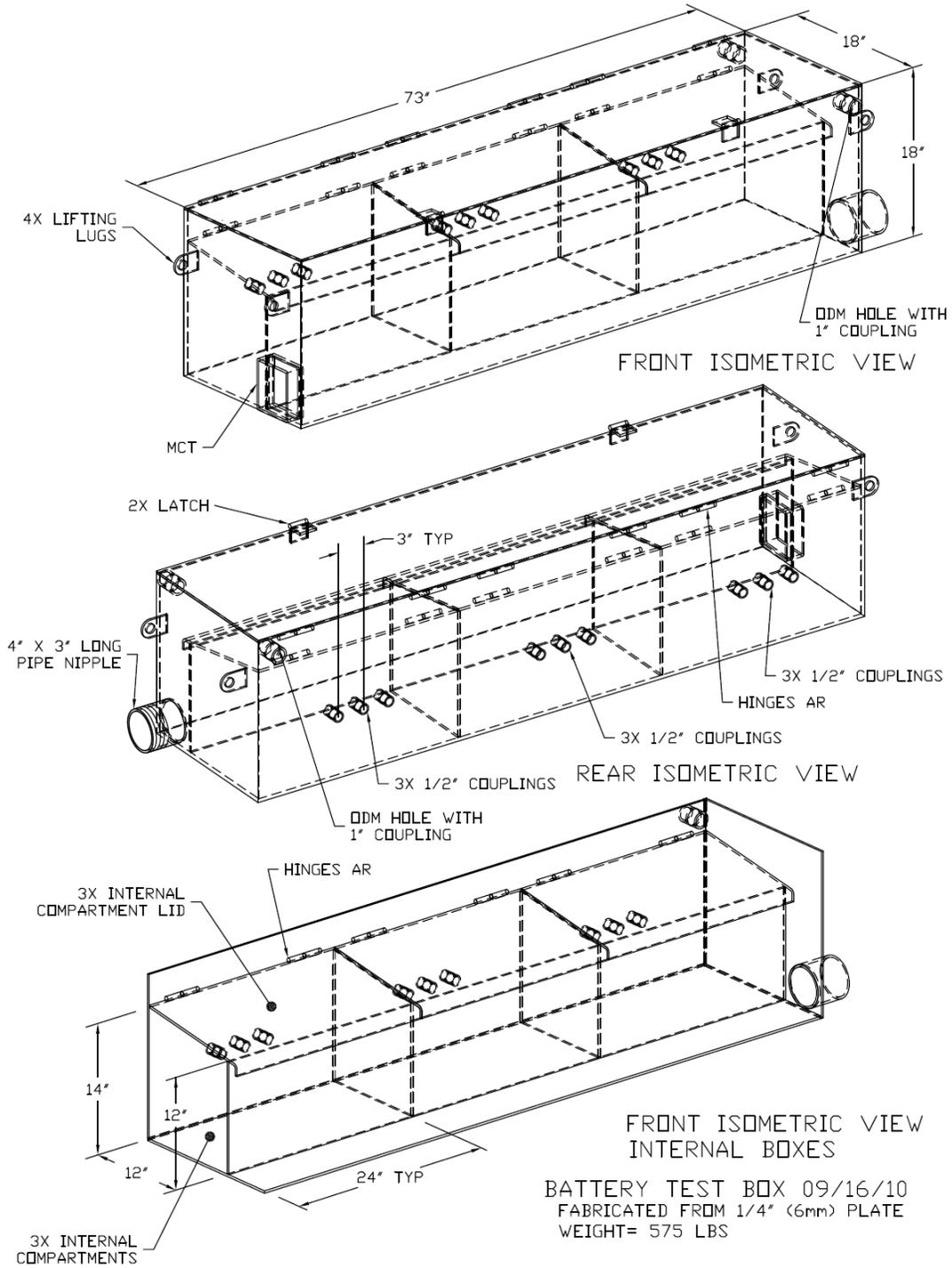3X INTERNAL COMPARTMENTS

73"

18"

18"

Fig. 12 — Prototype BSL schematic

10.2 Detection System Development History

During the development tests, the rectangular BSL was instrumented for both temperature and optical density so it could be determined if standard off-the-shelf heat and smoke detectors would be suitable for this application. In addition, two commercially available detectors were installed in the battery storage compartment: a heat sensing device (HSD) and an aspirated smoke detection system.

During the vast majority of the tests, there was no indication of the casualty outside the cell or pack prior to the event. Short-circuits or overcharge may produce sufficient local heating to be detected prior to the casualty if the battery pack is instrumented internally for temperature. A sudden increase or decrease in battery voltage may also indicate an ensuing battery casualty, but the voltage was not measured during these tests.

During the vast majority of the tests, the reaction of a single cell within the BSL produced effects that would be detectable using almost any of the available COTS technologies (i.e., heat and smoke). The battery compartment and the plenum space became obscure (80% to 100%) with smoke/aerosol particles during every casualty. COTS photoelectric type smoke detectors typically alarm when exposed to obscurations between 3% and 5%, making them a good option for this application. During many of the tests, there was a significant temperature increase (between 30 and 300 °C) in the battery compartment, indicating that temperature sensors would also work well in this application (i.e., inside the battery compartment to detect the battery casualty).

Ultimately, the results supported the selection of a photoelectric smoke detector for use as an early warning device to notify personnel.

10.3 Suppression System Development History

Table 22 provides an overview of the fire suppression systems considered and their anticipated capabilities for this application. Also included are a number of concerns associated with each technology/system.

Since a battery casualty typically cannot be detected prior to the first cell reaction (venting and/or fire), the suppression system for this application must be able to extinguish any fires in normal combustible materials, minimize the potential for secondary reactions (in adjacent cells and/or battery packs), and mitigate the hazards/exposures produced by the initial reaction (i.e., absorb the heat given off by the initial reaction, minimize the exposures to adjacent cells and batteries surfaces by cooling, and scrub some of the particles and compounds out of the vented gases).

Only water-based systems have the capabilities to meet these desired performance objectives. Gaseous agent systems have excellent fire extinguishing capabilities (they can extinguish most combustible materials in less than a minute of agent discharge) but have no cooling capabilities to help mitigate the hazard to adjacent cells or batteries.

The two systems that showed the most potential for this application were a water deluge (flooding) system and a sprinkling system. Additives such as foams would have been investigated if the "water only" systems could not meet the desired levels of performance. Ultimately, a closed head sprinkling system was selected for this application. The closed head sprinkling system has the advantage over other technologies of not needing a separate detection and activation system, making it the simplest, most cost effective, and easiest to maintain.

Table 22 — Suppression System Capabilities and Limitations

System	Capabilities	Limitations/Concerns
Seawater Flooding	Suppression, cooling, exposure protection	Shorting, collateral damage, electrolysis (hydrogen explosion)
Potable Water Flooding	Suppression, cooling, exposure protection	Shorting, collateral damage, electrolysis (hydrogen explosion)
Seawater Sprinkling	Cooling	Limited shorting collateral damage
Potable Water Sprinkling	Cooling	Limited shorting collateral damage
AFFF Sprinkling	Cooling	Limited shorting collateral damage
Medium Expansion or Compressed Air Foam	Suppression, cooling, exposure protection	Limited shorting collateral damage
High Expansion Foam	Suppression, cooling, exposure protection	Limited shorting collateral damage
Inert Gas	Suppression	No cooling
Halocarbons	Suppression	No cooling
Water Mist	Suppression, cooling	Limited shorting collateral damage
Powders/Aerosols	Suppression	No cooling
Aqueous Agents	Suppression, cooling	Limited shorting collateral damage

The suppression system chosen for the LBCMS consists of an individually thermally activated sprinkler (a closed head sprinkling system) installed above the center of each battery compartment. Standard Tyco pendent sprinkler heads (57 °C/135 °F) with k-factors of 80 lpm/bar$^{\frac{1}{2}}$ (5.6 gpm/psi$^{\frac{1}{2}}$) were selected and tested for this application. Additional information on the sprinkler heads is provided in Table 23.

During the development and validation tests, the system was designed to fill the battery compartment with water in less than 20 seconds from activation. The system was secured (turned off) about 40 seconds after activation. This corresponds to twice the amount of water required to fill a single battery compartment.

Table 23 — Sprinkler Head Information

Manufacturer and Model	Tyco Pendent Sprinkler Head
K-Factor	80 lpm/bar$^{\frac{1}{2}}$ (5.6 gpm/psi$^{\frac{1}{2}}$)
Temperature Rating	57 °C (135 °F)
Response Time Index (RTI)	32 (m-s)$^{\frac{1}{2}}$ (58 (ft-s)$^{\frac{1}{2}}$)
Photograph	

10.4 Mitigation Test Results

10.4.1 Rectangular BSL Suppression Test Results

The capabilities of the suppression system installed in the rectangular BSL were assessed against two battery packs: 24 18650 type E cells and 10 D type H-2 cells. These batteries were selected because they produce a burning reaction that readily propagates to all the cells within the pack. Also, the individual cells are obstructed from direct water spray impingement from the sprinkler head due to packaging material. Table 24 describes these battery packs.

Table 24 — Battery Packs Tested in the Rectangular BSL

No. of Cells	24	10
Cell Type	18650	D Cell
Manufacturer	E	H-2
Type	Secondary	Primary
Voltage	30 V	27 V
Capacity	7.2 Ah	11.1 Ah
Energy	207 Wh	300 Wh

During the first series of scoping tests, only one suppression test (H-2 pack) was conducted. The results suggested that a single individually thermally activated sprinkler head was a viable option for the battery compartment fire suppression system. During the second test series, four additional fire suppression tests and two baseline tests without suppression were conducted to further quantify the capabilities of the system. The results of these tests are summarized in Table 25.

Table 25 — Rectangular BSL Suppression System Test Results

Battery Description	Max. Battery Comp. Temp. (°C)	Max. Adjac. Battery Comp. Temp. (°C)	Max. Plenum Temp. (°C)	Sprinkler Activ. Time (sec)	Exting. Time* (sec)	No. of Cells that Reacted
One E pack of 24 cells	250	80	115	**5–10	NA	24 of 24
One E pack of 24 cells	165	25	30	5–10	~20	6 of 24
Three E packs, total 72 cells	200	30	85	5–10	~30	24 of 72
One H-2 pack of 10 cells	250	125	200	**5–10	NA	10 of 10
One H-2 pack of 10 cells	125	25	75	5–10	~15	4 of 10
Three H-2 packs, total 30 cells	145	175	***325	5–10	~35	15 of 30

* These are estimates due to the difficulty in determining the actual extinguishment time
** For this test, the water was not allowed to flow
*** The flammable electrolyte gases were burning outside of the battery compartment in the plenum

As shown in Table 25, three tests were conducted with each battery type: a single battery pack baseline test without suppression, a single battery pack test with suppression, and a test with three battery packs taped together to assess the ability of the system to prevent pack-to-pack propagation.

During the baseline tests, the casualty rapidly propagated through the entire pack(s), consuming all the cells in less than 2 minutes. In both cases (E and H-2), the plastic case continued to burn for another 2 to 3 minutes.

When repeated with the suppression system operational, the system activated within 10 seconds and the reaction was stopped before all the cells in the pack were consumed and before the battery case ignited (i.e., the fire was extinguished about 10 seconds after the start of discharge). Only 25% of the E cells were consumed and 40% of the H-2 cells were consumed.

When the tests were repeated with the three-pack configurations, the system again activated within 10 seconds and the reactions were stopped before all the cells in the pack of origin were consumed, but the fire did spread into one of the adjacent packs. This fire spread to the adjacent pack was an anomaly of the test configuration. Specifically, the wires/Calrod used to heat the cells in the center pack ran through the center of one of the adjacent packs. This wire run provided a path for the hot gases that were being released from the pack of origin to ignite the adjacent pack. However, in both three-pack tests, only one or two cells in the adjacent pack reacted prior to the suppression/extinguishment of the entire group of batteries. In both cases, the fire was extinguished less than 30 seconds after the start of discharge. Only 33% of the E cells were consumed and 50% of the H-2 cells were consumed in the pack of origin during these multiple pack tests.

With respect to thermal management, the sprinkler rapidly suppressed and extinguished the fires and prevented the spread of fire to batteries stowed in adjacent battery compartments (based on the temperatures measured in the adjacent areas).

10.4.2 Pressurizable Cylindrical BSL Suppression Test Results

Some lithium battery packs produce significant overpressure during a casualty. These pressures could not be contained in the rectangular design BSL. A pressurizable cylindrical BSL with three battery compartments was designed to handle up to 50 psig pressures with a vent.

The original battery pack intended to be stowed in the LBCMS, consisting of thionyl and sulfonyl chloride lithium cells (B-2, B-3, and B-4), was shown to be too energetic during casualty events to be contained within a reasonably designed BSL. Accordingly, notional battery packs were constructed using less energetic cells. These notional battery packs (referred to as Pack #1, Pack #2, and Pack #3) provide the necessary energy and power for some applications. The battery packs tested are described in Table 26.

Table 26 — Battery Pack Configurations

Battery Pack Designation (% of volume)	Cell	Manufacturer	No. of Cells	Configuration
Bulk	C	F	30	Three 10-cell boxes
1 Pack	18650	E	10	1 pack of 10 cells
Pack A	Large form	I-3	9	3 packs of 3 cells
Pack #1 – 25%	5/4 C	H-1	112	14 sticks of 8 cells
Pack #1 – 50%	5/4 C	H-1	224	28 sticks of 8 cells
Pack #1 – Full	5/4 C	H-1	416	52 sticks of 8 cells
Pack #2 – Full	18650	E	441	7 modules of 63 cells
Pack #3 – 25%	C	F	120	12 sticks of 10 cells
Pack #3 – 50%	C	F	250	25 sticks of 10 cells
Pack #3 – Full	C	F	480	48 sticks of 10 cells

The full battery pack configurations are shown in Fig. 13. In all cases, the cells that make up the pack were placed in an open-ended aluminum cylinder (8.5 in. internal diameter) to simulate the casing of a commercial battery pack. With respect to cell configuration/orientation, Pack #1 and Pack #3 consisted of a group of closely nestled cells packed end to end (in "sticks") that were physically held connected together in series by a layer of shrink wrap PVC tubing to simulate a nominal battery assembler's packaging. These "sticks" were secured to each other mechanically. Pack #2 consisted of seven 63-cell modules secured to each other by hot-melt glue.

Pack #1 – Full
H-1 5/4 C   Pack #2 – Full
                                 E 18650   Pack #3 – Full
                                                                F C cell

Fig. 13 — Typical battery stick and 63-cell module loading configurations

For testing, the open-ended aluminum cylinder was placed inside a cylindrical battery compartment and into the pressure vessel (Fig. 14). In most tests, the open ends of the aluminum cylinder were partially sealed to simulate the potential water flow obstructions of an actual battery pack (i.e., to reduce the flow rate of water into the center of the pack).

Fig. 14 — Pressurizable containment configuration

   Two series of suppression tests were conducted in the pressurizable BSL to assess the capabilities of the overall LBCMS. The first series tested against the reduced scale/partial battery packs (up to 50% of an all-up battery pack; see Table 26). In the second series, the capabilities were validated against the full battery packs (Table 26). Results of the ten tests are summarized in Table 27.

Table 27 — Cylindrical BSL Suppression System Test Results

Battery Pack Description (Pack #)	Max. Battery Comp. Temp. (°C)	Max. Adjac. Battery Comp. Temp (°C)	Max. Plenum Temp. (°C)	Sprinkler Activ. Time (sec)	Exting. Time* (sec)	No. of Cells that Reacted
30 F Cells	170	30	37	~90	~100	3
10 E Cells	80	30	36	<30	<30	4
9 I-3 Cells	135	35	110	7	16	1
112 H-1 Cells (#1, 25%)	65	25	29	10	10	2
** 224 H-1 Cells (#1, 50%)	325	70	260	15	10	28
416 H-1 Cells (#1, Full)	175	35	135	15	25	4
7 × 63 E Cells (#2, Full)	95	35	65	9	~60	16
120 F Cells (#3, 25%)	160	25	43	45	45	6
** 250 F Cells (#3, 50%)	385	55	125	15	15	100
480 F Cells (#3, Full)	95	35	80	10	37	6

* These are estimates due to the difficulty in determining the actual extinguishment time.
** The discharge of water was intentionally delayed to further challenge the LBCMS.

   Specific findings of the ten tests are summarized as follows:

- The BSL (and installed systems) met all LBCMS requirements to contain the casualty to a single battery and prevent products of combustion from escaping the LBCMS.
- The smoke detector (photoelectric) installed in the BSL alarmed early into the casualty during every test and could be heard outside the pressure vessel.
- Only the sprinkler in/above the battery compartment of origin activated during any of these tests.
- The sprinkler head typically activated early in the casualty and within a few seconds of water discharge, stopped the reaction/casualty (with only a few cells reacting).
- For fast growing casualties, the sprinkler head typically activated about 15 seconds into the event.
- The maximum temperatures measured in the battery compartment of origin for normal LBCMS operation (i.e., no delay in water discharge) ranged from 65 °C to 175 °C.

- The maximum temperatures measured in the plenum for normal LBCMS operation (i.e., no delay in water discharge) ranged from 29 °C to 135 °C and the maximum temperatures measured in adjacent battery compartments (also called pigeon holes) ranged from 25 °C to 35 °C.
- For normal LBCMS operation (i.e., no delay in water discharge), the maximum pressure produced in the BSL was less than 10 psi overpressure (pressure due to both the gas generated during the casualty and the water injected to suppress the casualty).
- The two primary hazardous gases produced during these battery casualties were CO_2 and CO. During these suppression tests, the amount (mass) of CO_2 produced ranged from 0.02 to 0.08 kg. The amount (mass) of CO produced ranged from 0.01 to 0.05 kg.

10.5   Suppression Summary

The ability of a suppression system to prevent secondary cell reactions within a complex battery pack is, in part, a function of the openness of the battery pack housing. If the cells are contained within a closed housing (air tight, water tight, or even just a fairly tight enclosure), the mitigation system will not be able to contain the reaction to the initial cell within a single battery, and in most scenarios, all of the cells within the pack will react, even if submersed under water.

If the battery housing is fairly open, a fast acting mitigation system may be able to reduce the exposures to the adjacent cells within the housing below the critical value (below the level at which adjacent cells react). The best way to achieve this objective is to rapidly submerse the battery pack in water. The severity of the initial reaction, the proximity of the adjacent cells, and the vulnerability of adjacent cells are variables associated with achieving this performance objective. A water spray system (versus a flooding system) has the ability to thermally manage the conditions around the pack of origin, but is unlikely to be effective in preventing the complete consumption/reaction of the initial pack.

The data in Table 27 are from tests in which the individual cells were loosely packed and thus water could surround and cool each cell. This prevented total destruction of the battery pack in the BSL.

11   UNMITIGATED BATTERY PACK REACTIONS INSIDE A PRESSURE VESSEL

Three tests were conducted to validate the capabilities of the LBCMS (using the cylindrical BSL) against a number of worst-case scenarios: unabated reaction of an entire battery pack within the BSL and pressure vessel. These tests were conducted with all-up battery packs (full 100% packs) and are summarized in Table 28.

Table 28 — Conditions Produced Inside a Pressure Vessel

	7 × 63 E Cells	416 H-1 Cells	480 F Cells
Casualty Duration (sec)	300	96	162
No. Cells Reacted	441	416	480
Reaction Rate (cells/sec)	1.3	4.3	3.0
Max. Temp. Battery Storage Compartment (°C)	600	880	1000+
Max. Temp. Plenum (°C)	400	310	435
Max. Temp. Adj. Battery Storage Compartment (°C)	80	80	100
Volume of Gases Produced (m^3)	5.6	9.4	9.3
Volume of CO_2 Released (m^3)	5.1	6.1	6.1
Volume of CO Released (m^3)	0.5	3.3	3.2
Total Mass of CO_2 Produced (kg)	6.4	10.9	9.4
Total Mass of CO Produced (kg)	0.73	3.8	3.4

11.1   BSL Worst-Case Thermal Conditions

The maximum temperatures measured in the center battery compartment of the LBCMS (the one containing the battery casualty) ranged from 600 °C to over 1000 °C. The maximum temperatures measured in the plenum ranged from 310 °C to 435 °C and the maximum temperatures measured in adjacent battery storage compartments ranged from 80 °C to 100 °C. Although some of the batteries in the adjacent battery storage compartments showed moderate thermal damage, none of the batteries stowed in the adjacent battery storage compartments reacted during any of these worst-case tests.

Figures 15 and 16 show the worst-case thermal conditions produced in the BSL during these tests, which occurred in the test conducted with 480 F cells. The reaction began about 61 minutes into the test. The battery compartment containing the casualty exceeded 1000 °C about 3 minutes into the casualty. The aluminum cylinder used to house the cells (surrogate battery case) was significantly damaged with only the bottom half remaining at the end of the test. The plenum temperature above the battery storage compartment reached 435 °C. The adjacent battery storage compartments remained below 100 °C for the entire test.
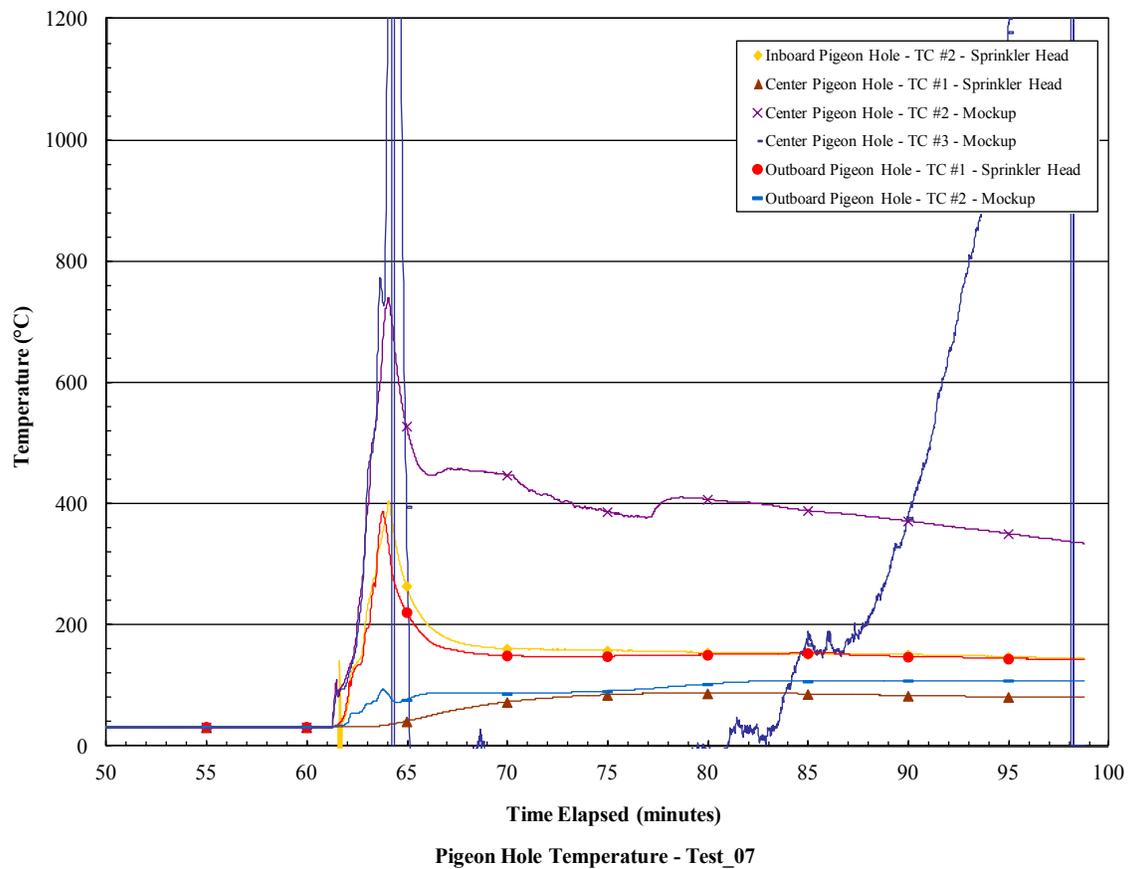
Pigeon Hole Temperature - Test_07

Fig. 15 — BSL worst-case thermal conditions in the compartment containing the battery (480 cells) (TC = thermocouple)

BSL Plenum Temperature - Test_07
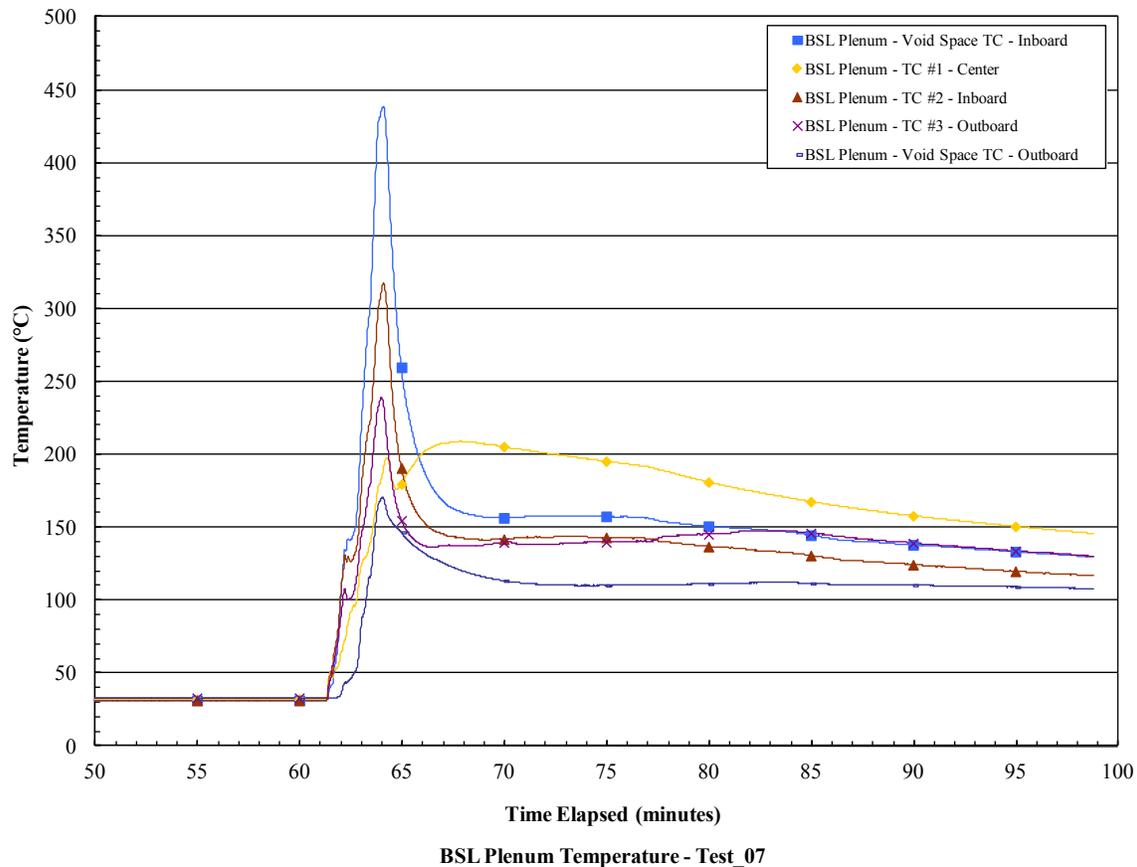
Fig. 16 — BSL worst-case thermal conditions in the plenum (480 cells) (TC = thermocouple)

The reactions of the battery pack significantly damaged the aluminum cylinder used to simulate a representative battery housing. Table 29 shows pre-test and post-test photographs of the battery packs and aluminum housings. As can be seen, some of the packs/cells released enough heat to completely destroy the housing.

The data collected during these tests provide valuable information on the reaction rates (cell-to-cell propagation) of a battery casualty in a confined space, involving a battery containing a large number of cells. The unabated cell-to-cell propagation rates (shown in Table 28) ranged from 1.3 to 4.3 cells per second. Surprisingly, the reactions continued inside the BSL even though there was no oxygen to support combustion of the vented products. It was assumed that the heat logged in the BSL prior to the complete consumption of oxygen was adequate to continue the reaction of the remaining cells in the pack. The reaction of these remaining cells still logged additional heat energy inside the BSL in the absence of combustion. Reactions of cells at low oxygen levels and the mechanism driving cell-to-cell propagation are topics that should be further investigated.

Table 29 — Damage Photographs

Battery	Pre-Test Photograph	Post-Test Photograph
7 × 63 E Cells		
416 H-1 LiMnO4 Cells		
480 F Cells		

11.2   Gas Production

During these worst-case tests, the volume of combustion gases released/produced during the reaction inside the BSL ranged from 5.6 to 9.4 m^3. About 65% of this gas was CO_2 and remaining was CO. On a mass basis, the amount of CO_2 produced ranged from 6.4 to 10.9 kg and the amount of CO produced ranged from 0.7 to 3.8 kg.

A significant quantity of unburned hydrocarbons was also produced but the amount could not be quantified with the instruments installed in the BSL and test compartment during these tests.

The cylindrical BSL was designed to vent the reaction gases when the pressure in the BSL reached 50 psi. Therefore, it was estimated that 85% of this gas vented outside the LCBMS.

12   BATTERY CASUALTY CLASSIFICATION

There are currently no established criteria for classifying the hazards associated with a lithium battery casualty. Table 30 provides a simplified approach to characterizing these events. A general description of these hazards follows.

Table 30 — Battery Hazard Classifications (Simplified Approach)

Hazard Parameter	Significant	Moderate	Insignificant
Explosion and Fragments	Will cause injury to unprotected personnel within the compartment of origin with compartment overpressures >1 PSIG or or release of any fragment with >15 ft/sec velocity or >20 ft-lb impact loading	Could cause injury to unprotected personnel in close proximity to the battery with compartment overpressures >0.25 PSIG or release of any fragment with >5 ft/sec velocity	Unlikely to cause injury (<0.05 PSIG overpressure) and no debris greater than 0.2 ft from battery
Fire/Thermal – HRR	PHRR > 100 kW for any duration	100 kW > PHRR >10 kW	PHRR < 10 kW
Fire – Fragments	Flaming fragments projected > 3 ft	Flaming fragments projected up to 3 ft	No flaming fragments
Aerosol Products	Loss of visibility within the compartment of origin and/or the production of explosive mixtures	Loss of visibility in close proximity to the battery (3 ft)	No loss of visibility
Gaseous Products (F)	Flammable concentrations within the compartment of origin	Flammable concentrations in close proximity to the battery	No flammable gases produced
Gaseous Products (T)	Toxic/hazardous concentrations within the compartment of origin for protected personnel	Toxic/hazardous concentrations in close proximity to the battery for unprotected personnel	No toxic/hazardous gases produced

PHRR = Peak Heat Release Rate   (F) = Flammable   (T) = Toxic

The same hazard parameters are typically produced during every reaction but to varying degrees: flammable by-products (aerosols, vapors, and liquids), toxic gases, flying debris (some burning), and sustained burning.

On a local scale, the exposures produced by the reaction are a function of the battery chemistry, the number of cells involved in the reaction, and the distance between the battery and the item of concern. On a global scale, the exposures produced by the reaction are a function of the battery chemistry, the number of cells involved in the reaction, and the size of the compartment in which the reaction occurs.

In the case of immediate ignition of gases as they discharge from a battery, the thermal exposures produced by the casualty are localized to a region around the reaction and significantly decrease with distance away from the battery/battery pack. Therefore, thermal exposures to equipment and personnel are only a concern in the region in close proximity to the battery (within a few feet of the battery). The main concern associated with these localized thermal conditions is the exposures to adjacent cells within the pack and adjacent batteries/battery packs within the storage device.

There is also a separate concern associated with nearby combustible materials. Based on limited data, it may be assumed that flaming debris from a battery casualty could cause ignition of combustible materials anywhere within the fragment zone/volume. Precautions should be taken to avoid or limit the storage of combustible materials near lithium batteries.

The primary hazard associated with a battery casualty appears to be the gases produced during the reaction. These gases have been determined to be toxic and in some cases flammable. The concentration of toxic and/or flammable gases is a function of the battery chemistry, the number of cells involved in the reaction, and the size of the compartment in which the reaction occurs. Due to the production of copious amounts of gases during the reaction of larger batteries and battery packs, it must be assumed that any battery casualty will render the storage compartment untenable for unprotected personnel (personnel not wearing a breathing apparatus).

Another significant concern is the production of a flammable mixture of gases (explosive mixture) within the storage compartment. If the resulting mixture is in the flammable range, the delayed ignition of the gases in the space can produce a large fireball and overpressures that could produce structural damage and additional battery casualties. In this scenario, the thermal exposure would be on a large scale, resulting in a hazard to personnel from thermal exposure, overpressures, and flying debris.

13 SUMMARY

The Naval Research Laboratory recently participated in, and completed, several major research programs initiated to characterize and mitigate lithium battery fire hazards for a number of applications. More than 100 battery casualty tests were conducted to characterize the conditions produced during a range of both unmitigated and mitigated casualties. This report summarizes the results of these tests.

The primary failure mode of a lithium battery is associated with a flaw or damage to the thin porous electrical insulation layer that separates the anode and the cathode (the separator). This is typically a microporous polyolefin layer in the Li-ion cells and a glass or ceramic paper in oxyhalide cells. Damage to the separator can result in an internal short circuit that produces enough heat to vaporize the electrolyte or in the case of a primary metallic lithium anode, melt and allow massive internal shorting and direct anode-catholyte reactions that result in a violent venting or explosive reaction. The separator can fail due to internal defects (production issues), physical damage (handling issues), exposure to high temperature (fire), and in the case of secondary cells, overcharging resulting in bridging of the separators. Once an internal short develops, a sudden release of stored energy occurs, commonly referred to as thermal

runaway. This event can cascade to adjacent cells and throughout an entire battery pack and ultimately destroy the device the battery is installed in and catastrophically impact the platform and personnel.

The requirements the U.S. Navy has adopted for the lithium battery safety program include a Preliminary Hazard Analysis, Battery Casualty Characterization Tests, Hazard Mitigation Tests, and a final Systems Hazard Analysis (SHA). There are two general types of tests conducted to characterize the battery casualty: reaction products testing and burning characteristics testing (heat release rate).

In the testing reported here, the reaction products were characterized for 19 different cells covering a range of chemistries, form factors, and capacities.

In general, when a cell casualty can be described as a venting reaction (no ignition), the majority of the products released are electrolyte constituents (i.e., carbonates or oxyhalides). These flammable gases and aerosols can accumulate and have the potential to produce an explosive atmosphere (explosion hazard). Explosive environments can be prevented by rapidly ventilating the space.

For the oxyhalides, the resulting dispersion generates an immediate risk to personnel from the acid gases (HCl, H_2SO_4, and HF). These products are also hazards to electronic equipment and have long-term effects on materials of construction.

For cell casualties that result in a burning reaction, the organic based electrolytes burn efficiently, producing CO_2 as the primary by-product, provided sufficient oxygen is available in the supporting atmosphere. Other products include CO and some amount of acid gases. Complete combustion is not assured, as the electrolyte and constituents are dense and may consume the limited oxygen in the cell, shifting the combustion products toward incomplete combustion with a large production of CO.

The acid gas production is directly related to the cell chemistry (and appears to be related to cell capacity and overall thermal effects), especially in the presence of high water vapor. Cells that contain sulfur produce sulfuric acid, cells that contain fluorine produce hydrofluoric acid, and cells that contain chlorine produce hydrochloric acid. It is proposed that for a given cell chemistry, the amount of acid gas produced should be directly proportional to the cell energy.

The heat release rates of the majority of the single cells were too low to measure using the 1 MW hood calorimeter on the ex-USS *Shadwell*. For future assessments, the heat release rates of the small commercial cells will be measured using a smaller hood calorimeter (10 to 100 kW). Ultimately, the HRRs of many of these cells were determined based on the results of tests on battery packs.

A wide range of battery pack configurations, groups of battery packs, and groups of battery modules were tested during these programs. There were significant differences in the types of reactions observed in the pack/module tests compared to the single cell tests. Specifically, except for the iron phosphate cells, almost all the packs/modules produced burning reactions, while many of the single cells only vented and never caught fire. In addition, during almost every unmitigated pack/module test, all the cells in the battery pack/module reacted and the casing materials were completely consumed.

The combustion energy potential was shown to be proportional to the electrical energy potential. The rationale is that the amount of combustibles (electrolyte and separator material) should be proportional to the electrical energy potential. However, the battery pack casing can provide a significant amount of fuel/energy to the fire. After adjusting the combustion energies to account for the case material, there is fairly good agreement between the results of the tests, suggesting that the combustion energy is typically about six times the electrical energy potential of the battery. The effect of a plastic case and packaging mass was found to be as high as 70% of the overall HRR with low thermal effect cells. Iron phosphate

based cells were combined and tested with ruggedized shipping containers and found to be fairly benign compared to other lithium batteries tested.

With respect to the fire hazard, the fire produced by the battery packs assessed during these programs was fairly energetic, but as a whole, should not be overmatching for a standard, properly attired fire response team. Most of the battery packs assessed during this program, with the exception of the large format battery packs, produced fires equivalent to the size of a large trashcan fire (20 to 50 kW). The large format battery packs contained an amount of energy equivalent to a gallon or two of JP-5 fuel (200 to 700 kW). In either case, suited-out responding personnel should be able to approach a battery casualty consisting of one of these and suppress/extinguish the fire through the application of copious amounts of water. However, for unmitigated bulk storage configurations, the fire has the potential to rapidly spread and can produce flashover conditions within the room.

Fire spread to adjacent batteries can be prevented by stowing the battery in a metal case and/or a segregated metal cabinet/locker. Fire insulation may also be required depending on the battery casualty characteristics, the thickness of the metal structure, and proximity to adjacent combustibles or batteries. Limitations of air and replenishment air will limit fire spread and may serve as a passive suppression system, although there is a possibility of back draft explosion as air is reintroduced to a hot room.

The precepts for the rapid control and suppression of a battery casualty were based on the development of a Battery Storage Locker similar to a commercial off-the-shelf flammable liquid storage cabinet. Tests were conducted to quantify the conditions produced in a prototype rectangular BSL and to assess/refine the design of an overall LBCMS. These conditions became the basis for the performance requirements for the system and components. The final design was a pressurizable cylindrical BSL. Two series of tests were conducted to validate the capabilities of the cylindrical BSL and the overall LBCMS.

Thirty-seven mitigation tests were conducted, all of which included some form of detection and 13 of which included active suppression.

The detection test results show that there are no universal precursors to a battery casualty that can be used for early warning detection for all types of batteries and systems. However, the results demonstrated that a smoke detector works well for detecting a casualty early into the event (i.e., after the first cell or group of cells have vented and/or caught fire).

The suppression system results show that water, or water-based agents, have good capabilities for managing the heat released during a battery casualty and have the potential to stop fire spread to adjacent batteries. The results demonstrate that cell-to-cell propagation within a large multicell pack can be stopped if the pack is rapidly submersed in water if the water can penetrate the battery pack. The final BSL design includes a sprinkler head installed inside each battery storage compartment. If battery packs (of the type studied) are colocated in adjacent storage areas, it is recommended they be protected from radiative and convective heat transfer.

REFERENCES

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2. F.W. Williams, X. Nguyen, J. Buchanan, J.P. Farley, J.L. Scheffey, J.T. Wong, H.V. Pham, and T.A. Toomey, "Ex-USS Shadwell (LSD-15): The Navy's Full Scale Damage Control RDT&E Facility," NRL Memorandum Report NRL/MR/6180--01-8576, August 24, 2001.

APPENDIX

VIDEO CLIPS FROM LITHIUM SINGLE CELL AND MULTICELL BATTERY CASUALTIES

Video clips (MP4 files) are on the enclosed DVD

A1   SINGLE CELL BATTERY CASUALTY VIDEO CLIPS

B-1 Cells Li/Li$_{0.5}$CoO$_2$ AA Size

File	Camera	Date	Start Time	SOC, %	Insult
146	Clip 8	11/3/2009	?	100	Heater
147	Clip 11	11/4/2009	?	100	Heater

B-2 Cells Li/SOCl$_2$ AA Size

File	Camera	Date	Start Time	SOC, %	Insult
123	5	8/20/2009	11:35:25	100	Propane

B-3 Cells Li/SOCl$_2$ D Size

File	Camera	Date	Start Time	SOC, %	Insult
151		4/15/2010	?	100	Heater
118		8/3/2010	12:47:20	100	Heater
119		10/13/2010	13:26:45	100	Heater

B-4 Cells Li/SO$_2$Cl$_2$-SOCl$_2$ D Size

File	Camera	Date	Start Time	SOC, %	Insult
157		4/16/2010	use all	100	Heater
120		8/6/2010	13:01:50	100	Heater

C-1 Cells LiFePO$_4$ 18650 Size

File	Camera	Date	Start Time	SOC, %	Insult
73	Exterior	1/4/2010	13:21:00	~40	Heater
74	Exterior	1/5/2010	10:15:15	100	Heater
75	Exterior	1/8/2010	14:21:30	discharged	Heater

D-2 Cell Li/LiFePO$_4$ 26650 Size

File	Camera	Date	Start Time	SOC, %	Insult
141*	Outside Chamber	7/19/2011	10:41:45	100	Heater

*Note: the banner on the video clip describes a18650 form fit, when actually it is a 26650 form fit.

E Cell Li/Li$_{0.5}$CoO$_2$ 18650 Size

File	Camera	Date	Start Time	SOC, %	Insult
83	Exterior	8/2/2010	13:56:00	100	Heater

F Cells Li/CF$_x$ C Size

File	Camera	Date	Start Time	SOC, %	Insult
142	Outside Chamber	4/12/2010	7:00	100	Heater
143	Outside Chamber	4/12/2010	3:40	100	Heater
163	Exterior	5/24/2010	10:31:00	100	Heater
86	Inside Box	8/2/2010	15:03:20	100	Heater
88	Outside Box	8/2/2010	15:03:16	100	Heater

H-1 Cell Li/MnO$_2$ 5/4 C Size

File	Camera	Date	Start Time	SOC, %	Insult
159	Outside Chamber	4/14/2010	?	100	Heater

H-2 Cell Li/MnO$_2$ D Size

File	Camera	Date	Start Time	SOC, %	Insult
158	Outside Chamber	4/12/2010	?	100	Heater

I-1 Cells LiNiCoAlO$_4$ Large Form Size

File	Camera	Date	Start Time	SOC, %	Insult
91	Exterior	6/21/2010	11:36:50	20	Heater
92*	Exterior	6/21/2010	11:40:00	20	Heater
96	Exterior	12/7/2012	9:19:10	100	Burner
94	Exterior	6/21/2010	13:54:38	100	Heater

*This is a continuation of file 91 same test later time

I-2 Cells LiNiCoAlO$_4$ Large Form Size

File	Camera	Date	Start Time	SOC, %	Insult
98	Exterior	12/6/2010	14:07:20	20	Burner
100	Exterior	6/22/2010	9:34:00	20	Heater
102	Exterior	6/22/2010	11:22:10	100	Heater
106	Exterior	6/24/2010	14:43:30	100+	Overcharge

I-3 Cells LiNiCoAlO$_4$ Large Form Size

File	Camera	Date	Start Time	SOC, %	Insult
108	Exterior	6/22/2010	13:53:25	20	Heater
109	Exterior	12/7/2010	12:26:50	100	Burner
112	Exterior	12/8/2010	13:28:28	100	Burner
110	Exterior	6/23/2010	9:54:20	100	Heater
113	2	6/24/2010	12:14:40	100+	Overcharge

J Cells LiCoO$_2$ Polymer Pouch Size

File	Camera	Date	Start Time	SOC, %	Insult
78	Exterior	12/8/2010	11:56:00	100	Burner
79	Exterior	6/23/2010	14:49:19	100	Heater
81	Exterior	6/25/2010	11:02:45	100+	Overcharge

Li/MnO$_2$ cell 18650 Size

File	Camera	Date	Start Time	SOC, %	Insult
162	Outside Chamber	6/17/2010	11:57:55	100	Heater

A2   MULTICELL LITHIUM BATTERY CASUALTY VIDEO CLIPS

Li/ Li$_{0.5}$CoO$_2$ 18650 Size

File	Camera	Date	Start Time	SOC, %	Insult
125		5/26/2010	14:-07:47	20	Heater
126		5/27/2010	9:45:04	100	Heater
127*			9:45:35		
128		5/28/2010	11:53:21	100	Heater
129**			11:53:54		

*Continuation of the test shown in File 126
**Continuation of the test shown in File 128

Simulated #3 Battery Li/CF$_x$ (480 cells) C Size

File	Camera	Date	Start Time	SOC, %	Insult
52*		9/22/2011	11:44:40	100	heater

*Pressure vessel with the relief valve set at 50 psi.

LiCoO$_2$ Polymer Pouch Size

File	Camera	Date	Start Time	SOC, %	Insult
61	Exterior	1/7/2010	13:51:50	100	Heater
63	Exterior	1/7/2010	16:42:10	100	Heater
11	Exterior	12/15/2010	14:27:48	100+	Overcharge
12	Infrared	12/15/2010	14:27:48	100+	Overcharge

Li/FePO$_4$ 18650 Size

File	Camera	Date	Start Time	SOC, %	Insult
58	Exterior	1/5/2010	13:24:00	100	Heater

Li/FePO$_4$ 26650 Size

File	Camera	Date	Start Time	SOC, %	Insult
57	Exterior	1/14/2010	11:21:00	100	Heater
54	Exterior	1/7/2010	15:43:30	100	Heater

Li/MnO$_2$ 5/4 C Size

File	Camera	Date	Start Time	SOC, %	Insult
68	2	8/4/2010	14:07:00	100	Heater
69	3	8/5/2010	9:55:15	100	Heater

LiNiCoAlO$_4$ Large Form Size

File	Camera	Date	Start Time	SOC, %	Insult
26	Passageway	12/16/2010	10:07:20	100+	Overcharge