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Summary of FAA Studies Related to the Hazards Produced by Lithium Cells in Thermal Runaway in Aircraft Cargo Compartments

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16. Abstract

This report is a compilation of test data and results from projects conducted by the Fire Safety Branch designed to determine the hazard from and possible hazard mitigation for the bulk shipment of lithium batteries/cells as cargo on transport airplanes. Though the main focus of this report is transport on passenger aircraft (effectiveness of Halon and effect on Class C cargo compartment), general hazard data is also applicable to freighters.

Initial testing found that current packaging did little to impede thermal runaway propagation from cell to cell and package to package. Lowering the state of charge (SOC) was shown to reduce the hazard. A 30% SOC in some cell chemistries stopped cell-to-cell propagation but did not eliminate the hazard from an external fire.

Full-scale tests in a 727 aircraft demonstrated that, even in the presence of Halon 1301, cell-to-cell propagation occurred. The tests also demonstrated that the pressure and off-gassing from the cells could reduce the Halon concentration at an accelerated rate, thereby causing the loss of fire protection earlier then designed.

Recent testing showed that lithium-ion cells in thermal runaway emitted H_2 gas that can be explosive even in a 5% Halon atmosphere. The ignition of the gases vented by a small number of cells in thermal runaway (the number depends on many factors, such as chemistry, design, and SOC of the cells, and size, design, and load factor of the compartment) can cause enough damage to a Class C cargo compartment as to render the Halon suppression system ineffective.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

FCC	Fire-containment cover
FRC	Fire-resistant container
LFL	Lower flammability limit
UFL	Upper flammability limit
LOC	Limiting oxygen concentration
MIC	Minimum inerting concentration
SOC	State of charge

EXECUTIVE SUMMARY

The 1999 LAX ramp fire involving lithium batteries was the basis for the FAA Technical Center initial investigation into the hazard of shipping these items by air. In the 1999 incident, a pallet of 120,000 lithium batteries was dropped on its side. The pallet erupted in flames 3 hours and 40 minutes later. Airport fire rescue had difficulty extinguishing the fire. This incident, coupled with the projected near exponential increase in lithium cell production, warranted investigation into the potential hazards of shipping these items by air. The likelihood that lithium cells may be involved in any cargo fire is directly related to the number of cells shipped as cargo.

The FAA has conducted numerous research projects from 2002 until the present date on the flammability hazard of lithium batteries. This report summarizes and consolidates the results of those studies. For more detailed information on each study, please see the referenced report or presentation.

Initial studies focused on the unique characteristics of lithium cells. It was found that lithium cells differ from other conventional batteries in that the lithium cells are constructed with a flammable electrolyte. This electrolyte can be forcibly released from a cell that is in a state of thermal runaway. Thermal runaway is a chemical reaction within the cell that results in a dramatic, uncontrolled temperature and pressure rise. This results in the cell expelling its contents, including the flammable electrolyte, which can be ignited by the hot cell case or burning packaging. Cells in thermal runaway can reach exterior case temperatures that exceed 1400°F. This is sufficient to ignite the typical fiberboard packaging in which the received cells were shipped. The heat produced by a single cell in thermal runaway may also be sufficient to heat adjacent cells, causing them to go into thermal runaway. This is a process called thermal runaway propagation and is key to understanding the hazard presented in shipping these cells. Auto-ignition tests revealed that heating a cell to 400°–450°F will induce thermal runaway. Experiments were performed to evaluate the effectiveness of Halon 1301, the fire-suppressant agent used in Class C cargo compartments, on a fire involving lithium-ion cells. It was found that the agent could suppress the electrolyte and burning packaging fires, but it had no effect on stopping the propagation of thermal runaway from cell to cell. Halon 1301 was also shown to be ineffective in suppressing an explosion of the gases vented during thermal runaway.

The concept of thermal runaway propagation was further investigated using lithium-ion cells packaged for shipment. It was found that the typical fiberboard packaging did little to impede thermal runaway propagation and, because it is flammable, may actually foster propagation. A single cell in thermal runaway will propagate from cell to cell and package to package until the entire shipment has been consumed.

The effect of cell state of charge (SOC) was investigated. The Portable Rechargeable Battery Association has stated that most types of lithium-ion cells are normally shipped at 50% SOC. The majority of the cells received in shipment were at or near 50% SOC. It was found that reducing the SOC of cobalt dioxide 18650 cells to 30% or less resulted in a less energetic thermal runaway event and greatly reduced the likelihood of thermal propagation from cell to

cell. These tests were conducted with cells from a limited number of manufacturers. The results can be extrapolated, in general terms, to other cells of this chemistry from other manufacturers.

Full-scale tests were performed in the Fire Safety Boeing 727 freighter test article to evaluate a transport aircraft's ability to withstand a fire involving a large number of lithium batteries. A typical test fire load consisted of 5000 lithium-ion cells, packaged as received in fiberboard boxes with cardboard separators containing 100 cells per box. Tests were conducted in both the Class E main deck cargo compartment and in the lower underfloor Class C compartment. Class E cargo compartments rely on oxygen starvation to control the fire. Class C compartments have a Halon 1301 total flood suppression system. Both compartments have ventilation controls and fire detection. It was found that the Class E compartment was able to slow the propagation of thermal runaway during the lithium-ion fire. Ceiling temperatures eventually exceeded test safety parameters, resulting in the termination of the test after 1 hour. The Class C compartment was able to control the lithium-ion fire under the test conditions. The agent suppressed the open flames from the burning electrolyte and packaging, but did not impede the propagation of thermal runaway. Cells continued to release the electrolyte and gases as thermal runaway propagated cell to cell and throughout the 50 packages until the test was terminated. Similar tests were conducted with lithium-metal cells. These cells are more energetic; neither the Class C nor the Class E compartments were able to withstand fires involving lithium-metal cells.

The flammability characteristics presented by batteries and cells of different chemistries and form factors were tested. Cylindrical lithium-ion, like the 18650 cells tested previously, and lithium-polymer cells are manufactured with similar chemistries. When exposed to heat, they react differently because of the form factor. The cylindrical cells, when induced into thermal runaway by heating, build a rapid increase of internal heat and pressure, resulting in pressure relief and a release of sprayed electrolyte that was then ignited. The lithium polymer cells are encased in a plastic film. When heated, the cells build pressure and inflate the film until reaching the bursting point, releasing the electrolyte all at once. This release feeds a rapidly escalating fire. From a flammability standpoint, the propensity to propagate thermal runaway is significant. It was found that cells of LiFePO4 chemistry yielded the lowest temperature rise in thermal runaway and were least likely to propagate. Cells of LiMnNi and $LiCoO_2$ exhibited the highest temperature rise in thermal runaway and were most likely to propagate. Halon 1211 handheld extinguishers were found to be effective in extinguishing the electrolyte fires of each cell type. However, the agent did not prevent reignition of lithium-ion polymer pouch cells.

The ability of various fire extinguishing agents to control lithium-ion cell fires was investigated. The agent must perform two roles in these types of fires: extinguish the electrolyte fire and cool remaining cells to stop the propagation of thermal runaway. It was found that gaseous agents were effective in extinguishing the electrolyte fire, but had no effect in stopping the propagation of thermal runaway from cell to cell. Aqueous-based agents were effective in both extinguishing the electrolyte fire and in stopping the propagation of thermal runaway. Hot-plate tests evaluated the cooling capacity of several agents; plain water was found to be effective, as were other aqueous agents.

Fire-containment covers (FCCs) for cargo loaded on pallets and newly developed fire-resistant containers (FRCs) are a viable means to control cargo fires on freighter aircraft. Both FCCs and FRCs control fires by means of oxygen starvation. The FRC can also be fitted with a fire suppression agent that is automatically discharged when a fire is detected. The ability of an FCC and an FRC to control a fire involving large numbers of lithium-ion cells was investigated. The fire load for each test consisted of 5000 lithium-ion 18650 $LiCoO_2$ cells, with the balance of the interior volume containing the standard fire test load of cardboard boxes filled with shredded paper. It was found that the FCC was unable to contain the cell fire; flames and burning gases escaping from beneath the cover caused the test to be terminated after 70 minutes. This is well short of the 4-hour containment requirement. Two FRC tests were conducted with surprising results. In each case, flammable gases released by the propagation of thermal runaway by the lithium-ion cells reached explosive concentrations. The gases were ignited by burning cells or packaging, causing an explosion that destroyed the container. The proprietary powder-type extinguishing agent used in these tests was not effective in suppressing the explosions. Analysis of the batteries consumed in the fire indicated that only a small fraction of the 5000 cells had vented and caused the explosion. Further FRC development is ongoing to reduce the risk of explosion posed by burning lithium-ion batteries.

Following the explosive results of the FRC tests, an analysis was conducted to determine the constituents of the gases vented by lithium-ion cells in thermal runaway. This study yielded two key results. The first is that the volume of gases emitted during thermal runaway is dependent on the SOC of the cell. Higher SOCs yield greater volumes of flammable gases. The second is that, in addition to the expected hydrocarbons, a large amount of hydrogen gas is also produced. Hydrogen gas has a very large flammability range, but more importantly, a high concentration of Halon 1301 is required to suppress a hydrogen-gas explosion. Tests were conducted in a 10-cubic-meter explosion chamber to evaluate the ability of Halon 1301, the agent used in Class C cargo compartments, to suppress an explosion caused by the ignition of vented gases from lithium-ion 18650 $LiCoO_2$ cells in thermal runaway. It was found that a concentration of 10% Halon 1301 is required to suppress an explosion from these gases. This is significant because the design concentration of Halon 1301 in an aircraft Class C compartment is an initial concentration of 5%, with a maintained 3% concentration for the duration of the flight. Halon 1301 had previously been found effective at suppressing the open flames from burning electrolyte and packaging. These results show that it would not be effective at suppressing an explosion of the vented gases.

The flammability of hydrogen and the effectiveness of Halon 1301 were evaluated at sea-level conditions in the tests described above. A study was undertaken to examine the flammability of hydrogen at reduced pressure and oxygen, representative of high altitudes and simulating the conditions of an aircraft in flight. It was found that hydrogen retains a wide range of flammability limits, even under reduced pressure and oxygen levels. Further tests confirmed that a concentration of Halon 1301 greater than the available 5% in a Class C cargo compartment is required to suppress a hydrogen explosion. Tests with vent gases from lithium-ion 18650 $LiCoO_2$ cells in thermal runaway, consisting of various hydrocarbons and hydrogen gases, revealed that an 8.6% concentration of Halon 1301 is required to suppress an explosion.

Recognizing the implication of the explosive vent gases, a study was conducted to determine the amount of vent gas that, when contained and ignited, would cause an over-pressure condition in a Class C cargo compartment. Class C cargo compartments rely on the integrity of the cargo liners to keep the fire-suppressant agent from leaking out. If the leakage rate exceeds design limits, the concentration of Halon 1301 would be reduced, making it less effective at suppressing cargo fires. Cargo compartments are designed with pressure-relief devices, which are generally non-resettable, to prevent pressure differentials between the compartment and the rest of the aircraft. This prevents structural damage in the case of depressurization. These pressure-relief devices activate at a psi differential between 0.6 and 1.1 psi. Therefore, an explosion that causes a pressure increase inside a Class C compartment of somewhat less than 1 psi or greater will activate the pressure-relief devices and allow the Halon 1301 agent to leak out. Reduced agent concentrations will allow existing fires to intensify, endangering the aircraft. Tests were conducted in the 10-cubic-meter explosion chamber configured to resemble the free airspace in a loaded 737 Class C cargo compartment. It was found, under ideal conditions, that the gases from only a small number of cells were required to cause an explosion and pressure increase of 1 psi. Tests were repeated in a Boeing 737 test article with similar results. The vent gases from six 18650 $LiCoO_2$ cells in thermal runaway at 100 % charge or 20 cells at 50% charge, when ignited in a loaded 737 Class C cargo compartment, caused a pressure rise of 1.2 psi. This pressure rise dislodged the pressure-relief panels. These tests represent ideal theoretical conditions, but the implications are clear: only a small number of cells can produce enough explosive gases to cause an overpressure inside a Class C compartment. The number will vary depending on compartment volume but is insignificant in comparison to bulk shipment of cells that can be in the thousands.

Improved packaging may provide a means to mitigate the hazard of shipping lithium-ion batteries. Tests were conducted to investigate the effect of modifications to existing packaging on the rate of thermal runaway propagation. Some of the modifications tested were different separator materials, intumescent paints, and water delivery systems. The separator material changes and intumescent paints were largely ineffective. The water delivery systems have the potential to stop thermal runaway propagation, and the package design should also preclude a lithium-cell shipment from becoming fuel for an external fire.

1. INTRODUCTION

The tests described in this report are included in an effort to assess the flammability characteristics of lithium cells and the potential hazard associated with shipping them on transport aircraft. This report summarizes the main findings from this ongoing research project.

The shipping of lithium cells presents a unique hazard that is unlike other common cell chemistries and almost all other cargo. Traditional batteries and cells such as alkaline, nickel metal hydride, nickel cadmium, and lead acid all use a water-based electrolyte. Lithium batteries and cells use a hydrocarbon-based electrolyte. The hydrocarbon electrolyte is flammable, whereas water-based electrolytes are not flammable. Lithium-metal cells also contain highly flammable metallic lithium. Therefore, lithium cells become fuel for a fire.

Lithium batteries and cells are also capable of being ignition sources. Lithium cells can reach a state called thermal runaway. A cell in thermal runaway undergoes a chemical reaction within the cell that results in an uncontrolled temperature rise. The exterior temperature of the cell casing can reach temperatures in excess of 1400°F. As the temperature rises, the pressure within the cell increases and activates the pressure-relief ports. This results in the release of the electrolyte. The electrolyte may ignite from contact with the hot cell cases or from burning packaging ignited by the hot cells. Lithium-metal cells can self-ignite from burning lithium.

Thermal runaway may be initiated by many circumstances. These include internal cell failure, heating (exposure to an external fire), physical abuse, rapid discharge, over-charging, or the latent manifestation of a manufacturing contaminant.

A cell in thermal runaway produces enough heat energy to cause adjacent cells to heat up. Once these adjacent cells reach a threshold temperature, they too go into thermal runaway. This is a process referred to as thermal runaway propagation. The typical fiberboard bulk packaging does not prevent the propagation of thermal runaway.

2. THERMAL RUNAWAY CHARACTERISTICS

A series of tests was conducted to determine the flammability characteristics of 18650-type rechargeable $LiCoO_2$ lithium-ion cells and lithium-metal manganese dioxide 123A and CR2 cells, both individually and as packaged for bulk shipment onboard cargo and passenger aircraft [1, 2]. The tests were designed to determine the conditions necessary for cell ignition, the characteristics of the cell fire, the effect of state of charge (SOC), the potential hazard to the aircraft as a result of the fire, and the effectiveness of the standard Halon 1301 fire-suppression systems used to extinguish the fire.

Several methods were examined to initiate thermal runaway, including physical damage, overcharging, shorting, and heating. Heating was found to be the simplest and most repeatable method of initiating thermal runaway. It was found that a relatively small fire source is sufficient to heat the lithium cell above the temperature required to activate the pressure-release mechanism in the cell. This causes the cell to forcefully vent its electrolyte through the relief ports near the positive terminal. The electrolyte is highly flammable and easily ignites when exposed to an open flame or hot surface. Fully charged lithium-ion cells released small white sparks along with the electrolyte. Lithium-metal cells released larger particles of burning lithium. Figure 1 shows a lithium-ion 18650 $LiCoO_2$ cell in thermal runaway. Failure of the pressure-relief mechanisms can cause catastrophic disassembly of the cell expelling the contents all at once, as shown in figure 2.

Figure 1. High-speed video capture of lithium-ion $LiCoO_2$ cell in thermal runaway

Figure 2. High-speed video capture of a lithium-ion $LiCoO_2$ cell in catastrophic disassembly

2.1 AUTO-IGNITION TEMPERATURE

Tests were conducted to determine the temperature needed to induce a cell into thermal runaway. It was found that externally heating the cells to a temperature of approximately 400°F, measured on the external cell case, would initiate the thermal runaway reaction within the cell.

2.2 HALON 1301 EFFECTIVENESS

Halon 1301, the fire suppression agent installed in transport category aircraft, was found to be effective in suppressing the electrolyte fire at both the 5% knockdown concentration and the 3% suppression concentration. Halon 1301 has no cooling effect and did not prevent the release of the electrolyte and gases from heated cells, nor the propagation of thermal runaway.

2.3 PRESSURE PULSE

Ignition of the electrolyte released by overheating a lithium cell produces a pressure pulse that can raise the air pressure within a cargo compartment. Exposing only a few 18650 $LiCoO_2$ cells to a small alcohol fire was sufficient to increase the air pressure by more than 1 psi in an airtight, 10-cubic meter pressure vessel. Cargo compartments are only designed to withstand an approximate 1-psi pressure differential. A fire involving a bulk-packed lithium-ion shipment may compromise the integrity of the compartment by activating the pressure-relief panels. This can allow the Halon 1301 fire suppressant to leak out of the compartment, reducing its effectiveness and the time duration of protection. Moreover, smoke and combustion products from the fire may also leak out, posing a danger to the passengers and crew.

Fully charged 18650 $LiCoO_2$ cells produced a larger pressure pulse and more forceful venting than cells at a lower SOC.

3. CELL PROPAGATION, HALON EFFECTIVENESS, PACKAGING EFFECTIVENESS

The tests described in this study were designed to increase knowledge of the flammability of lithium-ion and lithium-metal cells generated in earlier test efforts and to address their safe shipment [3]. Based on previous work at the FAA William J. Hughes Technical Center Fire Safety Branch, tests were conducted with a larger number of cells and simulated self-ignition (thermal runaway) conditions. The effectiveness of Halon 1301 was evaluated from the perspective of open-flame suppression and the ability to halt the propagation of thermal runaway within a shipment.

The capability of existing shipping containers to contain a lithium-ion and lithium-metal cell fire was evaluated. Currently available robust shipping containers, such as metal pails and drums recommended by the International Civil Aviation Organization, were not effective in controlling lithium-metal cell fires, but some types were effective in containing lithium-ion cell fires. The airtight metal drums and pails failed because of pressure buildup within the container, resulting in the lid attachment failing. A cardboard overpack designed to safely ship oxygen-generator canisters was tested in a 100-cell 18650 $LiCoO_2$ lithium-ion cell fire. The overpack successfully contained the fire; however, smoke and gases were released. Though the oxygen-generator overpack failed to contain the smoke and gases, the lightweight foil/ceramic insulator was sufficient to contain the fire and heat. This technology may be transferrable to an improved method of packaging lithium-ion cells.

3.1 THERMAL RUNAWAY PROPAGATION TESTS

A cell failure resulting in thermal runaway generates an external cell case temperature in excess of 1400°F. The cell will also vent, causing a spray of flammable electrolyte. The heat generated is sufficient to (1) ignite the packing materials and (2) heat adjacent cells, causing them to go into thermal runaway. Typically, a cell will undergo thermal runaway when heated to approximately 400°–450°F. The propagation of thermal runaway from cell to cell is related to heat transfer by overheated cells and by the burning packaging.

Propagation tests were conducted with full bulk shipping boxes of 100 18650 $LiCoO_2$ lithium-ion cells. The boxes were the original fiberboard shipping packages as received, meeting all UN and ICAO Technical Instruction requirements. A single cell was removed and replaced with a cartridge heater to simulate a cell in thermal runaway, as shown in figure 3.

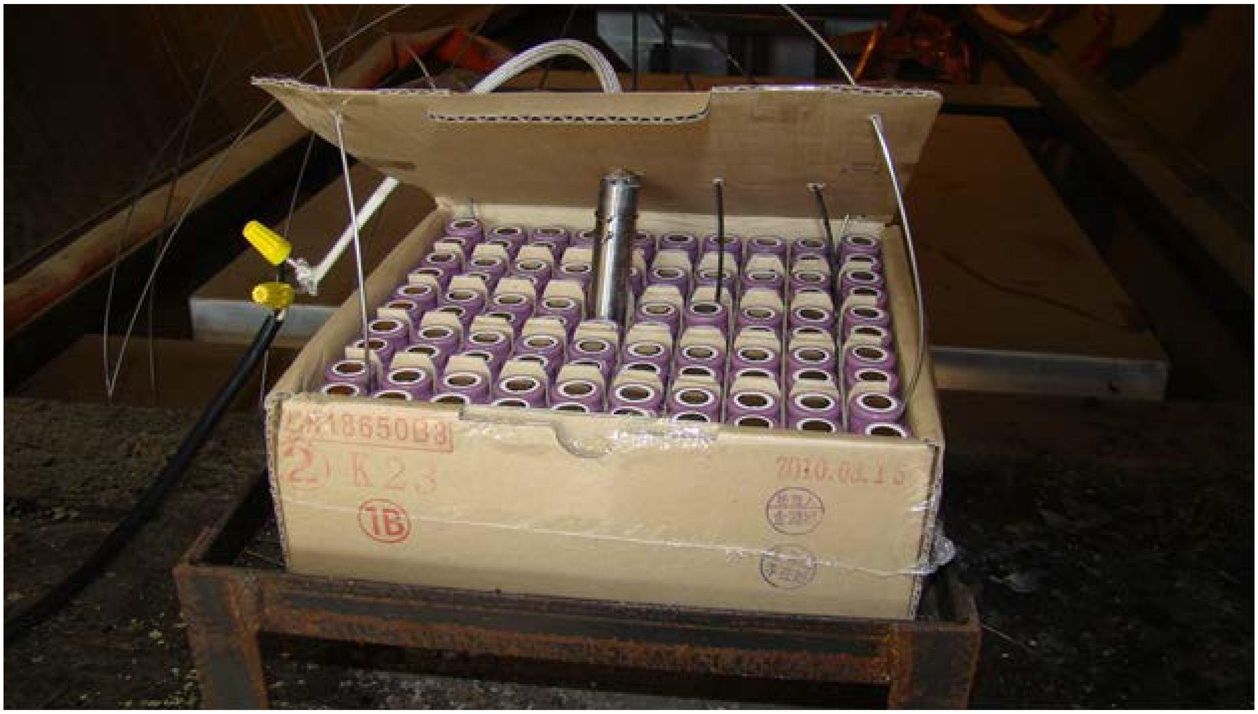


Figure 3. Shipping box with interlocking cardboard separators for 100 18650 $LiCoO_2$ lithium-ion cells

3.1.1 Baseline Test Results

The cartridge heater temperature reached 1000°F at the 9-minute mark, peaking at 1250°F at approximately 19 minutes. The power to the cartridge heater was shut off at this time. The cardboard box began to smoke 8 minutes into the test. The box caught fire at the 11-minute mark. As cells went into thermal runaway, strong torch flames erupted from the box as the electrolyte was vented and ignited by the burning cardboard. The fire continued to burn vigorously until the 45-minute mark, when all cells were consumed, as shown in figure 4.

Figure 4. Baseline post test

3.2 IMPROVED PACKAGING TEST

The standard bulk packaging for lithium-ion 18650 cells consists of a fiberboard box with interlocking cardboard separators. One possible way of reducing the radiant heat transfer from a cell in thermal runaway to adjacent cells is to replace the cardboard separators with a heat-resistant material. For this test, the cardboard separators were replaced with a fiberglass material used as a flame barrier in aircraft thermal-acoustic insulation. The fiberglass was cut to the same dimensions as the cardboard separators. The installed fiberglass separators are shown in figure 5.

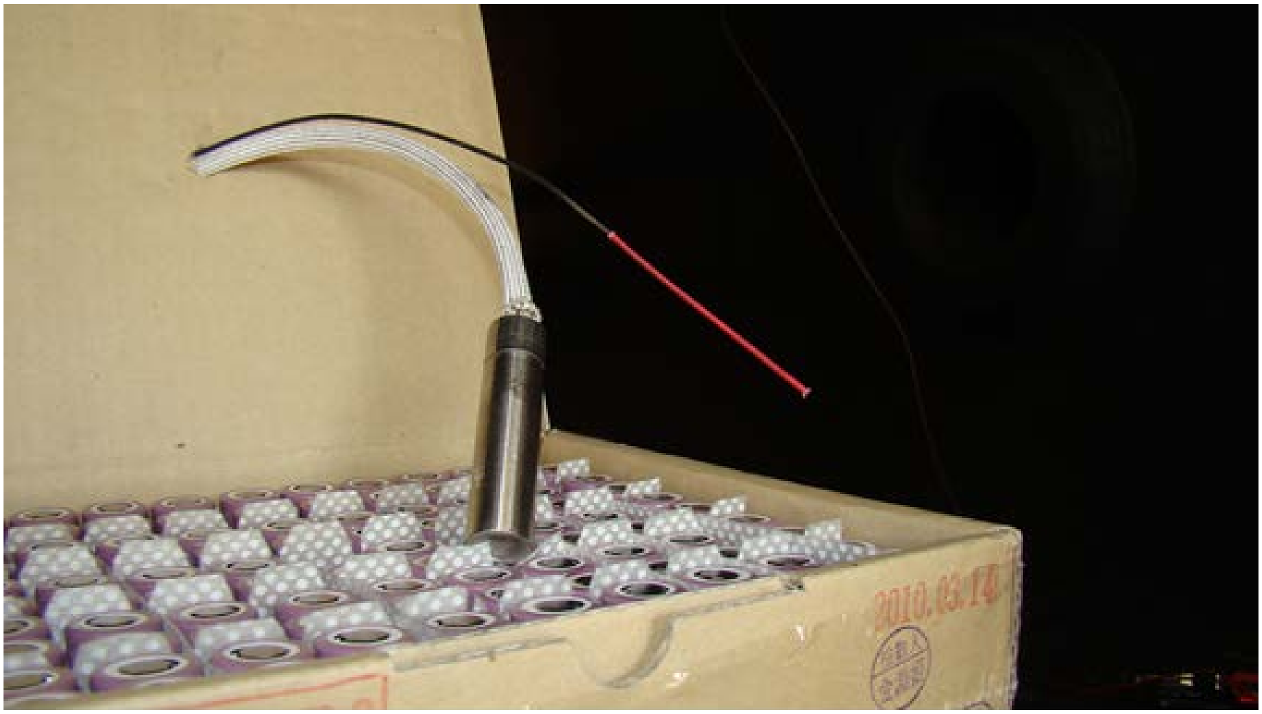


Figure 5. Fiberglass separators

The results from the improved packaging test revealed that the fiberglass separators did not perform as well as the original cardboard separators. The propagation of thermal runaway proceeded at a faster rate than the baseline test, consuming all of the cells in less time.

3.3 HALON 1301 EFFECT ON FLAMMABILITY AND PROPAGATION RATE

Early tests with small numbers of cells predicted that the Halon 1301 extinguishing agent would suppress the open flames but not prevent the propagation of thermal runaway from cell to cell [1]. This test examined the effect of Halon 1301when cells were packaged for shipment, and it was prepared exactly like the baseline test. The test chamber was flooded with a 6% Halon 1301 concentration at the first indication of open flames. The agent extinguished the open flame and prevented open flames for the duration of the test. Thermal runaway continued to propagate throughout the box until all cells were consumed. The rate of propagation was identical to the baseline rate. The results from these tests confirmed that Halon 1301 is effective in suppressing open flames from lithium-ion cells in thermal runaway. The Halon, as expected, was totally ineffective at stopping the progression of cell-to-cell thermal runaway. Even in the presence of Halon 1301, all cells in the shipment were consumed.

3.4 OXYGEN-GENERATOR OVERPACK TEST

In the past, a specification was developed for an overpack designed for shipping oxygen generators on passenger aircraft. This specification is defined in Pipeline and Hazardous Materials Safety Administration Rule HM224B. The oxygen-generator overpack is designed to protect the contents from a cargo compartment fire exterior to the overpack. The external fire threats are the same for a bulk shipment of lithium-ion cells exposed to a suppressed cargo fire. A test was designed to determine if the specification would protect against an internal lithium-ion fire.

The overpack was tested against a fire load consisting of 99 18650 lithium-ion $LiCoO_2$ cells in the same configuration as the propagation tests. Thermal runaway was initiated by energizing the cartridge heater and allowed to propagate until all cells were consumed. The overpack successfully contained the fire to within the package, but allowed smoke and gases to escape because of increased pressure, as shown in figure 6.

Figure 6. Oxygen-generator overpack test

The box was opened after 3 hours. The inside of the overpack was soot covered but undamaged. (see figure 7). The exterior of the fiberboard box was not discolored, except for the soot coating on the top. The top flaps were slightly brittle but intact. The fiberboard shipping box that contained the cells was charred but intact. All the cells were consumed. This container successfully contained the lithium-ion fire, but allowed smoke and gases to escape. The ability of the overpack to prevent thermal runaway was not evaluated in relation to an external fire event.

Figure 7. Oxygen-generator overpack post test

4. SOC EFFECT ON FLAMMABILITY AND PROPAGATION OF THERMAL RUNAWAY

The effect of SOC was investigated on the most common cell chemistry and size: $LiCoO_2$ 18650 cells [4]. Three charge states were tested: 100%, 50%, and 30%. The nominal shipping charge from the manufacturer is 50%. Flammability was evaluated in two ways; first, by exposing the cells to a low-intensity alcohol fire and, second, by measuring peak heat release using a cone calorimeter. Thermal runaway propagation was measured using an inline fixture. The results of these tests showed that, for cells of this size and chemistry, propagation of thermal runaway from cell to cell did not occur at a SOC of 30% or below.

4.1 FLAMMABILITY EVALUATION: ALCOHOL FIRE HEAT SOURCE

The intensity of the thermal runaway is affected by the SOC. The higher the SOC, the more intense the thermal runaway characteristics become. The results of three states tested for this chemistry are as follows:

1. 100% charge: produced flammable electrolyte, large pressure pulse, strong torching fire, sparks, vent 4:00 minutes, ignition of electrolyte 4:28 minutes.
2. 50% charge: produced flammable electrolyte, large pressure pulse, vent 3:46 minutes, ignition of electrolyte 4:56 minutes.
3. 30% charge: produced flammable electrolyte, small pressure pulse, vent 3:39 minutes, ignition of electrolyte 5:07 minutes.

The 30% SOC produced a reduced-intensity event. The electrolyte release was much less forceful than at the two higher SOCs. The pressure pulse produced was also reduced.

4.2 CONE CALORIMETER RESULTS FOR A RANGE OF SOCs

The cone calorimeter peak heat release data generally tracked the SOC; high SOCs produced the largest heat release. There is some data scatter due to the propensity of cells at high charge states to catastrophically disassemble during the heating process. Five $LiCoO_2$ 18650 cells were tested at 100%, 70%, 30%, and 20% charge, and four cells were tested at 50% SOC. The results are shown in figure 8.

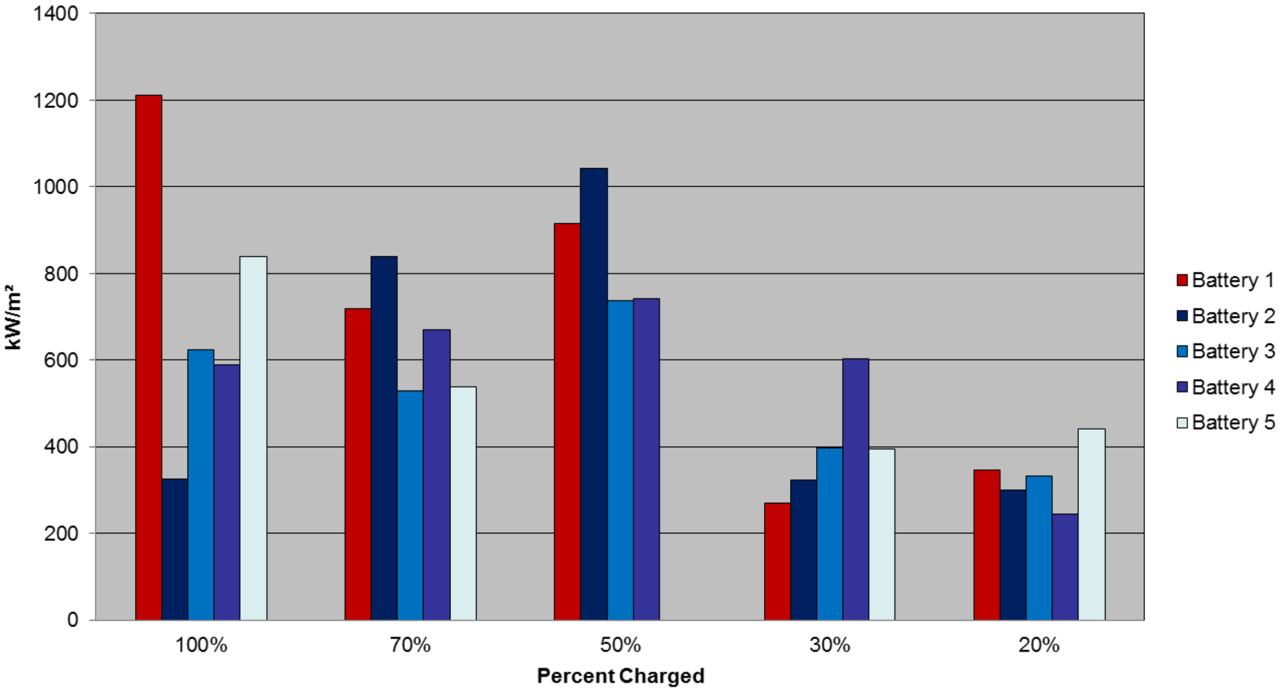


Figure 8. Peak heat release for $LiCoO_2$ 18650 cells at different SOCs

4.3 EFFECT OF SOC ON THERMAL RUNAWAY PROPAGATION

A test was designed to measure the effect of SOC on the propagation of thermal runaway. The test consisted of an insulated cell holder, a 100-watt cartridge heater, and four cells, all arranged in a line, as shown in figure 9. Thermocouples were attached to each cell and the heater.

Figure 9. Propagation test configuration

Five charge states were tested: 100%, 50%, 40%, 30%, and 20%. Two tests were conducted at 100% SOC. In both of these tests, the cell adjacent to the heater catastrophically disassembled. This resulted in the cell rapidly cooling, and no further propagation was noted. The results from the 100% tests are shown in figures 10 and 11.

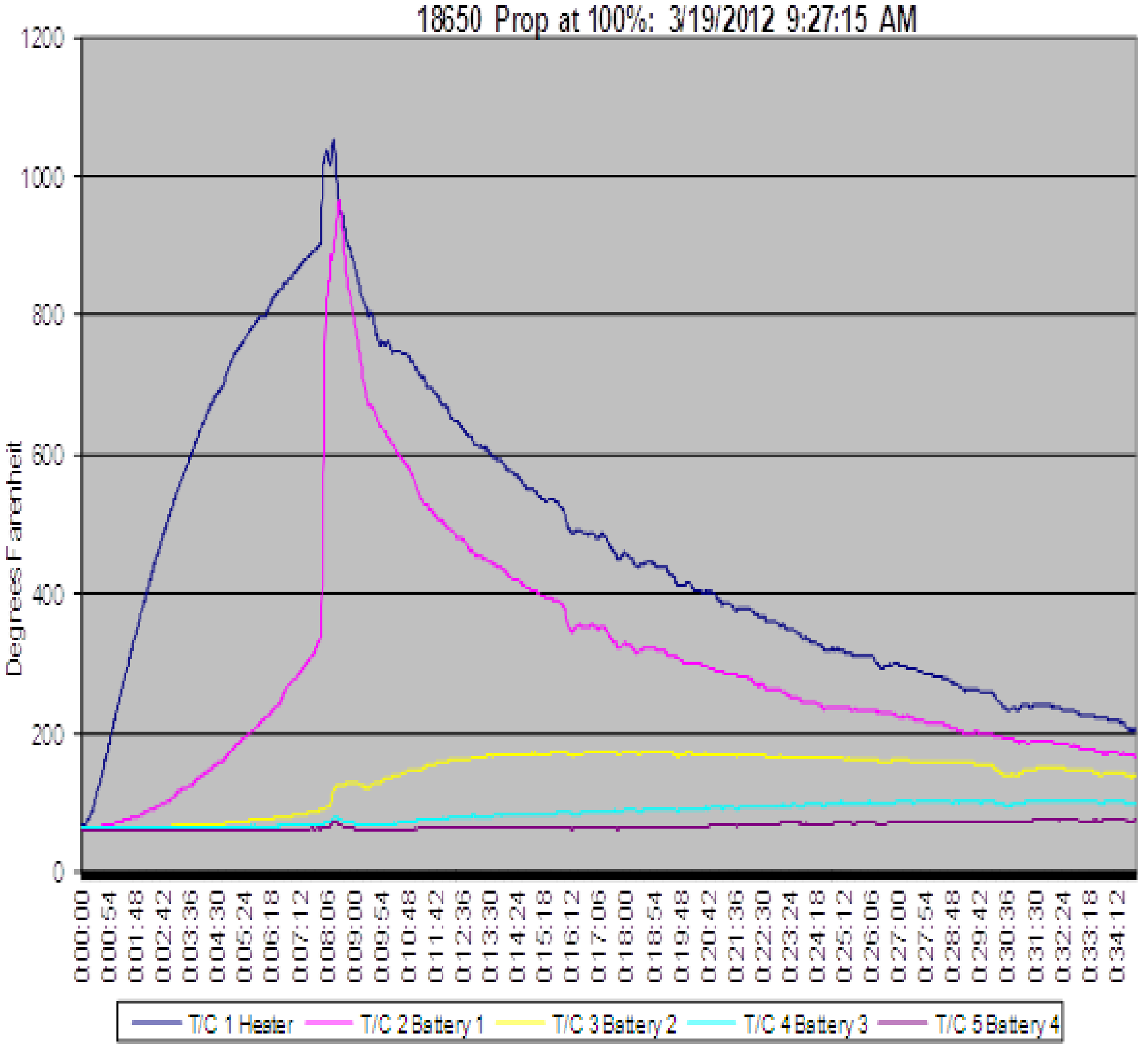


Figure 10. The $LiCoO_2$ 18650 cell 100% SOC propagation test 1

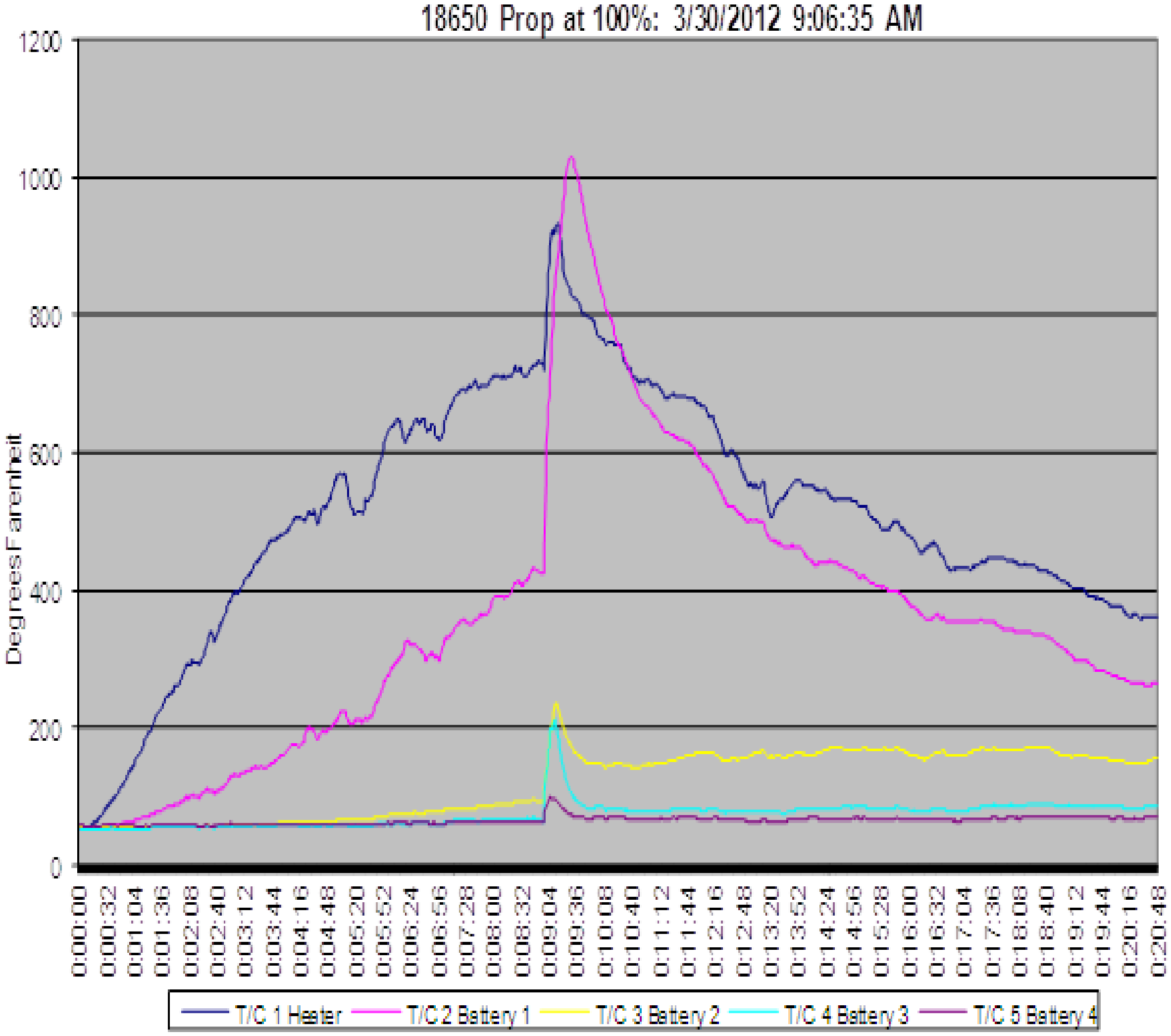
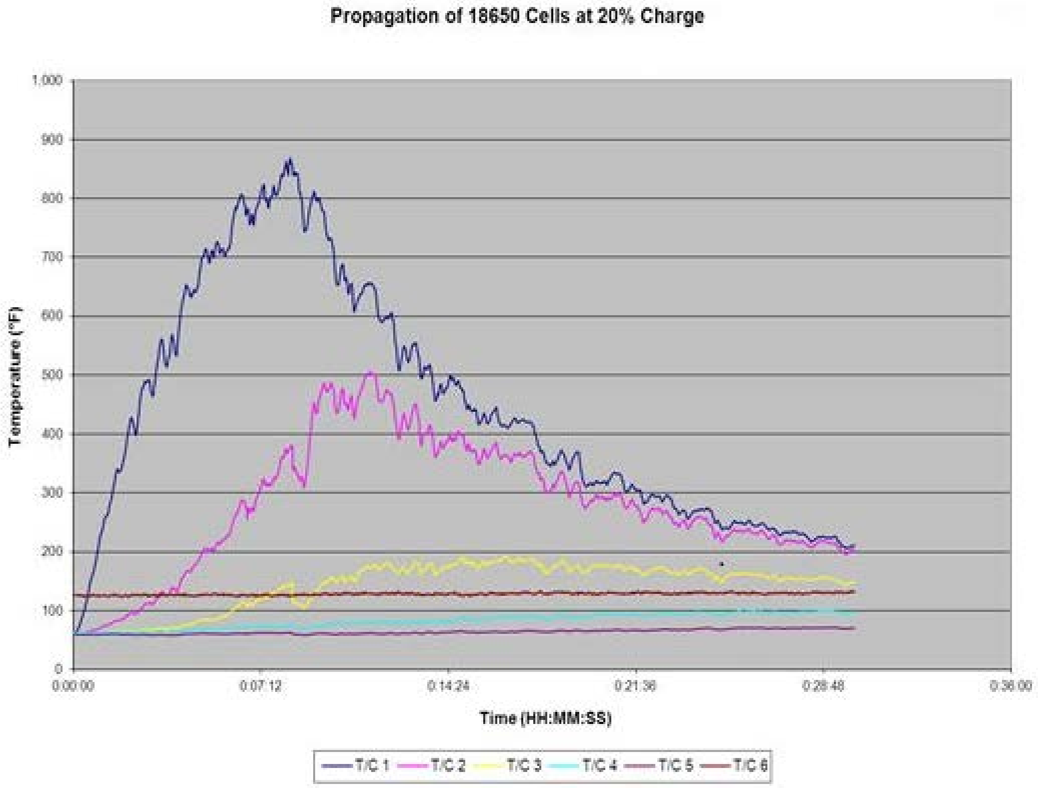


Figure 11. The $LiCoO_2$ 18650 cell 100% SOC propagation test 2

The results for 20%, 30%, 40%, and 50% SOCs are shown in figure 12.



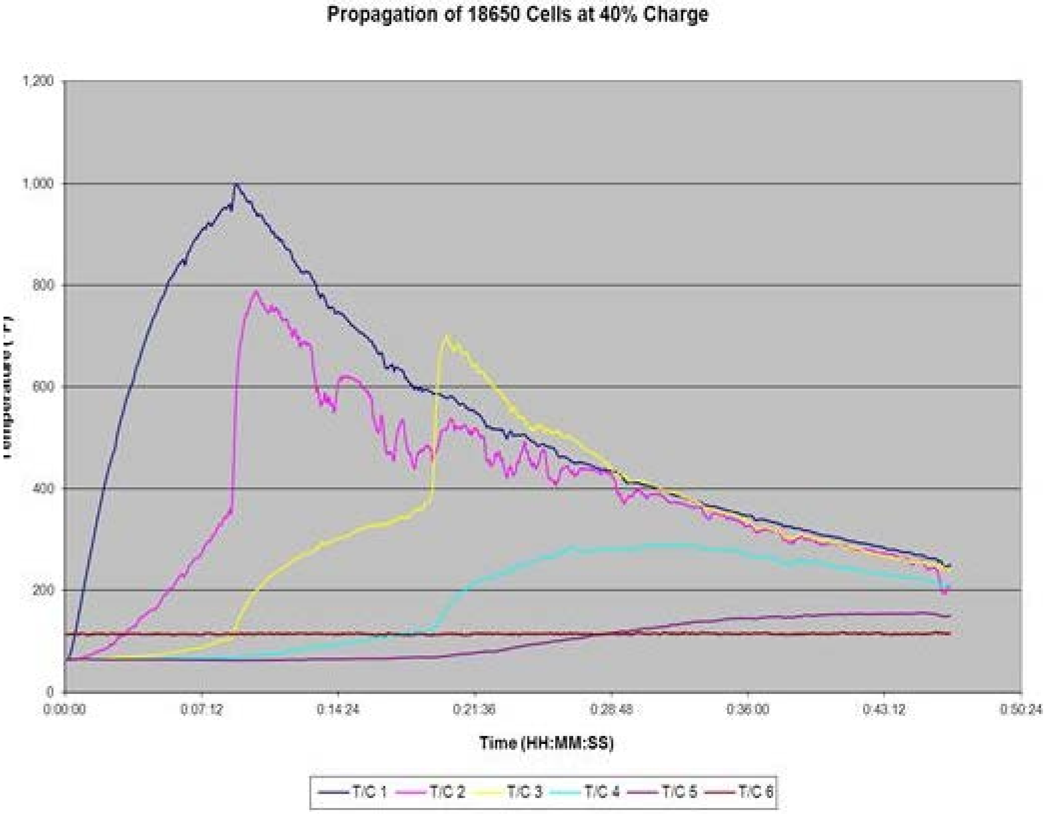
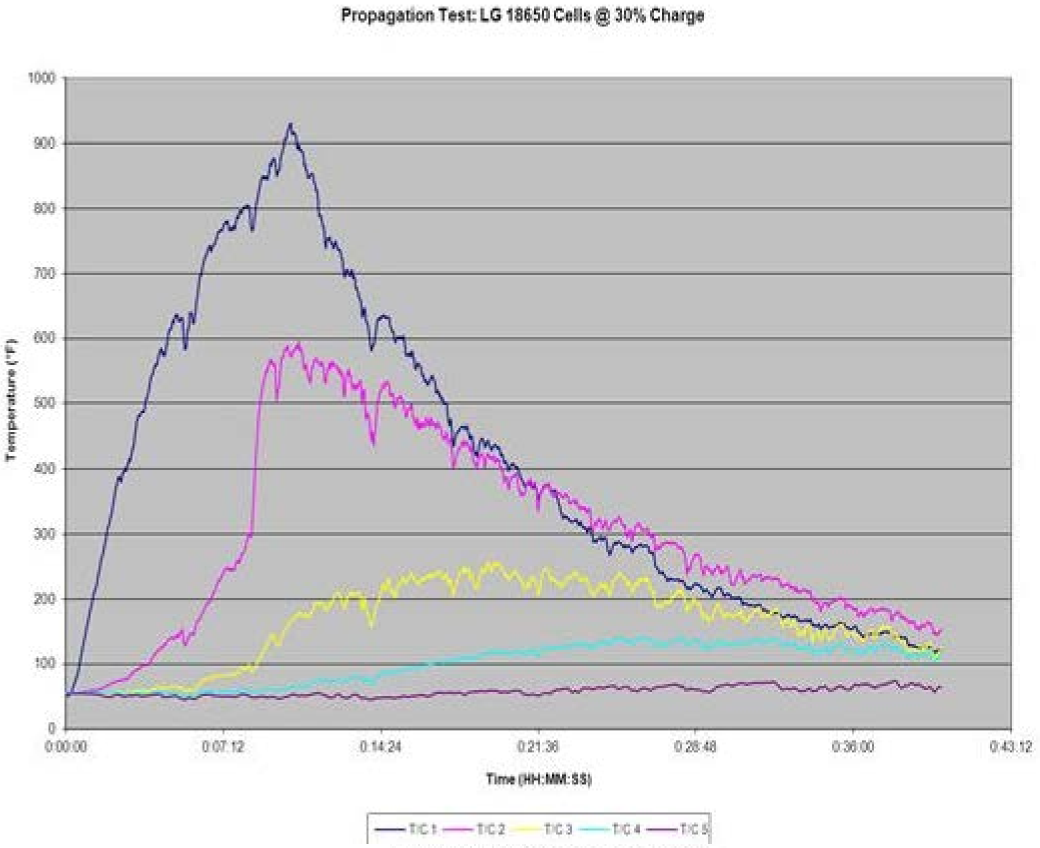


Figure 12. The LiCoO2 18650 cell SOC thermal runaway propagation tests



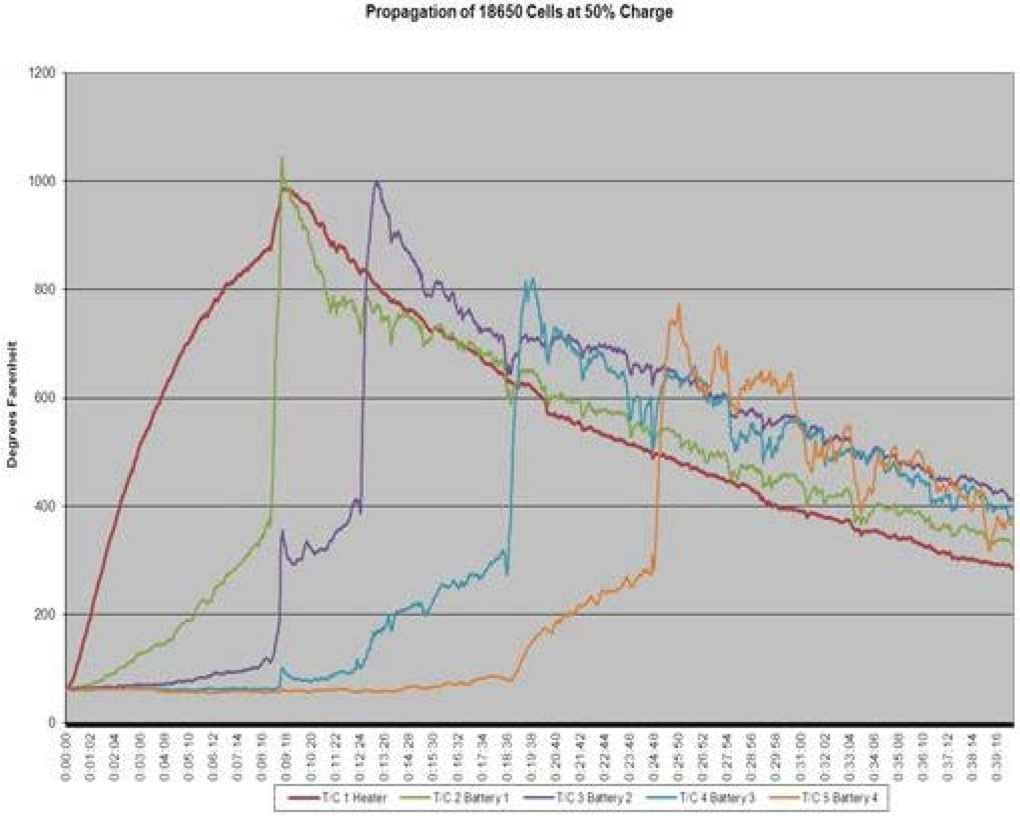


Figure 12. The $LiCoO_2$ 18650 cell SOC thermal runaway propagation tests (continued)

The results can be summed up as follows:

- The 100% cell exploded in both tests, and rapid cooling was observed. Peak temperature: 1030°F.
- The 50% test consumed all cells. Peak temperature: 1044°F.
- At 40%, two cells were consumed, and the peak temperature 760°F decreased after thermal runaway in Cell 2.
- At 30%, venting occurred in Cell 1 with no thermal runaway. Peak temperature: 560°F.
- At 20%, venting occurred in Cell 1 with no thermal runaway. Peak temperature: 502°F.

For cells of this size and $LiCoO_2$ chemistry, SOCs at 30% and below prevented propagation of thermal runaway from cell to cell.

4.3.1 SOC as a Predictor of Cell Energetics

SOC has been shown to be a good predictor of thermal runaway propagation. A 30% SOC for 18650 $LiCoO_2$ cells has been shown to minimize the propagation of thermal runaway from cell to cell in a bulk-packed shipment of cells. Prediction of the cell charge necessary to prevent thermal runaway propagation for other chemistries may be possible by measuring the electrical energy of the cell. Analytical analyses of cells of different chemistries indicate that electrical energy rather than SOC or fractional charge may be an indicator of the propensity of a cell to propagate thermal runaway [5]. Some chemistries may not propagate at charges above 30%, whereas others may require less than 30% to prevent the propagation of thermal runaway, as shown in figure 13, assuming the propensity to propagate is related to the total heat release. $LiCoO_2$ cells currently make up the bulk of consumer cells, making the 30% number applicable to the majority of cells shipped today and an excellent interim safety measure.

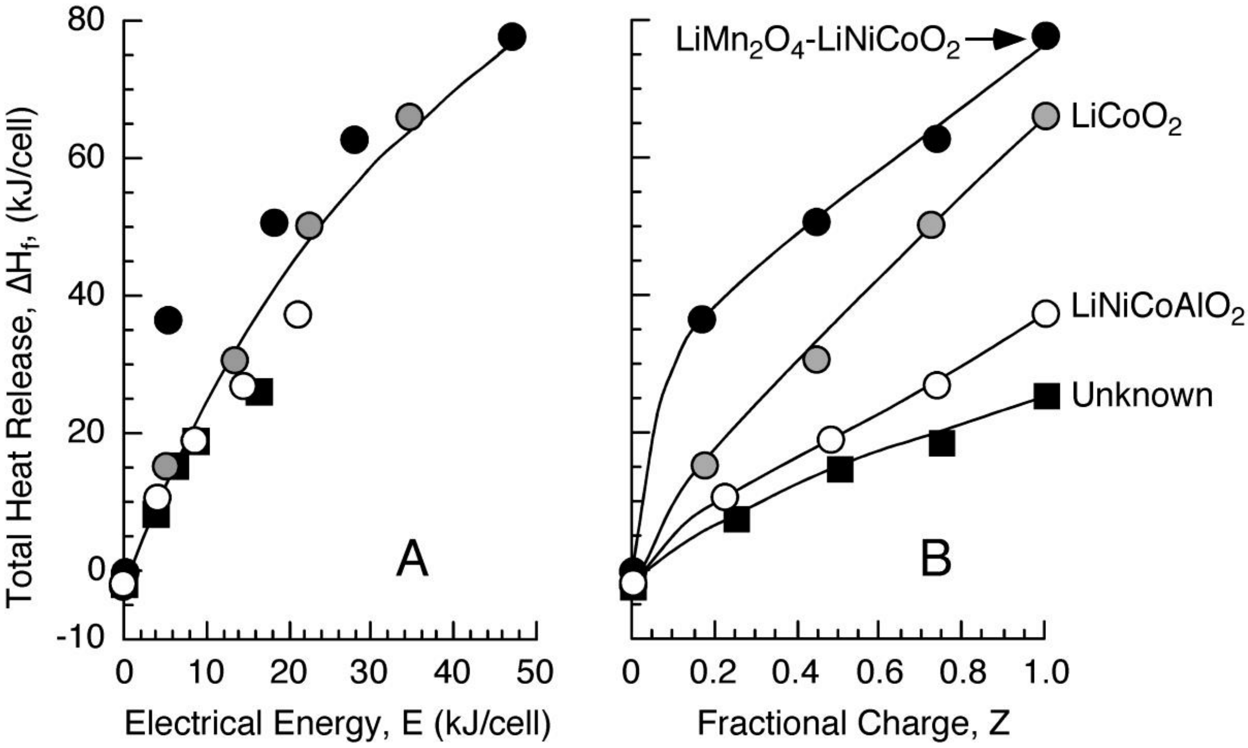


Figure 13. Total energy release, ∆Hf versus: (A) electrical energy, E, and (B) fractional charge, Z, for the different lithium-ion battery cathode chemistries

5. FULL-SCALE LITHIUM-CELL FIRE TESTS

A series of tests were conducted in the Fire Safety Branch Boeing 727 freighter test article to determine the effect on the aircraft of a large-scale lithium-cell fire [6]. Tests were conducted in both the Class E main deck and the Class C below-deck cargo compartments. Three fire loads of different cell types were evaluated, with two types of ignition. These included a mix of alkaline/nickel-metal hydride/nickel-cadmium cells, lithium-ion, and lithium-metal cells. Each test was performed twice: once with a simulated thermal runaway as the ignition source, and the second time with an external fire ignition source. The aircraft was configured to simulate the internal airflows that would be experienced at altitude in emergency conditions. Measurements were made in the cargo compartments including: air temperatures; fire temperatures and heat flux; smoke density; cabin pressure; and CO, O2, and CO_2. The conditions on the flight deck were also monitored for temperature, smoke, and CO, O2, and CO_2. There was extensive video documentation, including visible light and infrared cameras. The aircraft was fitted with a 60 gallon per minute water deluge system to extinguish the fire and protect the aircraft as needed.

The mixed-cell fire load, 1666 Alkaline AA cells, 1666 nickel-metal hydride cells, and 1667 nickel-cadmium cells served as the baseline for each compartment and to illustrate the difference between these chemistries and lithium-ion and metal cells. The cells were packed in 11 cartons.

The lithium-ion fire load consisted of 5000 18650 $LiCoO_2$ cells for each test. The cells were conditioned to a 50% SOC. The cells were packaged as received in the original shipping boxes, 100 cells to a box, two boxes per outer carton, with the fire load consisting of 25 cartons. The cartons were stacked on a metal pallet, in the open, with no plastic wrap used.

The lithium-metal fire load consisted of 4800 lithium-metal 123A Li-MnO_2 cells for each test. The cells were packaged as received, 400 cells per box, three boxes per outer carton, with the fire load consisting of four cartons.

5.1 CLASS E TESTS

The upper-deck main cargo compartment on most freighters are Class E. Class E compartments are required to have fire detection systems, the means to shut off ventilation flow, and the means to exclude hazardous quantities of smoke, flames, and noxious gases from the flight crew compartment. There are no active fire suppression agents in a Class E compartment.

The ventilation system on the aircraft was configured to provide an air exchange rate in the Class E compartment of one air exchange every 47.72 minutes. The air exchange rate in the flight deck was set to one air exchange every 1.71 minutes. These numbers are consistent with those that would be expected in flight during the shutoff of ventilation flow on detection of a fire. Fire control for this type of compartment is by oxygen starvation.

5.1.1 Mixed-Cell Test

There was no simulated thermal runaway test conducted because none of the tested cells are flammable. The external fire test resulted in ignition of the fiberboard outer cartons and charring between cartons as shown in figure 14. Ceiling temperatures remained low, peaking at 119°F at the 40-minute mark. Moderate temperatures were measured within the cell stack, peaking at 975°F at 44 minutes. The compartment gradually became obscured by smoke, but there was no smoke penetration into the flight deck. The test was terminated at 102 minutes from initiation.

Figure 14. Mixed cell post test

5.1.2 Lithium-Ion Tests

The results of the two tests, one with each type of ignition, were almost identical. The tests were terminated at 57 minutes from ignition by means of the water deluge system. In each test, approximately 3000 cells were consumed, as shown in figure 15. The ceiling temperatures above the fire peaked at 1490°F at the 49-minute mark. Peak cell fire temperatures were measured at 1300°F at the 55-minute mark.

Figure 15. Lithium-ion cells consumed post test

Oxygen depletion slowed the fire progression by approximately one-third when compared to baseline tests in open air. The fire would build up, consume the oxygen, slow down until the oxygen level recovered, and then build up again. This is consistent with expectations for a Class E compartment fire.

Some light smoke was observed on the flight deck near the end of the test. There was significant damage done to the cargo liner and interior of the cargo compartment. Temperatures measured above the ceiling cargo liner were used as “stop” criteria to avoid catastrophic damage to the aircraft, including the electrical cables, and were the reason the test was terminated.

These results indicate that a lithium-ion fire in a decompressed Class E compartment will progress at a slower rate than in a non-decompressed compartment. The conditions in the compartment slowed the progression of thermal runaway, but the fire and high temperatures seriously damaged the cargo liner and would have done further damage if the test was allowed to continue. Note that two cargo liners were installed above the fire load to fire harden this area and protect the attic space above.

5.1.3 Lithium-Metal Tests

The tests with the simulated thermal runaway ignition source and the external fire ignition source yielded similar results. In each case, the tests were terminated at 16 minutes from ignition to prevent severe damage to the aircraft. Very high ceiling temperatures were measured, peaking at 1700°F 16 minutes from test initiation. Temperatures measured within the cell stack peaked at 2250°F at the 12-minute mark. Oxygen starvation had little or no effect on the intensity of the fire. The compartment rapidly filled with smoke. Smoke was visible on the flight deck less than 4 minutes from the first observable fire and became fully obscured in less than 6 minutes. There was significant damage to the cargo liner. Approximately one-half of the cells were consumed prior to extinguishing the fire with water, as shown in figure 16.

Figure 16. Lithium-metal cells post test

These results indicate that a lithium-metal fire in a decompressed Class E compartment will progress at the same rate as in a non-decompressed compartment.

5.2 CLASS C TESTS

The Class C cargo compartments are located under the floor in the belly of the aircraft. All US passenger aircraft have Class C compartments. Some freighters also have Class C, but not all. Class C compartments have smoke- or fire-detection systems; built-in fire extinguishing or suppression systems controllable from the flight deck; means to exclude hazardous quantities of smoke, flames, or extinguishing agent from any compartment occupied by the crew or passengers; and a means to control ventilation and drafts within the compartment.

The ventilation system on the aircraft was configured to provide an air exchange rate of 5.75 minutes on the main deck and 1.68 minutes on the flight deck. These numbers are consistent with in-flight expectations. Fire control in a Class C compartment is by suppression with Halon 1301 extinguishing agent at a nominal 5% initial concentration and maintenance of a 3% concentration for the duration of the flight. Cargo liner integrity must be maintained to keep the Halon from leaking out of the compartment.

5.2.1 Mixed-Cell Test

The fire load consisted of 1666 AA sized alkaline cells, 1666 AA sized nickel-metal hydride cells, and 1667 nickel-cadmium cells packed as received in 13 cartons. An external fire was used as the ignition source. Halon 1301 was discharged when visible flames were observed. The Halon 1301 extinguishing agent suppressed the surface fire, though the fire continued to smolder in the tight spaces between the boxes, as shown in figure 17. Ceiling temperatures remained very low, rising only a few degrees from ambient. All smoke was contained within the compartment. There was no damage done to the cargo liner.

Figure 17. Mixed cell post test

5.2.2 Lithium-Ion Tests

The 5000 lithium-ion 18650 $LiCoO_2$ cells were packaged in the same manner as in the Class E tests.

The results of the simulated thermal runaway ignition test were very different from the results of the external fire test. The Halon 1301 fire suppression system in each test was activated when visible flames were detected. In the case of the external fire ignition, the Halon system extinguished the fire before any lithium-ion batteries were induced into thermal runaway. The outcome was different for the simulated thermal runaway ignition. The Halon system was again activated at the first sign of visible flames. The Halon did extinguish the burning cardboard packaging and also suppressed the burning electrolyte from cells in thermal runaway. However, the Halon did not stop the propagation of thermal runaway from cell to cell, box to box, or outer carton to carton.

The test was allowed to proceed for 1 hour and was terminated by activation of the water deluge system. Ceiling temperatures in the compartment remained low to moderate above the cell shipment. Temperatures measured in the cell shipment were quite high where cells were in thermal runaway, peaking at 1150°F. Smoke was contained within the compartment and little or no damage was done to the cargo liner. In the 1-hour time frame, approximately 1200 cells were consumed by thermal runaway propagation, as shown in figure 18. The cardboard shipping boxes and cartons were charred, but no open flames were observed, consistent with Halon 1301 suppressed fires.

Figure 18. Image of the 1200 lithium-ion cells that were consumed

These results suggested that a Class C compartment could suppress the open flames from a non-containerized shipment of lithium-ion cells and slow but not stop the propagation of thermal runaway from cell to cell and package to package. Later tests showed the additional hazard of unburned flammable gas buildup inside a cargo container and the inability of Halon 1301 to suppress an explosion of those gases (see sections 8–12).

In addition, analysis of the data by Boeing engineers revealed that the pressure rise in the compartment due to thermal runaway of the cells may cause the Halon concentration to erode faster than the design leakage rate allows for. The reduced Halon concentration levels would contribute to shorter protection times and could reach a level that results in re-ignition of the suppressed fire and open flames.

5.2.3 Lithium-Metal Tests

The 4800 lithium-metal 123A cells were packaged in a similar manner to the Class E tests. The test with the external fire source was similar to the previous tests with mixed cells and lithium-ion cells. The Halon 1301 suppression agent was discharged at the first sign of visible flames. The Halon suppressed the open fire, though there was some smoldering between the cartons. No lithium-metal cells were involved.

The test with the simulated thermal runaway ignition source yielded very different results. The Halon was again discharged at the first indication of visible flames. The agent suppressed the cardboard and electrolyte fire, but had little effect on the rapidly escalating lithium-metal cell fire. Thermal runaway propagated rapidly between boxes despite the Halon and extremely low oxygen levels. Smoke and gases escaped the compartment and penetrated into the mix bay, the Class E compartment above, and the flight deck. There was a rapid reduction in the concentration of the Halon agent. The test was terminated because of high ceiling temperatures, loss of Halon, and smoke penetration into other areas of the aircraft. The fire consumed 3450 cells, as shown in figure 19. The results of these tests show that a Class C compartment is not capable of withstanding a lithium-metal cell fire caused by a cell in thermal runaway.

Figure 19. Lithium-metal cells post test

There was an explosion event as the test was being terminated. The oxygen levels in the compartment began to rise as the Halon concentration neared zero. A single cell in thermal runaway, visible on the infrared camera view, ignited the flammable gas mixture and caused a flash fire in the cargo compartment. The pressure rise from the flash fire forced open the pressure-relief panels separating the compartment from the mix bay. This caused ignition of the built-up gases in the mix bay with catastrophic results. The floorboards above the mix bay were blown upward leaving a large hole in the Class E compartment floor, as shown in figure 20. The pressure rise due to the explosion bowed the flight deck bulkhead and blew the door off its hinges and into the flight deck, as shown in figure 21.

Figure 20. Hole in floor above the mix bay

Figure 21. Flight deck bulkhead damage and door

6. LITHIUM-CELL HAZARD EVALUATION

Two studies were undertaken to evaluate the hazard characteristics of lithium cells based on cell chemistry, type, and size. In the first study [7], tests were performed to examine the fire safety hazards that cylindrical and polymer-type lithium-ion batteries may pose onboard aircraft. Tests were conducted on individual, manufacturer-supplied cells to determine how the cells would react in a fire situation. Tests were also conducted to determine what potential fire hazard the cells themselves may pose and to determine the effectiveness of a typical handheld extinguisher on a fire involving the cells. The cells that were tested were all commercial off-the-shelf products that were being considered by manufacturers for aircraft battery power usage.

The results of the tests showed that the lithium-ion and lithium-ion polymer cells can react violently when exposed to an external fire. The cylindrical cells vented in a manner by which the electrolyte would spray out forcefully and ignite, increasing both temperature and pressure. The lithium-ion polymer cells had 3.5 to 7 times the capacity of the cylindrical cells and did not have vent locations. Instead, they were designed with a seam around the perimeter of the cell that would open, thereby exposing the flammable electrolyte. The failure of these cells greatly fueled the existing fire as the full amount of the electrolyte was exposed instantaneously to the fire source. In both single- and multiple-cell tests, the lithium-ion polymer cells, which are of a different chemistry and had a much higher energy density and power capacity (8 ampere-hour [Ah] per cell versus 1.2 and 2.3 Ah for the cylindrical cells), resulted in significantly higher temperature and pressure increases compared to the cylindrical cells.

Attempts to cause the cells to reach their thermal runaway point via (external) short circuiting were unsuccessful on all three cell types. Auto-ignition tests showed that cells failed, venting their flammable electrolyte at temperatures ranging between 330° and 527°F.

Tests conducted with a handheld Halon 1211 fire extinguisher showed that the Halon was able to extinguish all three cell-type fires. However, for the lithium-ion polymer cells, even after several attempts, the Halon extinguishing agent was not able to prevent the cells from reigniting.

Figure 22 and table 1 show the three cell types that were tested and their respective specifications. The results from this testing, for single cells only, are summarized in tables 2–4, which show the fire exposure test results, pressure pulse test results, and auto-ignition tests results, respectively. Additional results for groupings of four and eight cells of each cell type and Halon extinguishment results can be found in the final report.

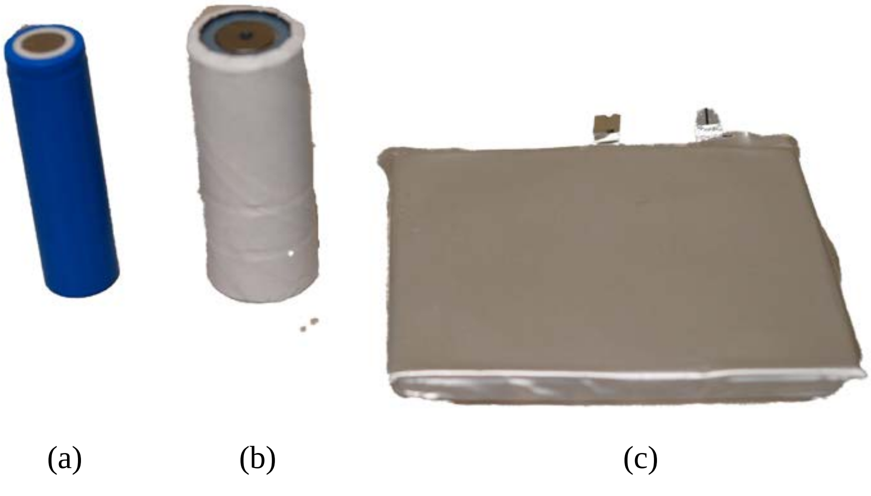

(a) (b) (c)

Figure 22. Cells used in the tests: (a) 18650, (b) 26650, and (c) Li-Po cell

Table 1. Summary of cell specifications

	Cell 1	Cell 2	Cell 3
Cell type	Cylindrical Li-ion	Cylindrical Li-ion	Li-ion Polymer
Cell size	18650	26650	3 1/2″ x 4″ x 1/4″
Chemistry	Lithium Iron Phosphate	Lithium Iron Phosphate	Lithium Cobalt Dioxide
Capacity (mAh)	1150	2300	8000
Nominal voltage	3.3	3.3	3.7
Charge voltage	3.85	3.6	4.2

Table 2. Fire exposure test results—single cell

Cell Type	Approximate Time to First Event (min)	Peak Temperature (°F)	Approximate Time to Reach Peak Temperature (min)	Fire Duration (min)
1	1.00	450	1.25	4.00
2	1.00	605	1.50	3.25
3	0.75	780	0.75	2.75

Table 3. Pressure pulse test results—single cell

Cell Type	Peak Pressure Rise (psi)	Approximate Time to Reach Peak Pressure (min)	Peak Temperature (°F)
1	0.70	3	420
2	1.40	4	500
3	2.15	1.75	770

Table 4. Autoignition test results

Cell Type	Trial 1			Trial 2		
	Ignition Temperature (°F)	Peak Temperature (°F)	Resulting Temperature Increase (°F)	Ignition Temperature (°F)	Peak Temperature (°F)	Resulting Temperature Increase (°F)
1	440	572	132	490	649	159
2	480	664	184	527	639	112
3	340	741	401	330	788	458

A second study details testing that was conducted to evaluate the failure effects of a variety of lithium-ion, lithium-pouch, and lithium-metal cells with various cell cathode materials, sizes, and constructions [8]. The results showed that the majority of cells had the potential to undergo thermal runaway. The major characteristic of a cell that demonstrated its safety was the likelihood of thermal runaway to propagate to additional cells. The likelihood of propagation was closely related to the thermal runaway onset temperature of the cell and its resulting temperature rise.

As a result of the external heating, many of the cells exploded. These explosions expelled a large quantity of gases and would have the potential to result in a dangerous situation, specifically on aircraft. However, failure of cells that exploded was less likely to propagate to adjacent cells. Several of the cells tested did not contain adequate pressure-relief mechanisms. All of these cells resulted in an explosion.

The event that followed after a cell was heated was observed to be dependent on the cell chemistry, case construction, and, in some cases, the orientation of the cell (vertical versus horizontal). In addition, various chemistries achieved the onset of thermal runaway at different temperatures.

In general, of all of the lithium-ion cells that were tested, $LiFePO_4$ would be considered the safest cathode material because of the relatively low temperature rise and the resulting low likelihood for thermal runaway to propagate. $LiCoO_2$ and LiMnNi would be considered the most hazardous because of the relatively large temperature rise and high probability for propagation of thermal runaway to adjacent cells.

To determine the relative safety of a lithium-metal cell, three hazards must be considered: fire, explosion, and toxicity. In terms of fire, LiMnO2 is the most hazardous chemistry. Explosion hazard is the highest in hermetically sealed cells without safety vents, such as found in some of the LiSOCl2 cells. However, a LiSOCl2 cell with a safety vent may be the safest cell for explosion and fire hazards, but SOCl2 gas that could be released from the cell is also known to be dangerous to breathe. LiSO2 and LiFeS2 chemistries were relatively safe compared with LiMnO2.

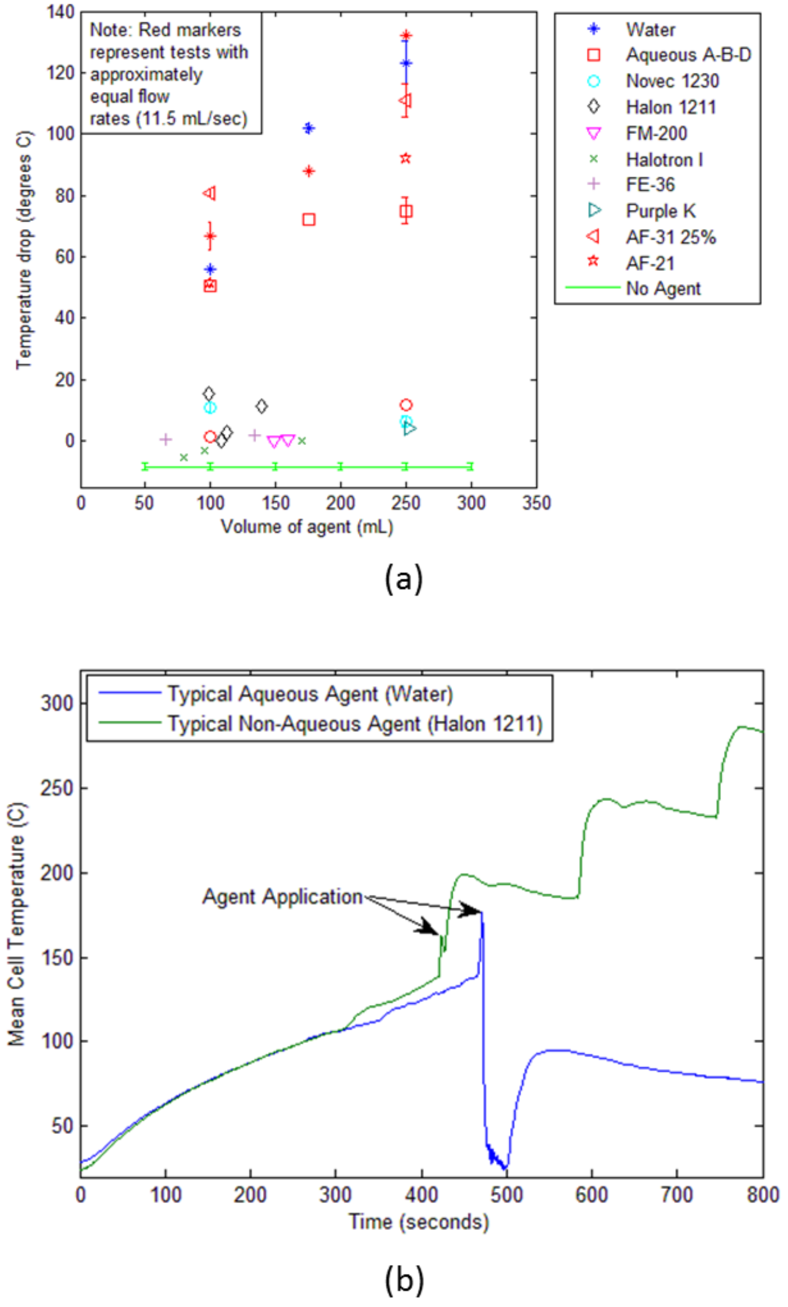
The button cells, all containing less than 0.3g lithium, were much less energetic than the larger cylindrical or pouch cells. None of them achieved full propagation to all of the other cells, though the 2025 $LiMnO_2$ cell did result in propagation to two additional cells beyond the initial one that was placed into thermal runaway. Some of the button cells did result in flames/sparks during the thermal runaway event, but the sparks were momentary and did not appear to pose a significant safety concern. Further testing may be required to determine if larger quantities of button cells have the same safety characteristics.

Aside from the generalizations that were made, there was a large variability among tests. In addition to the cell chemistry, the resulting hazard would also depend on the materials that surrounded the cells, the spacing between the cells, the number of cells, and the orientation of the cells. Because of the many factors involved in the hazard, each case should be evaluated on an individual basis.

7. EXTINGUISHMENT OF LITHIUM-ION BATTERIES

The objective of this study was to compare the effectiveness of fire extinguishing agents for the extinguishment of lithium-ion cell fires and the termination of cell-to-cell propagation of thermal runaway [9].

Tests were performed in a 64-cubic-foot test chamber with a sealable door. Quantitative tests were first done to compare the ability of “streaming” extinguishing agents, used primarily in handheld extinguishers, to cool a hot plate. The effectiveness of the agent’s ability to cool was quantified by the average temperature drop measured by five surface thermocouples. Water and other aqueous extinguishing agents were the most effective coolants, and they increased in effectiveness with increased volumes. The non-aqueous agents were essentially ineffective and showed little improvement with increased volumes, as shown in figure 23(a).



(a)

(b)

Figure 23. The (a) temperature drop of a hot plate from extinguishing agents, and (b) temperature plot of the extinguishment of lithium-ion batteries in thermal runaway for verification of hot-plate tests

Next, fire tests were performed with exposed lithium-ion cells to determine the capability of different agents to extinguish a small cell fire and prevent thermal runaway propagation. Five cells were placed side-by-side in an insulated holder and thermal runaway was initiated in a single cell with a cartridge heater. Tests were performed four times with lithium-ion cells to verify that thermal runaway would consistently propagate without the presence of an extinguishing agent. Once this was verified, streaming agents were applied with a handheld extinguisher from the distance suggested on the extinguisher bottle, and liquid agents were poured on the cell fire using a 500mL water bottle. These results also showed that aqueous extinguishing agents were most effective at halting thermal runaway propagation (see figure 23(b)). The gaseous agents were effective at extinguishing the electrolyte fires.

On occasion, cells would explode and terminate thermal runaway propagation. The propagation would terminate because hot internal cell components would eject away from the exploded cell and reduce the available heat to be transferred to the next cell.

In summary, the tests showed that the extinguishing agents that contained water were most effective at preventing thermal runaway propagation for small numbers of lithium-ion cells and that the effectiveness increased with increased volumes. The gaseous streaming agents were ineffective at preventing propagation and showed little improvement with increased volume.

8. LITHIUM-CELL FIRES IN FIRE-CONTAINMENT COVERS AND FIRE-RESISTANT CONTAINERS

In recent years, there have been many developments to protect bulk cargo compartment shipments from fires due to fire accidents on air freighters. Bulk cargo in air freighters is carried in one of two ways: on pallets that might or might not be covered or in cargo containers. Cargo that is carried on pallets can be covered with fire-containment covers (FCCs) that suppress fires on pallets by starving the fire of oxygen. Cargo containers were initially made of an aluminum frame with panels made of a polycarbonate material or aluminum. Polycarbonate materials melt at approximately 300°F, which leads to fires within such containers to spread to adjacent containers. Fire-resistant containers (FRCs) were developed of materials that could withstand high temperatures and starve the fire of oxygen by maintaining a low air exchange rate.

Tests were conducted to observe the effectiveness of FCCs to suppress Class A fire loads [10]. A nominal Class A fire load consists of 18″x18″x18″ cardboard boxes that are each filled with 2.5 lb of shredded paper. One such box, named ignition box, is packed with a Nichrome wire wrapped around paper towels to act as the ignition source. The ignition box is perforated with nine 1″ holes to provide sufficient oxygen to sustain the fire. The cardboard boxes are covered with the FCC as per its protocol, as shown in figure 24. The test is initiated when the ignition box is lit. The test is considered a pass if the FCC is able to suppress or contain the fire within its confines for a period of 4 hours.

Figure 24. Full-scale fire-test setup of an FCC

Tests showed that the FCCs were able to successfully suppress the fire for a period of 4 hours, as shown in figure 25. There were noticeable pockets of fire on the surface of the FCC that would last for a short duration. Off-gassing of the coating material of the FCC is believed to have caused these pockets of fire. The external fires helped melt the cargo netting that holds the FCC together onto the pallet. The cargo netting also caused hot spots on the surface of the FCC, but did not lead to the failure of the test. Figure 26 shows that the FCC contained the fire but collapsed on itself, thereby reducing the available free space within.

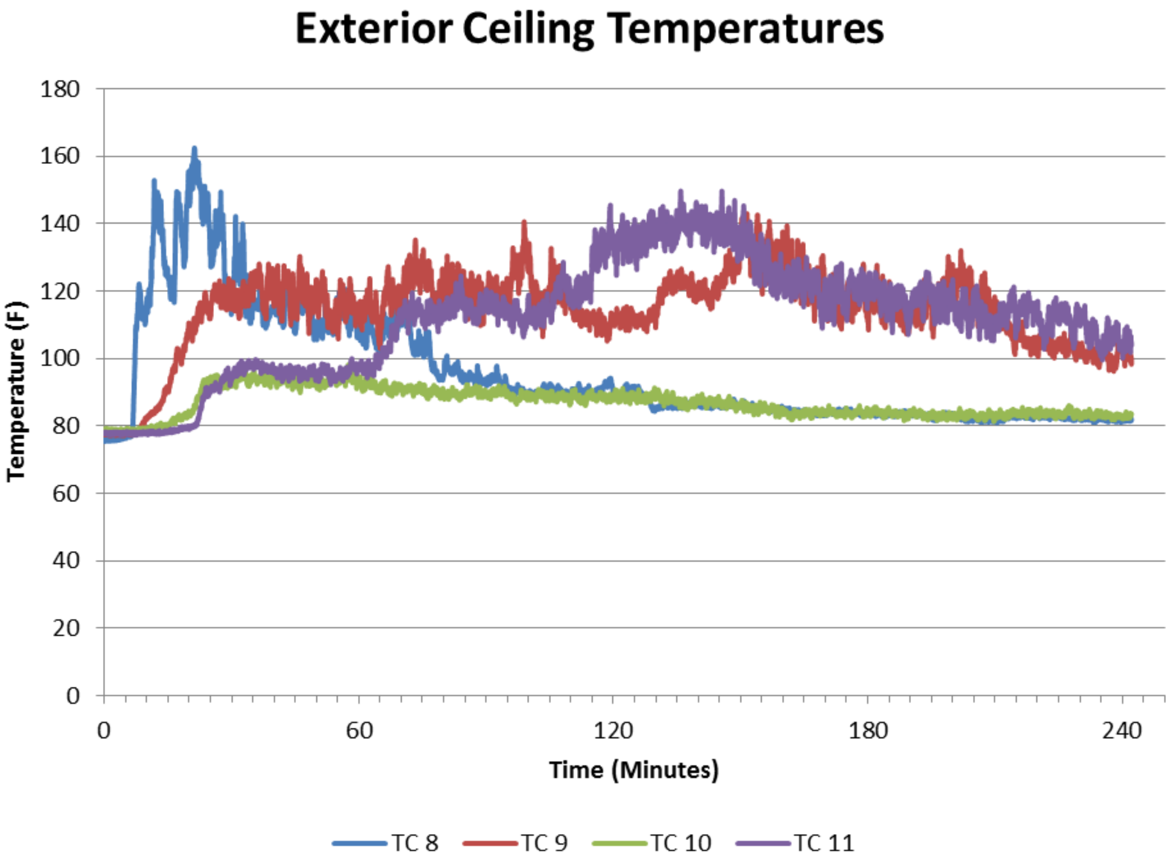


Figure 25. Results from a full-scale fire test of an FCC

Figure 26. Full-scale fire test of an FCC

Tests were also conducted to observe the effectiveness of the FCC against a lithium-cell fire threat. Some of the cardboard boxes within the FCC were replaced with 5000 lithium-ion 18650 $LiCoO_2$ cells or 4800 lithium-metal 123A Li-MnO2. The ignition source was a cartridge heater that replaced one of the cells, which replicated a cell in thermal runaway.

The lithium-ion cell test was terminated approximately 70 minutes after starting the test, as shown in figure 27. As thermal runaway propagated through the lithium-ion batteries, the fire intensified and the FCC could not contain the fire.

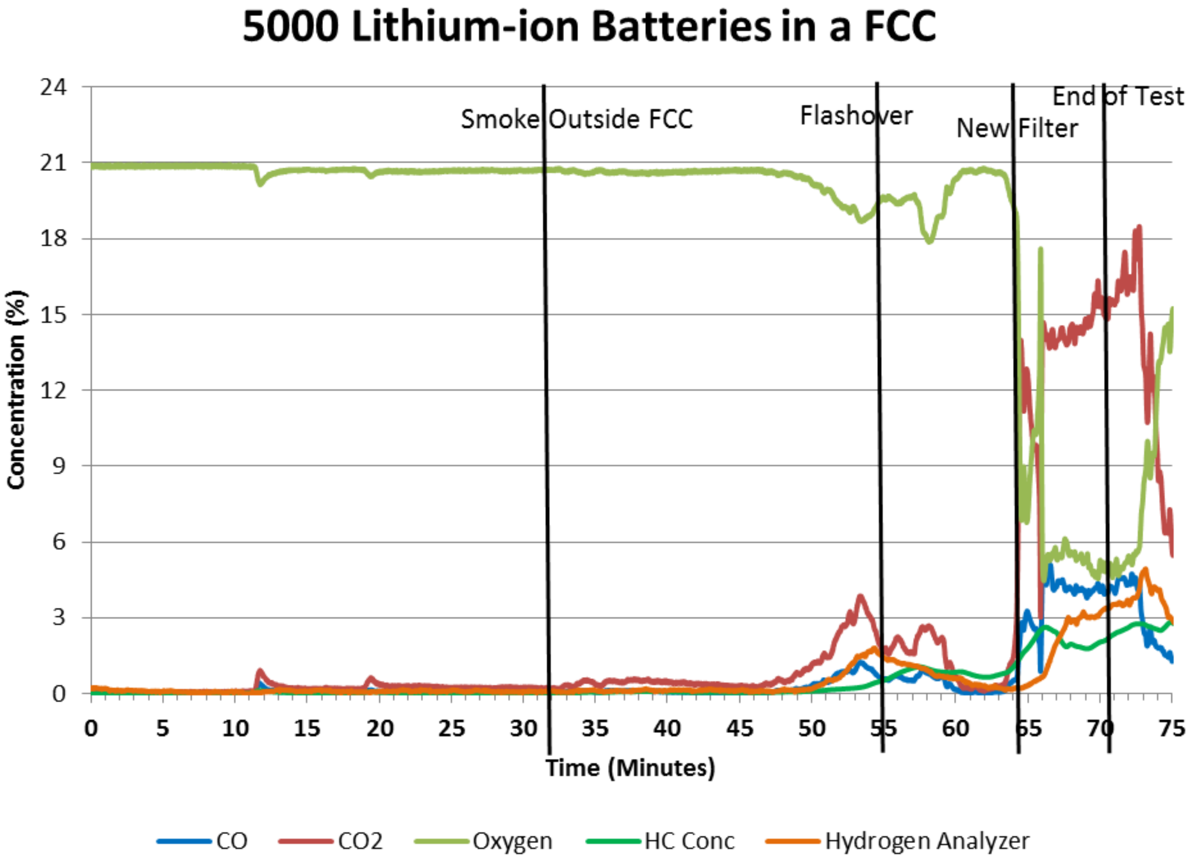


Figure 27. Gas analysis of the 5000 lithium-ion cell fire test

The lithium-metal cell test was terminated within 16 minutes of starting the test, as shown in figure 28. The burning lithium batteries consumed most of the oxygen within the FCC and filled the FCC with smoke, CO, CO_2, hydrogen, and hydrocarbons. The mix of gases leaked out from under the FCC and spontaneously ignited in the oxygen-rich surrounding air environment. Multiple sustained fires occurred outside the FCC.

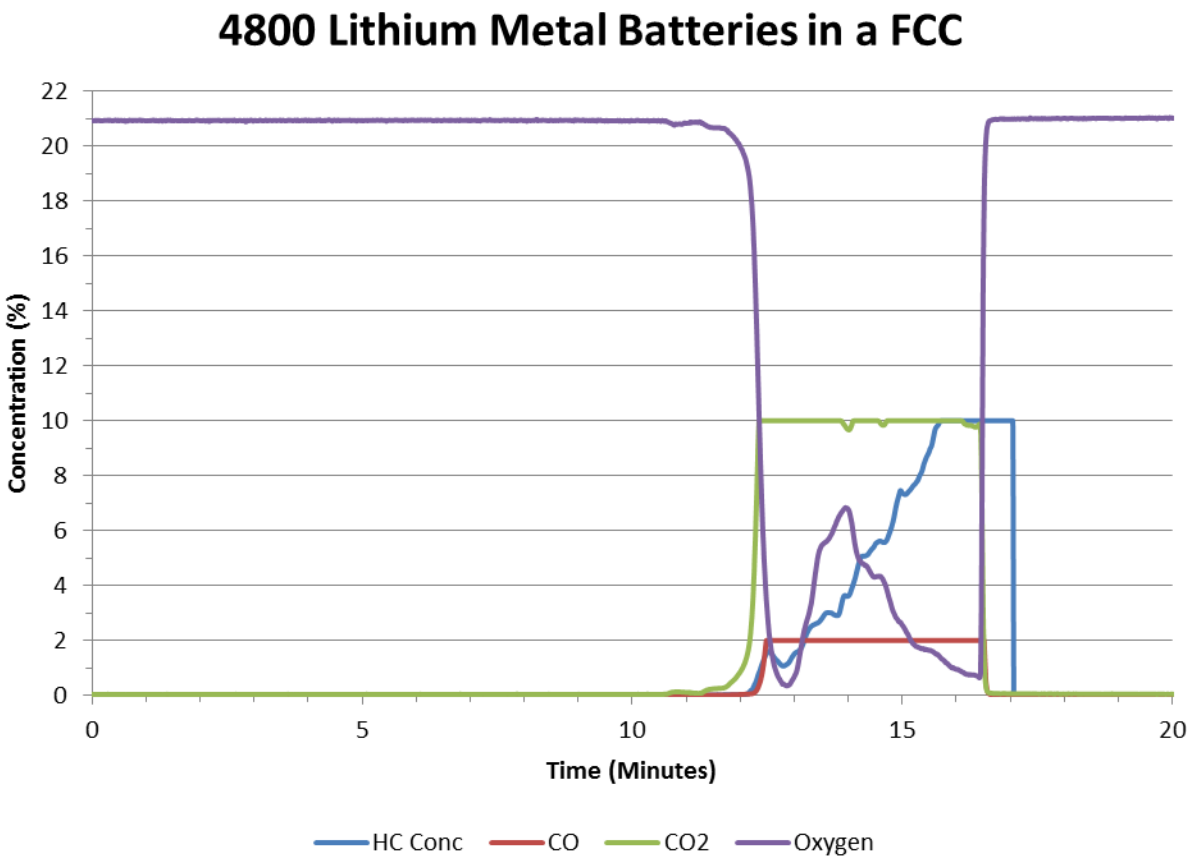


Figure 28. Gas analysis of the 4800 lithium-metal 123A Li-MnO2 cell fire test

The effectiveness of FRCs having a self-activated aerosol fire suppression system was evaluated against the same fire threats: Class A fire load, lithium-ion cell fire load, and lithium-metal cell fire load. Figure 29 shows an AAY-sized FRC in which the tests were conducted. AAY unit load devices are sized to fit on the main-deck Class E cargo compartment of a B737 aircraft. AAY ULDs measure 88″ deep by 125″ wide and can contain 410 cubic feet of cargo.

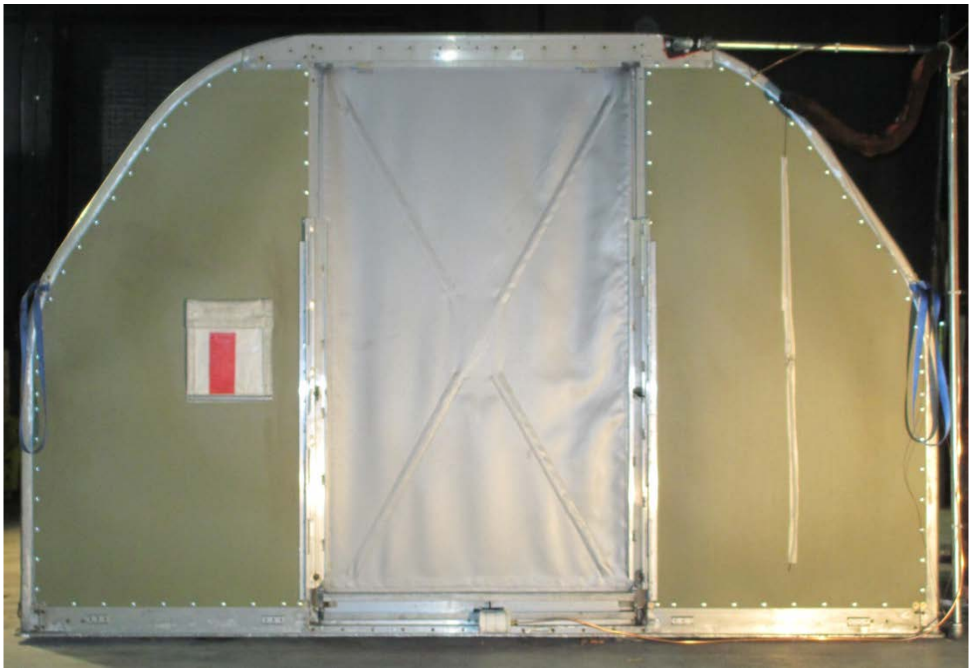


Figure 29. An FRC

The test conducted with a Class A fire load within a FRC was successful in containing a fire within by oxygen starvation for a period of 4 hours. When the doors were opened at the end of the test, the embers within the FRC reignited, causing a flashover. The test conducted with a self-activating fire extinguishing aerosol performed similar to the prior case, with the only difference being that there was no flashover when the container was opened at the end of the test. The aerosol was able to extinguish the fire at its source.

The test conducted with the 5000 lithium-ion 18650 $LiCoO_2$ cells caused the container to explode at approximately 45 minutes. Lithium-ion batteries produce flammable gases when they are in thermal runaway. Because of the manner the cells were packaged and loaded in the container and the low air exchange rate, the flammable gases collected inside the container. The fire-extinguishing aerosol activated during the test as programmed based on the conditions within the container. As oxygen concentration increased within the FRC, as shown in figure 30, the pocket of flammable gases ignited and created an explosion. Walls of the container blew out, spilling cargo into the surroundings, and the container and its contents were destroyed by the ensuing fire. The aerosol had no apparent effect on the outcome.

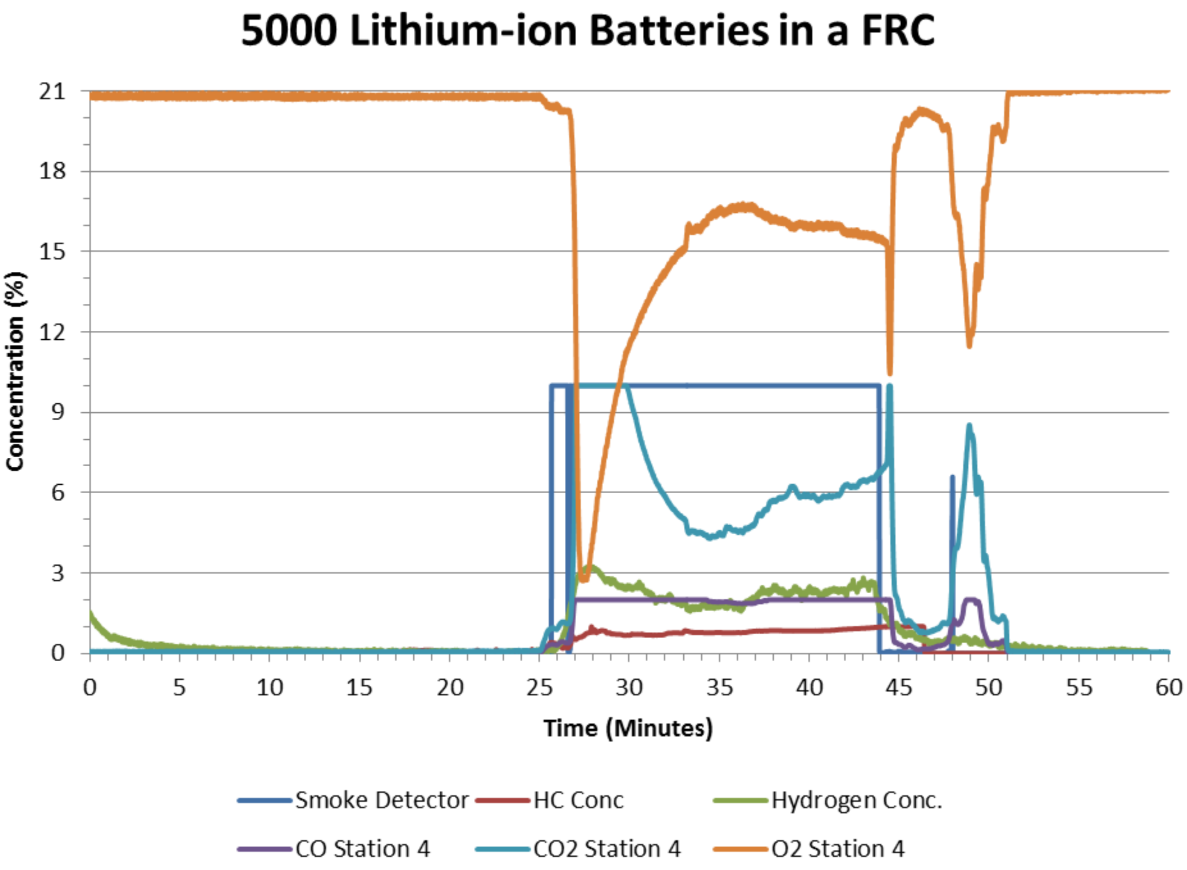


Figure 30. Gas analysis of 5000 lithium-ion 18650 $LiCoO_2$ cells in a FRC full-scale test

The test conducted with 5000 lithium-metal 123A Li-MnO_2 cells burned through the FRC within 3 minutes. The fire-extinguishing aerosol did not appear to have any effect on the outcome.

In summary, the FCCs and FRCs were effective means of suppressing and containing Class A fires. Both approaches use oxygen starvation to suppress and contain the fires. In the case of the FRC, the fire-extinguishing aerosol system mounted within extinguished the Class A fire. Both the FCCs and FRCs were not effective in containing lithium-ion or lithium-metal cell fires. In the case of a lithium-ion cell fire in the FRC, an explosion occurred because of the accumulation and ignition of flammable gases vented by the batteries in thermal runaway, causing a more catastrophic outcome.

9. LITHIUM-ION CELL THERMAL RUNAWAY VENT-GAS ANALYSIS

Tests were conducted to analyze the gases that are vented from lithium cells in thermal runaway and to evaluate the risk of the buildup and ignition of lithium-ion cell gases within an aircraft cargo compartment environment [11].

Small-scale tests were carried out in a 21.7-liter combustion sphere, where a gas chromatograph, non-dispersive infrared analyzer, paramagnetic analyzer, and pressure transducer were used to quantify the individual gases released from lithium batteries. Once the gas constituents were quantified, tests were performed to measure the pressure increase from combustion. Large-scale tests were then conducted in a 10.8 m^3 pressure chamber, a volume comparable to that of a small cargo compartment loaded with cargo, to validate the small-scale tests and to evaluate the effect of Halon 1301 on cell vent-gas combustion.

Results of the small-scale tests showed that the volume of gas (H2, CO, and total hydrocarbons) emitted from cells increased with SOC (see figures 31 and 32). Scaling calculations using the measured gas concentrations determined the minimal number of cells required to create an explosive mixture in an empty LD3 cargo container (see figure 33). Combustion of the gases at varying concentrations showed a lower flammability limit (LFL) of 10% and an upper flammability limit (UFL) that varied between 35% and 45%, depending on SOC. The combustion tests also measured a maximum pressure of more than 70 psia at altitude (see figure 34) and more than 100 psia at sea level.

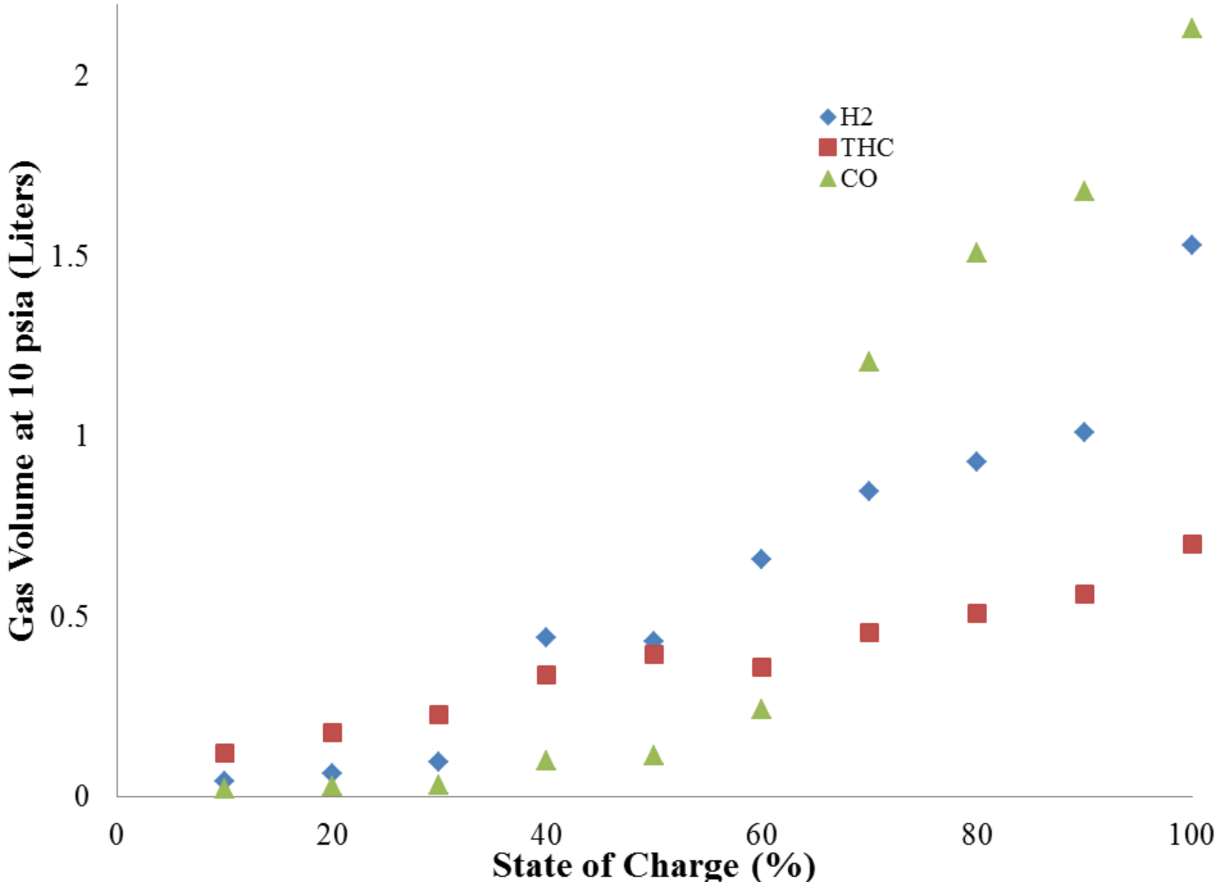


Figure 31. Flammable gases emitted from $LiCoO_2$ 18650 cells

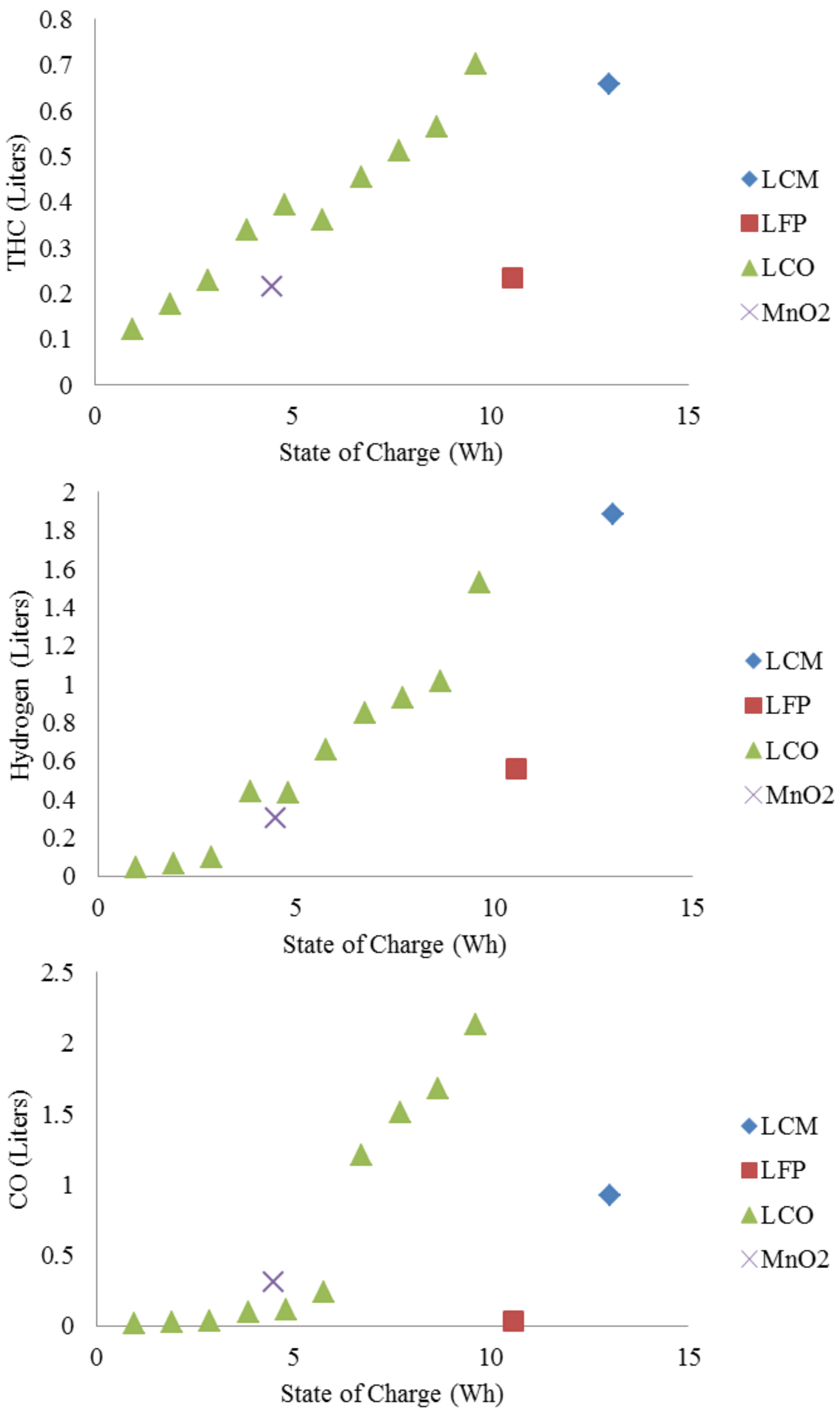


Figure 32. Flammable gases for various cell chemistries

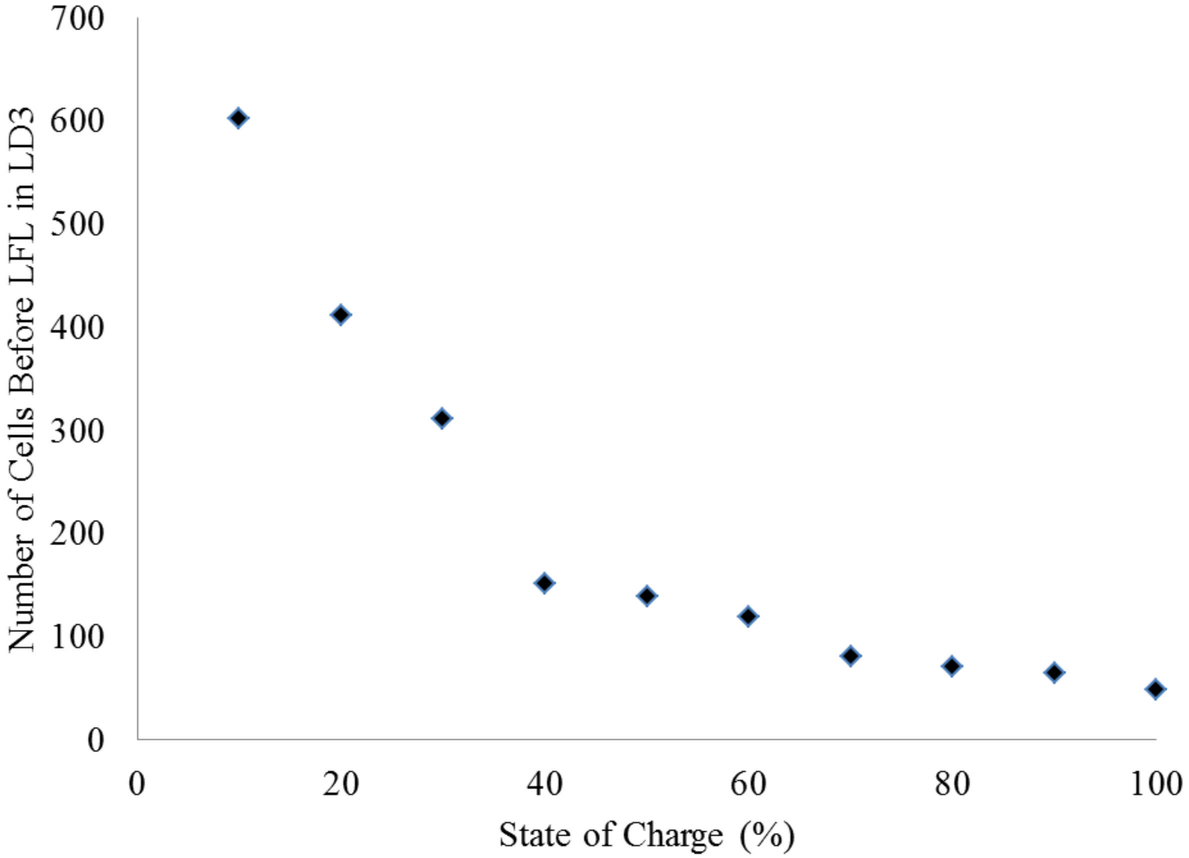


Figure 33. Number of 18650 cobalt-dioxide cells required to create an explosive mixture in empty LD3

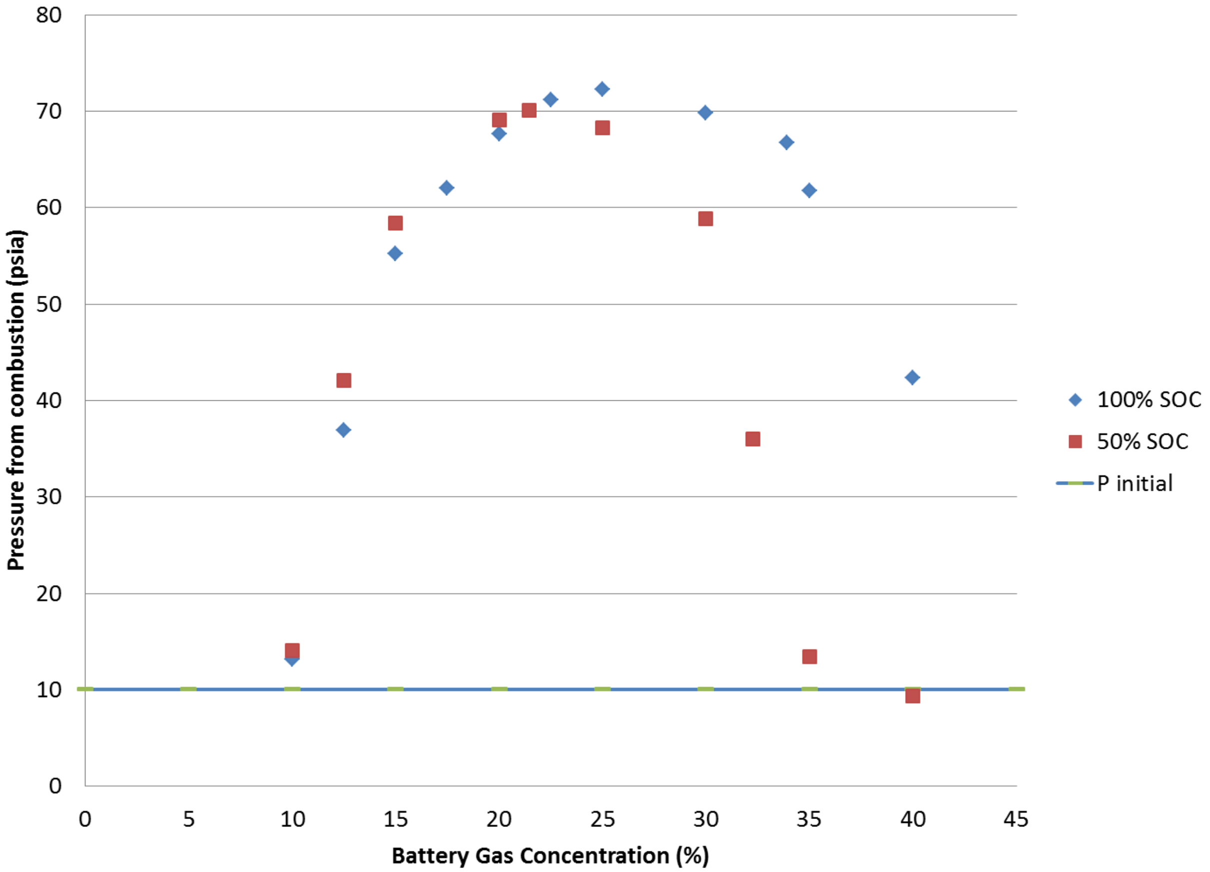


Figure 34. Pressure rise for various concentrations of cobalt-dioxide cell vent gases

Tests conducted in the pressure chamber with a mixture of flammable cell gases generated by thermal runaway and an approximately 5% Halon concentration, which is the design concentration for aircraft cargo compartments, did not prevent an explosion. The measured pressure rise profile was practically identical to that without Halon. A Halon concentration of approximately 10% would be required to inert the cargo compartment and prevent ignition of the cell gases (see figure 35).

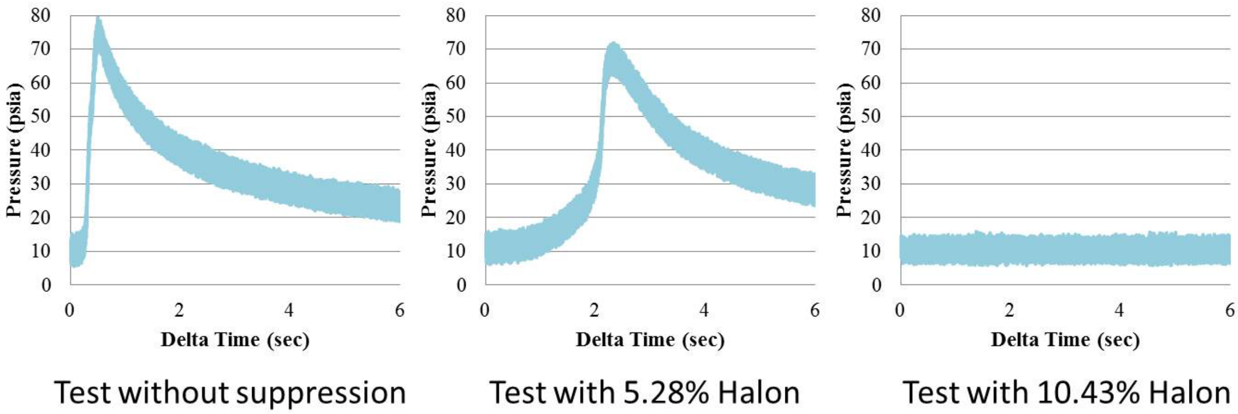


Figure 35. High-speed pressure profile for combustion of three Halon concentrations

In summary, the results of these tests showed that the SOC significantly affected the volume of flammable gases produced by lithium batteries in thermal runaway. The Halon 1301 design concentration of 5% did not prevent the ignition and resulting explosion of a flammable mixture of these gases, which would compromise the safety of an aircraft.

10. IMPACT OF LITHIUM-ION CELL GASES ON PRESSURE-RELIEF PANELS

During thermal runaway, a significant quantity of hydrogen and hydrocarbons may accumulate in the shipping boxes and free space within the cargo compartment. Should these gases ignite, a pressure pulse may dislodge pressure-relief panels designed to protect the airplane against the effects of a rapid decompression and may also dislodge cargo liners. These openings would compromise the safety of the aircraft by allowing for extinguishing agent leakage and combustion products to spread throughout the aircraft.

Tests were conducted to determine the minimum quantity of 18650 sized cells required to produce a flammable gas mixture capable of dislodging pressure-relief panels [12]. To control and vary the experimental conditions, a bottled gas mixture was used that was similar to the flammable gas composition of the vented gases. The bottled gas mixture was metered with air into a balloon to fix the location of the flammable gas mixture. Previous tests established the relationship between flammable gas volume, which was varied, and the number of batteries vented.

The bottled gas mixture was metered into a balloon with 78.3% air previously shown to maximize the pressure rise due to combustion. A spark generator located within the balloon was then activated to ignite the mixture. To verify that the pressure rise from combustion of the bottled gas mimicked the pressure rise of actual cell gas, a comparison test was conducted. The results showed identical pressure rise (see figure 36).

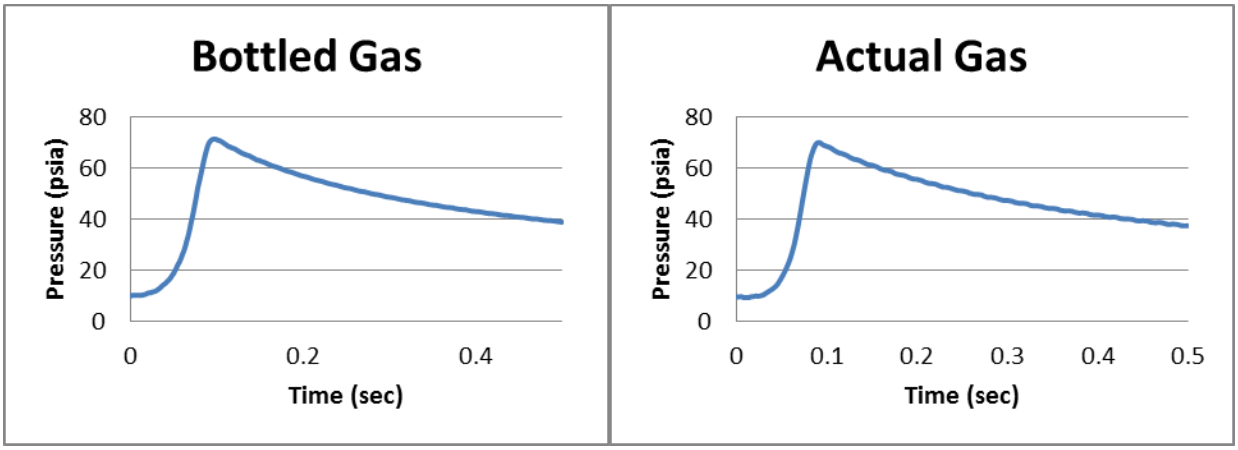


Figure 36. Comparison of pressure rise between vented cell gas and bottled gas

The tests were conducted in two test articles. First, tests were carried out in a 10.8 m^3 pressure chamber to determine the relationship between the volume of lithium-cell vent gases and the pressure rise in the overall chamber. The chamber was filled with boxes to represent a cargo compartment that was 70% loaded. Later, tests were performed in a 737 forward cargo compartment that was also 70% loaded with boxes to determine the impact of the measured pressure rise on the pressure-relief panels and cargo liners. In both test articles, the volume of bottled gas corresponded to a predetermined number of vented lithium-ion batteries. Figure 37 and 38 show the test setup in the pressure chamber and 737 cargo compartment, respectively. A summary of all of the tests that were conducted is shown in table 5.

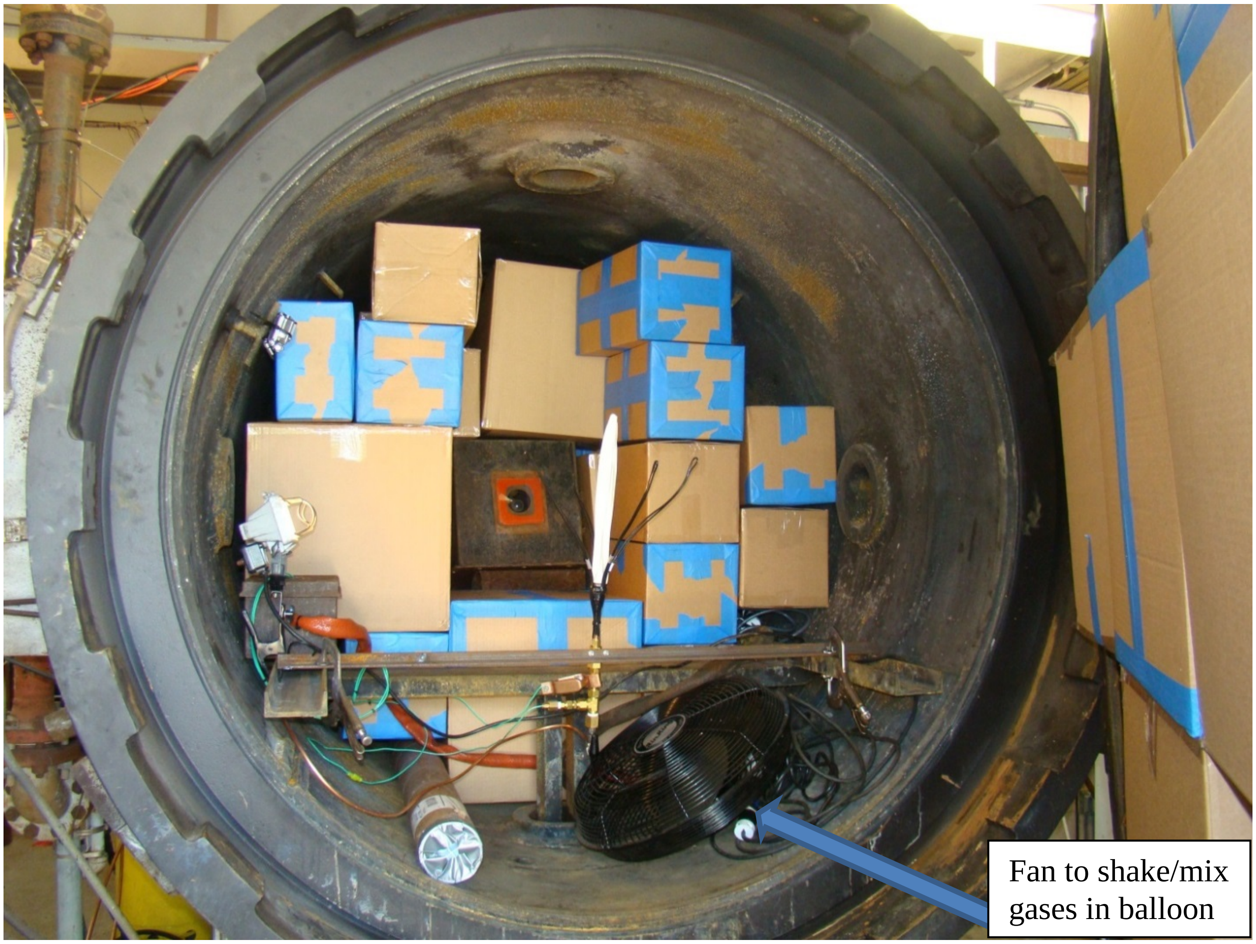


Figure 37. Pressure chamber used to simulate 70% loaded cargo compartment

Figure 38. A 737 forward cargo compartment

Table 5. Tests performed in pressure chamber

Ambient Pressure	Combined Air and Cell Gas Volume (Liters)	Equivalent Number of Cells 100% SOC	Equivalent Number of Cells 50% SOC
Sea Level	48.6	2.2	6.8
Sea Level	35.6	1.6	5
Sea Level	78.4	3.5	11
Sea Level	35.6	1.6	5
Sea Level	48.6	2.2	6.8
Altitude	52.4	1.6	5
Altitude	31.4	1	3
Altitude	10.5	0.3	1
Sea Level (in aircraft)	35.6	1.6	5
Sea Level (in aircraft)	141.2	6.4	20
Sea Level (in aircraft)	57	2.6	8

The pressure chamber test results are shown in figure 39 at sea level and in figure 40 at altitude. The data show that the pressure rise varies linearly with the number of vented batteries corresponding to the bottled gas volume. In addition, the higher the SOC, the fewer number of batteries required to produce a given pressure rise. For example, assuming that 1 psi is required to dislodge pressure-relief panels, the required number of batteries (cells) at altitude is only one cell at 100% SOC and 3 cells at 50% SOC.

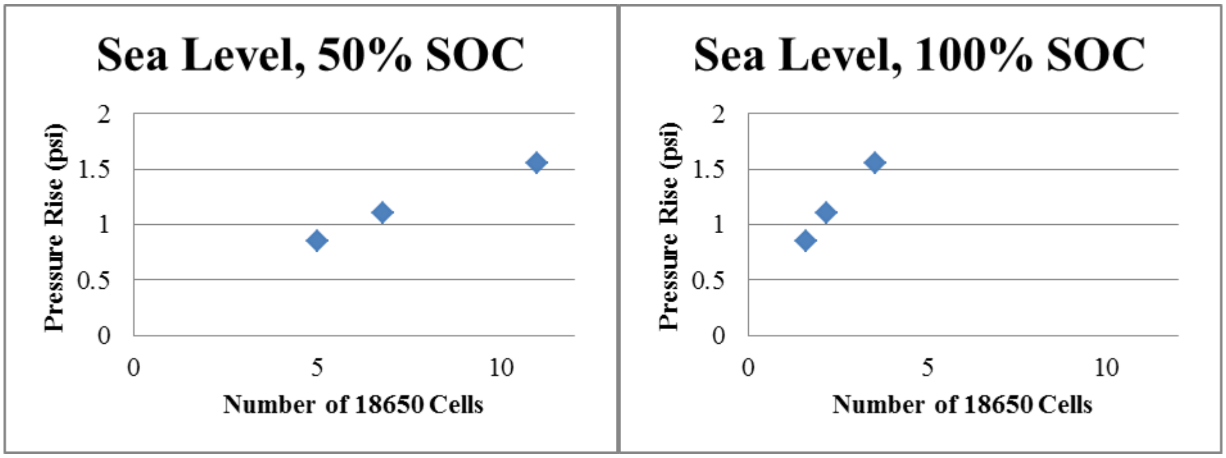


Figure 39. Pressure rise in chamber at sea level

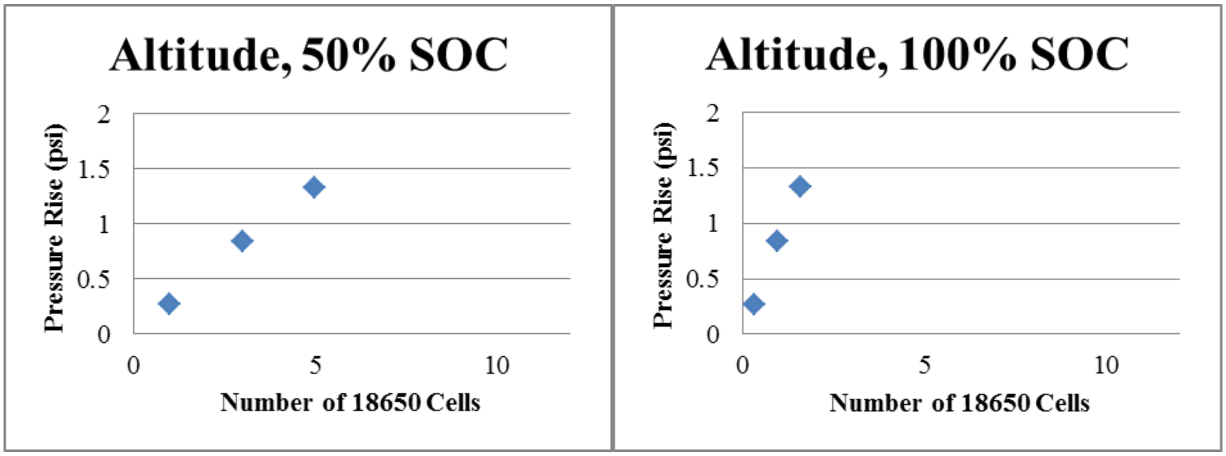


Figure 40. Pressure rise in chamber at altitude

The test results in the 737 forward cargo compartment (at sea level pressure) are shown in figure 41. At the lowest mixture gas volume, the resultant pressure rise, approximately 0.25 psi, had no impact on the pressure-relief panels. However, the higher gas volumes produced greater pressure rises and impacted the pressure-relief panels. At a gas volume of 57 liters, the measured pressure rise was 0.6 psi, causing a bulkhead pressure-relief panel to open slightly. The highest volume produced a pressure rise of 1.2 psi, dislodging the bulkhead pressure-relief panel and opening the pressure-relief panel above the door (see figure 42). In addition, the cargo liner was also damaged in one location. The volume of flammable cell gas ignited to produce a 1.2 psi pressure rise corresponded to only 6.4 cells at 100% SOC or 20 cells at 50% SOC.

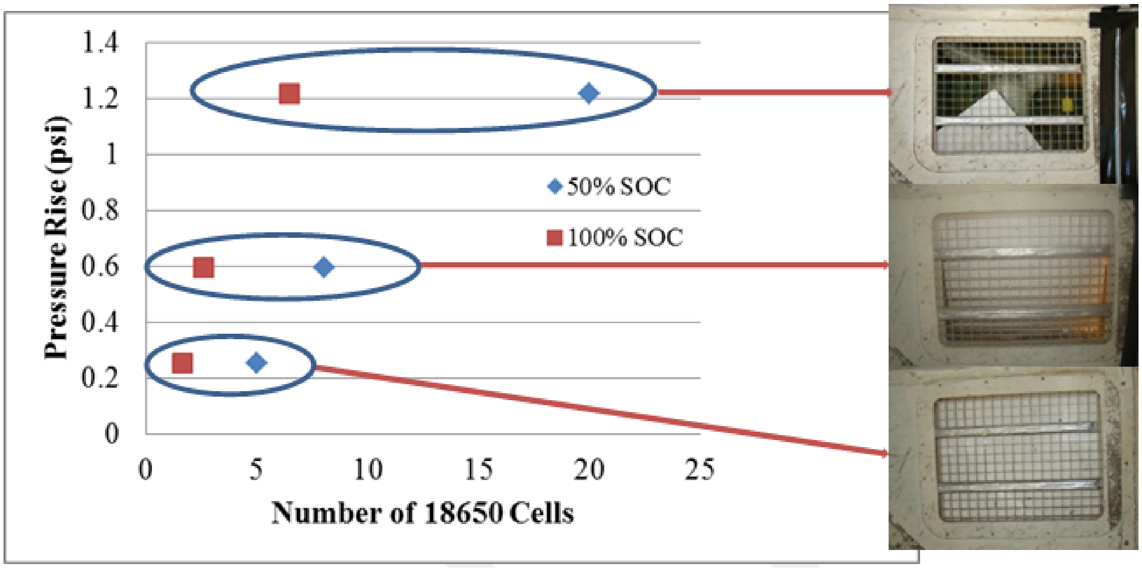


Figure 41. The 737 test results

Figure 42. Pressure-relief panel above door after 6.4 cells at 100% and 20 cells at 50%

The volume of vented lithium-cell gas (if ignited) and the corresponding number of batteries that would create the relatively low pressure rise capable of dislodging pressure-relief panels is dependent on many factors, including the type of cell, its SOC, and the volume of the cargo compartment. Nevertheless, the required number of batteries is relatively small, and the consequences are a safety concern in that the aircraft fire suppression system would be less effective, leaving the aircraft vulnerable to an uncontrolled fire.

11. HYDROGEN FLAMMABILITY IN AIR AT SUB-ATMOSPHERIC PRESSURES AND REDUCED OXYGEN CONCENTRATIONS

The flammability of hydrogen was measured in air at pressures replicating sea level, 15,000, 30,000, and 40,000 feet of altitude [13]. At these conditions, the LFLs and UFLs; maximum explosion pressures; flammability properties in oxygen-depleted air; and limiting oxygen concentrations (LOCs) were determined. All testing was done in a 20-liter stainless steel chamber based on the Bureau of Mines design for a 20-liter explosibility test chamber for dusts and gases. During each test, the chamber was evacuated and refilled with any concentration of hydrogen, nitrogen, and air, measured by partial pressures. Any mixture was considered flammable if the pressure increased by 3% or more over the initial pressure.

The flammability was determined over the full range of hydrogen concentrations in pure air and with 20%, 40%, and 60% nitrogen added at each altitude. The flammability limits of hydrogen and the limiting concentrations of oxygen and nitrogen are shown in table 6. These are the boundaries in which no ignition will take place. The data is shown in graphical form in figure 43. All combinations of gases inside the curves are flammable. At high altitudes, the gas mixtures, for the most part, remained flammable across a wider range of hydrogen concentrations, but the lower-altitude tests produced much higher peak pressures due to the increased mass of hydrogen and oxygen present. The highest pressure measured in all of the tests performed was at stoichiometric hydrogen and air at sea level. The pressure increased 100.8 psi over the initial pressure and reached that peak 12 ms after the spark. This and all other tests completed that were not near the flammability limits produced very powerful explosions that could be catastrophic in an aircraft.

Table 6. The LFL, UFL, LOC, and limiting inerting concentration of hydrogen in air at each altitude tested

Altitude (ft)	LFL, %H_2	UFL, %H_2	LOC, %O_2	LIC, %N_2
0	4.70%	78.18%	4.21%	78.06%
15,000	4.41%	78.87%	3.89%	79.87%
30,000	4.07%	77.86%	3.61%	81.83%
40,000	3.89%	76.87%	3.49%	82.09%

LIC = limiting inerting concentration

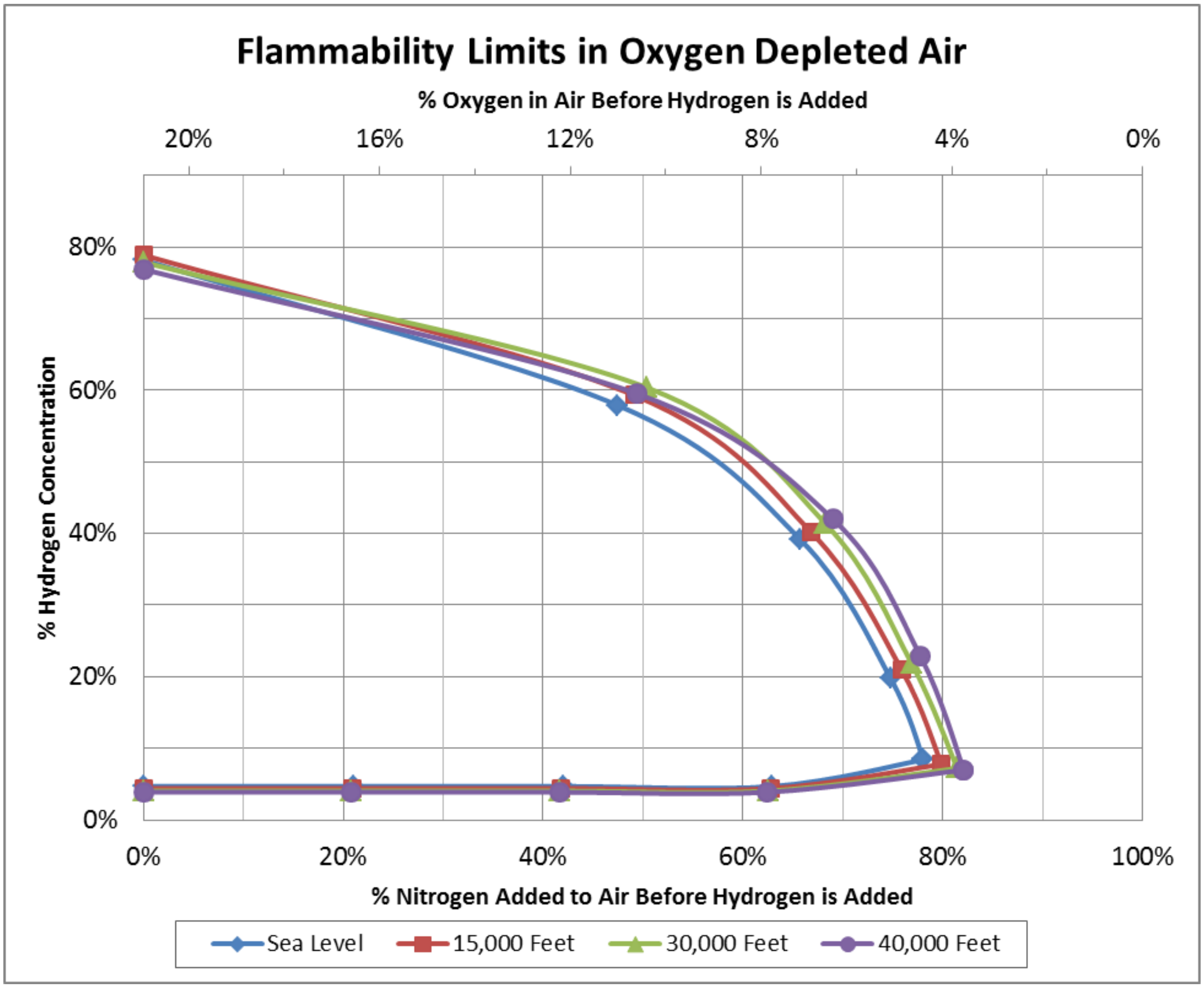


Figure 43. Flammability limits of all possible combinations of hydrogen, nitrogen, and air at each altitude tested (each combination inside the curve is flammable)

12. HYDROGEN FLAMMABILITY IN AIR WITH AND WITHOUT HALON 1301 ADDITION

The flammability of hydrogen, a major component in the flammable gases vented by lithium batteries, in an air mixture with Halon 1301, the extinguishing agent used in aircraft fire suppression systems, was measured in the 20L test vessel [13]. For these inerting tests, the mixture was considered flammable if the pressure increased by 5% over the initial pressure, instead of 3%.

The 5 % Halon 1301 by volume knockdown concentration and the sustained 3 % Halon 1301 by volume in a Class C cargo compartment were incapable of inerting hydrogen and air mixtures, though Halon can reduce the flammability range, as shown in table 7. Without Halon, the LFL and UFL of hydrogen and air mixtures is 4.95 ± 0.40 % and 76.52 ± 0.42 % hydrogen by volume. With 10% and 20% Halon, the LFL and UFL of hydrogen in air is 9.02 ± 0.51 % and 45.72 ± 0.41 % hydrogen by volume and 11.55 ± 0.48 % and 28.39 ± 0.47 % hydrogen by volume, respectively. The minimum inerting concentration (MIC) of Halon 1301 in hydrogen and air mixtures is 26.72 ± 0.43 % Halon 1301 by volume, as indicated in table 8. The MIC protects against the entire possible range of hydrogen in air mixtures. Figure 44 shows the complete flammability range of Halon 1301, hydrogen, and air mixtures.

Table 7. Flammability limits of hydrogen and air mixtures with and without Halon 1301 addition

Mixture	LFL, % Hydrogen Vol	UFL, % Hydrogen Vol
Hydrogen–Air	4.95 ± 0.40	76.52 ± 0.44
Hydrogen–Air–10 % Halon 1301	9.02 ± 0.51	45.70 ± 0.41
Hydrogen–Air–20 % Halon 1301	11.55 ± 0.48	28.39 ± 0.47

Table 8. Halon 1301 MIC of hydrogen in air

Mixture	MIC, % Halon 1301 Vol
Hydrogen–Air–Halon 1301	26.72 ± 0.43

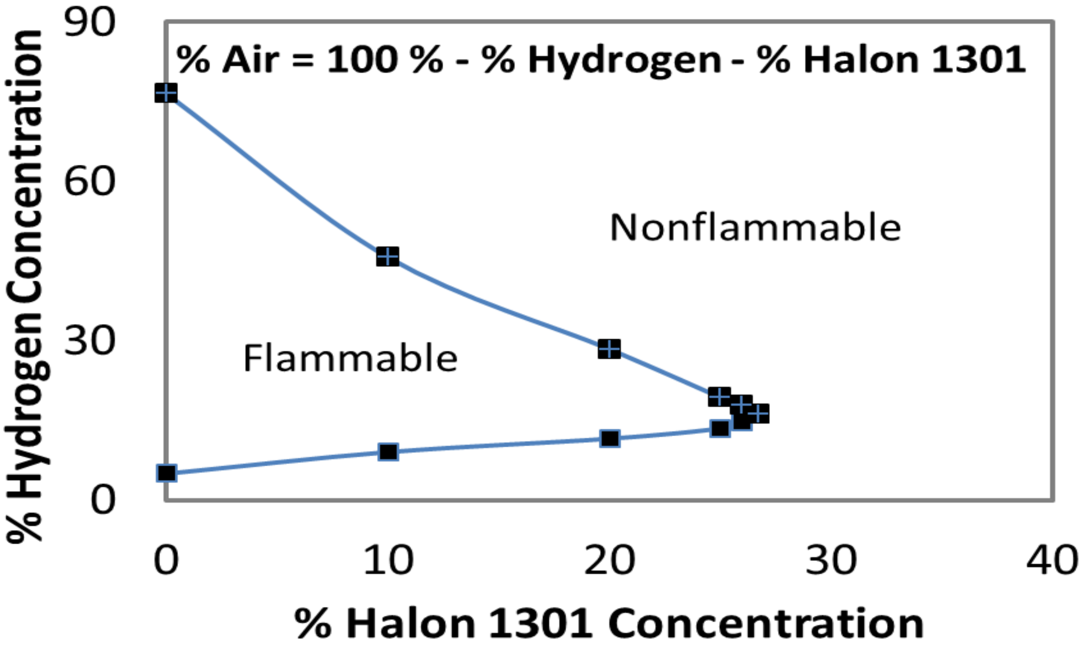


Figure 44. Flammability curve of hydrogen, air, and Halon 1301 mixtures

13. LITHIUM CELL THERMAL RUNAWAY VENT-GAS FLAMMABILITY IN AIR WITH AND WITHOUT HALON 1301 ADDITION

Tests were also conducted in the 20L test vessel to examine the Halon inerting characteristics of the bottled cell vent-gas mixture used in the previously described pressure chamber and 737 cargo compartment tests [14]. As shown in table 9, the LFL and UFL of lithium-cell vent gas and air mixtures is 7.88 ± 0.41 % and 37.14 ± 0.42 % by volume. At 5%, 7%, and 8% Halon 1301 concentration, the LFL and UFL is 13.80 ± 0.49 % and 26.07 ± 0.43 %, 16.15 ± 0.40 % and 23.31 ± 0.44 %, and 17.62 ± 0.52 % and 24.84 ± 0.65 %, respectively. The MIC of Halon 1301 in lithium-cell vent gas and air mixtures is 8.59 ± 0.52 % (see table 10). This is consistent with the previously described pressure chamber results, which demonstrated Halon inerting at approximately 10.4 % but ineffective at 5.3%. The flammability envelope for lithium-cell vent gas and Halon 1301 in air mixtures is shown in figure 45.

Table 9. Flammability limits of lithium-cell vent gas and air mixtures with and without Halon 1301 addition

Mixture	LFL, % Hydrogen Vol	UFL, % Hydrogen Vol
Lithium Cell Vent Gas–Air	7.88 ± 0.41	37.14 ± 0.42
Lithium Cell Vent Gas–Air–5% Halon 1301	13.80 ± 0.49	26.07 ± 0.43
Lithium Cell Vent Gas–Air–7% Halon 1301	16.15 ± 0.4	23.31 ± 0.44
Lithium Cell Vent Gas–Air–8% Halon 1301	17.62 ± 0.52	21.84 ± 0.65

Table 10. Halon 1301 MIC of lithium-cell vent gas in air

Mixture	MIC, % Halon 1301 Vol
Lithium Cell Vent Gas–Air–Halon 1301	8.59 ± 0.52

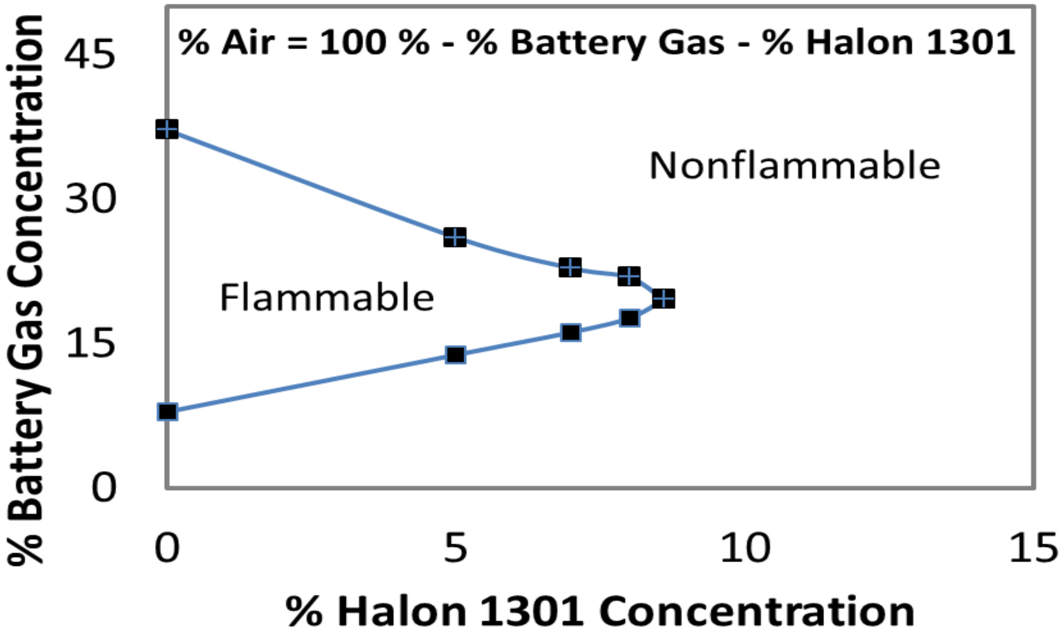


Figure 45. Flammability curve of lithium-cell vent gas, air, and Halon 1301 mixtures

14. PASSIVE PROTECTION OF LITHIUM-CELL BULK SHIPMENTS

In an earlier study, tests were performed to demonstrate the effectiveness of various shipping configurations and concepts at containing a bulk shipment lithium-cell fire initiated by a simulated single cell in thermal runaway. The configurations tested included an oxygen overpack box, a steel drum, and a decrease in cell packaging density in standard cardboard boxes. The tests demonstrated that the oxygen-generator overpack successfully contained the fire from a lithium-ion cell thermal runaway, but was unsuccessful in containing a lithium-metal cell fire. In either case, the overpack did not contain smoke or gases. Note that the overpack is designed to protect oxygen storage containers from activating or venting during an external suppressed cargo compartment fire and not to contain a fire generated from within. The secured lid was launched off of the steel drum in one of the tests because of the rapid pressure rise caused by thermal runaway propagation. Clearly, shipping lithium batteries in an air-tight container will not prevent thermal runaway propagation but instead causes a sudden and large release of the decomposed and chemical reaction products ejected by the batteries. The experiment with decreased cell packaging density (half the cells removed) failed to prevent thermal runaway propagation. Even the superior insulation properties of air did not prevent propagation.

The objective of the current study was to further evaluate the effectiveness of various types of shipping materials and configurations to prevent or minimize the propagation of thermal runaway in lithium-ion cell shipments [15].

Tests were performed in square cardboard boxes with a capacity for 16 18650-sized cells. A cartridge heater was placed on the inside corner of the box to initiate thermal runaway, and a thermocouple was attached to each cell for temperature measurement (see figures 46 and 47). The SOC and material between each cell was varied. An additional test evaluated the effectiveness of a packet of water placed above the cells. During thermal runaway, the packet material melts, releasing the water contents and cooling the batteries.

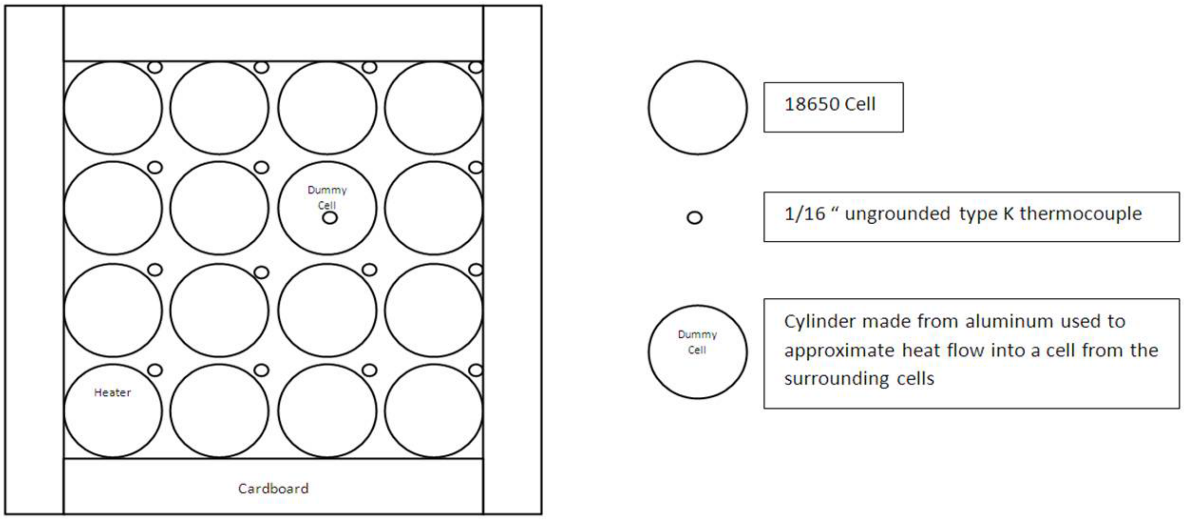


Figure 46. Layout of the 18650 cell box (the separators in between each cell are absent from this figure for simplicity)

Figure 47. Test chamber and setup

The tests showed that thermal runaway propagated at charge levels greater than 30% with typical cell package material. Divider materials with improved insulation properties increased the SOC required for propagation. Conductive divider materials delayed the onset of thermal runaway because there was more heat transfer away from the heater, but decreased the time between thermal runaway events once propagation had begun. Higher cell charge levels increased cell temperatures and decreased the amount of time for an entire package to undergo thermal runaway. The results are shown in figures 48–50. In figure 48, the peak temperature is the maximum value measured for all of the batteries; the average temperature in figure 49 is the average of the peak temperatures for the 16 batteries. In figure 50, the test time is the time from the beginning of the test until the activation of the last cell. The importance of SOC is evident. At the lowest SOC, thermal runaway propagation did not occur. At the higher charges, some batteries exploded and others ejected their core materials. Lowering the charge also increased the time required for thermal runaway to propagate throughout the package. The pack of water above the cells prevented thermal runaway propagation at a 50% SOC (see figure 51).

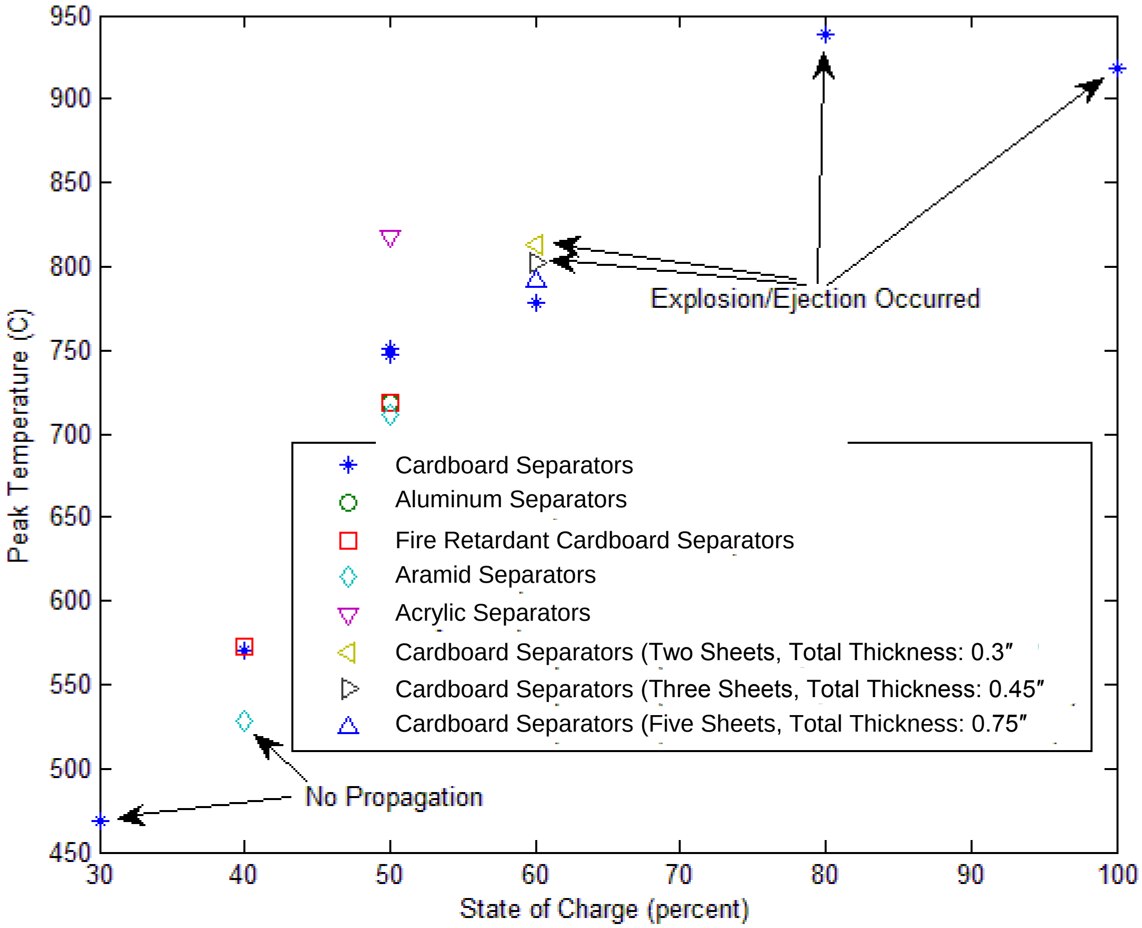


Figure 48. Peak temperatures during tests

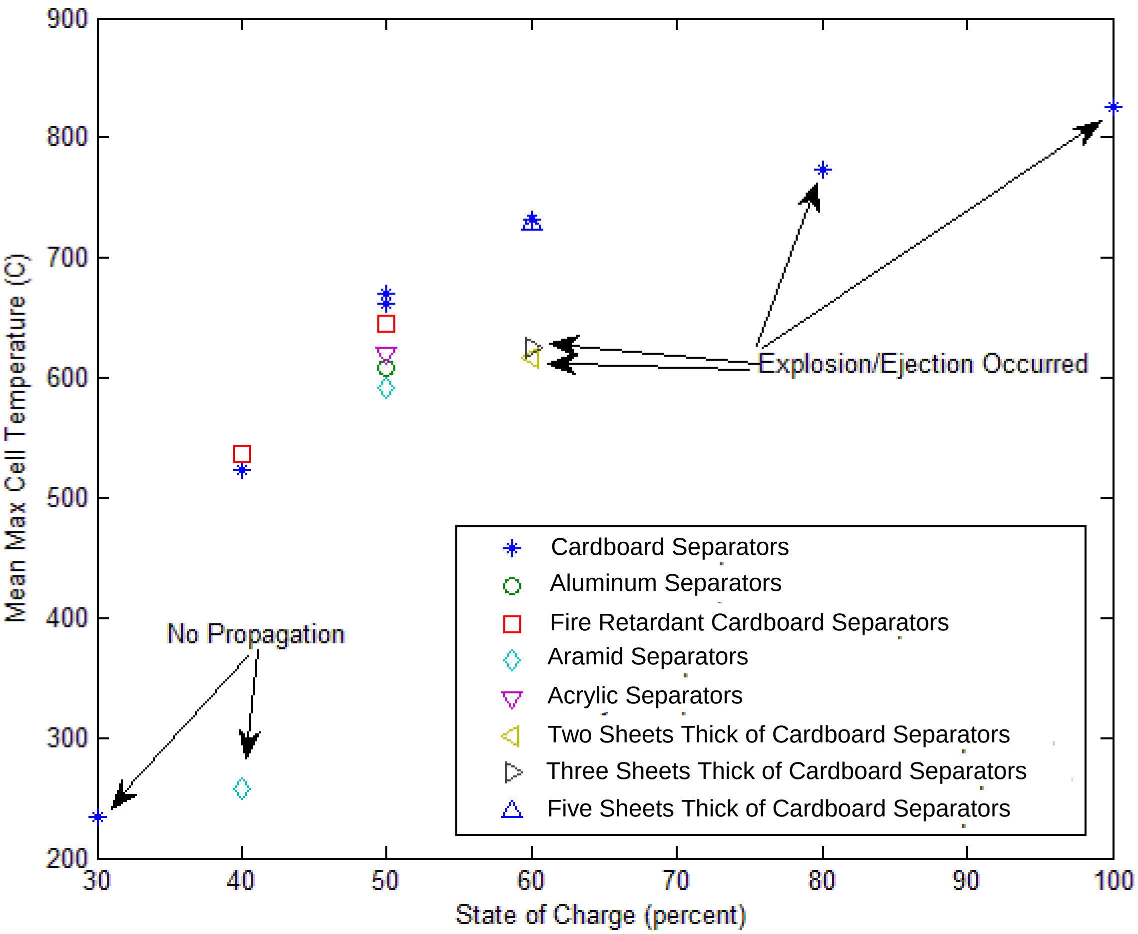


Figure 49. Average of the maximum of the cells in the tests

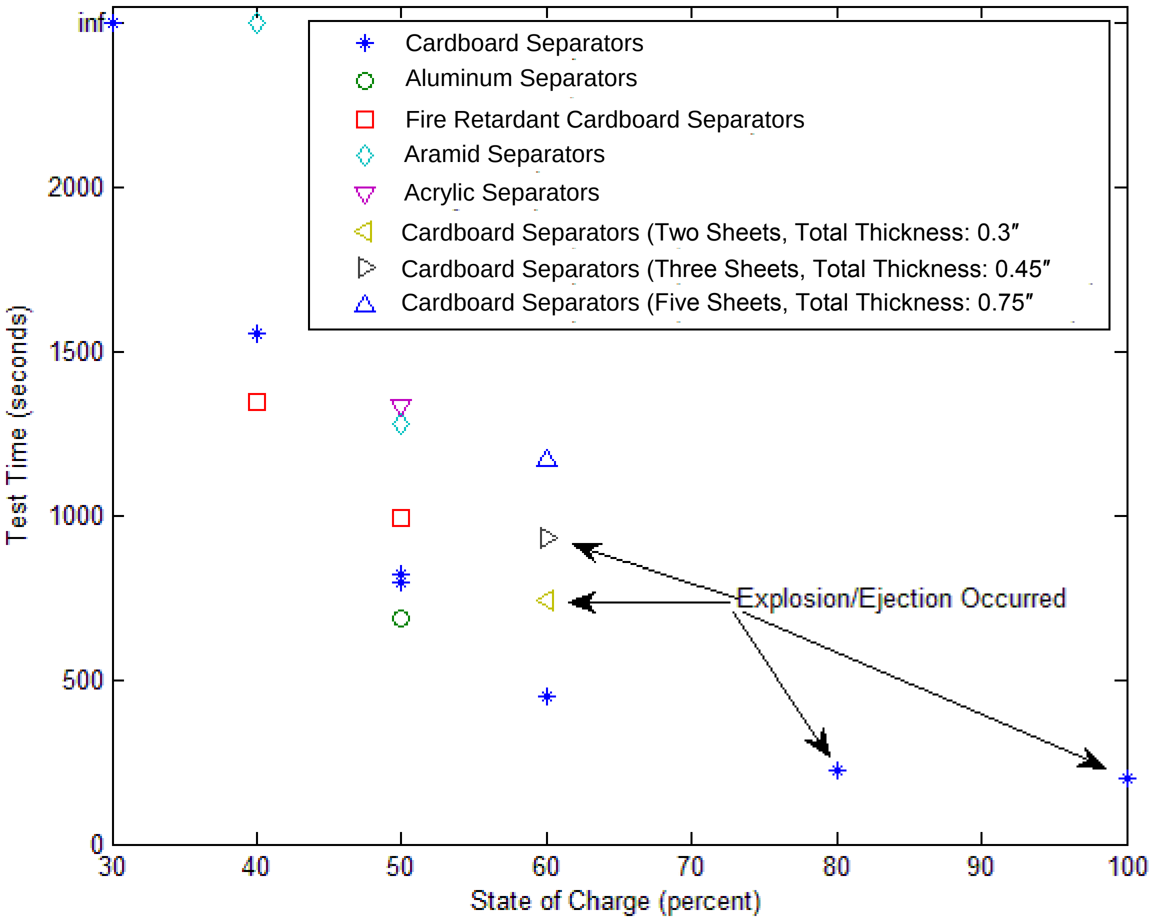
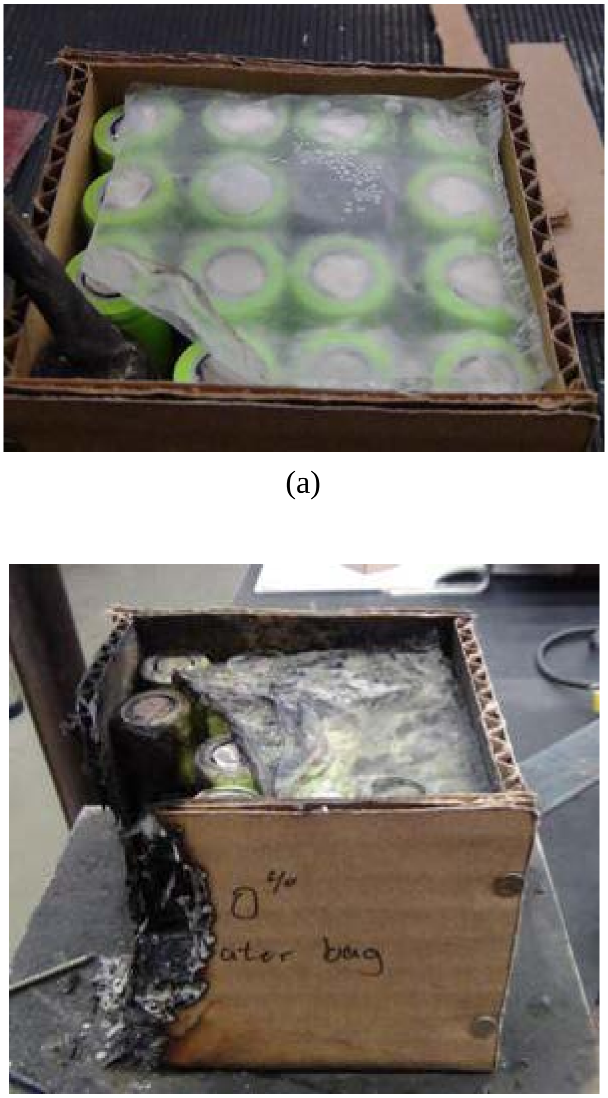


Figure 50. Test time for various configurations



(a)

(b)

Figure 51. Result of the test with water above the cells: (a) before and (b) after

The effectiveness of intumescent paint, which chars into an insulation layer when exposed to a flame, as a method to decrease the propagation of thermal runaway was also tested (see figure 52) [16]. During experiments with exposure to a direct flame, intumescent paint was minimally effective on organic materials and significantly effective on conductive materials. Intumescent paint was slightly effective when tested against a radiative heat source at a low heat flux; at higher heat fluxes, the intumescent paint was unable to deflect the heat away from the organic material. In the lithium-cell tests, the replacement of cardboard dividers with those that were coated with intumescent paint or aluminum foil only delayed adjacent batteries from being driven into thermal runaway (see figure 53) and did not prevent thermal runaway propagation.

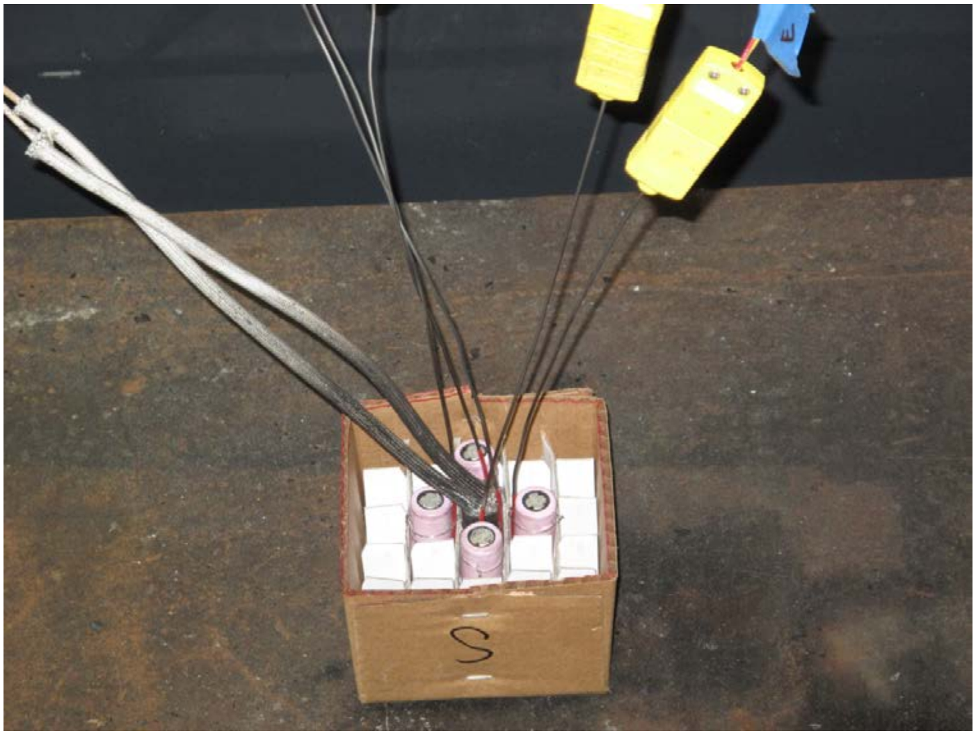


Figure 52. Setup of a lithium-ion cell fire source test

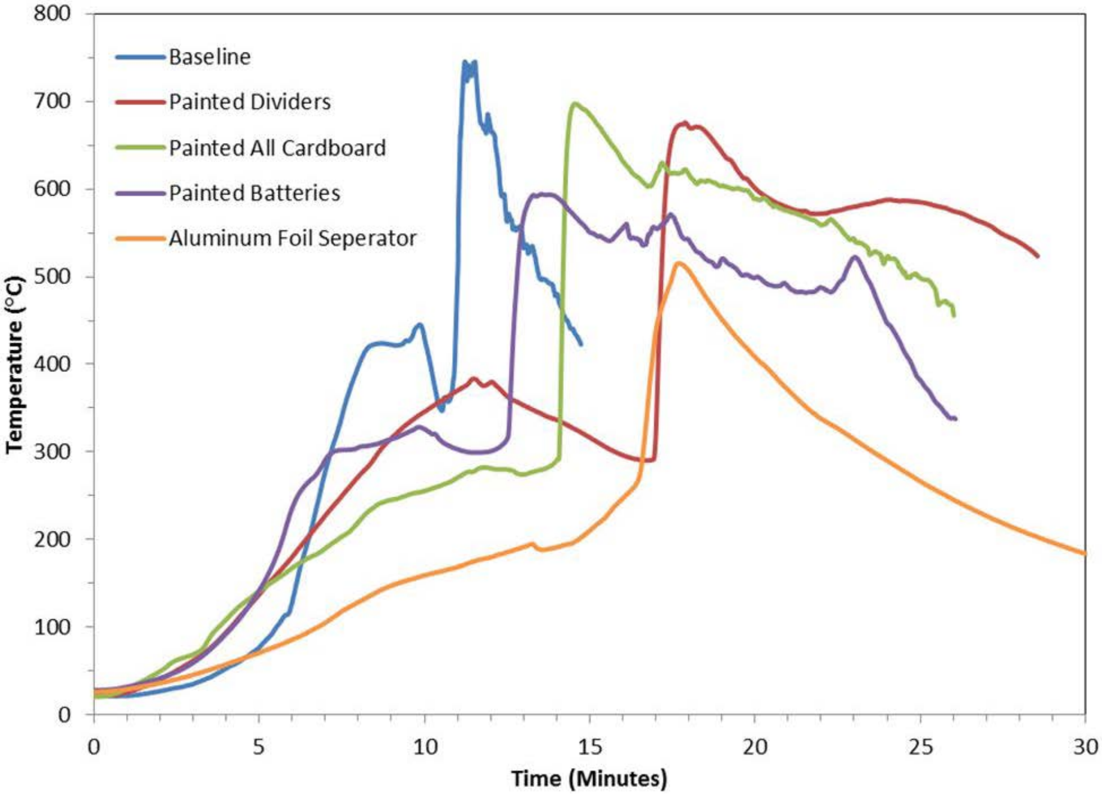


Figure 53. Timelines for first cell to enter thermal runaway

The improved insulation separation materials helped to reduce the time to initial thermal runaway. Conductive materials increased the onset time but decreased the propagation time once thermal runaway was initiated.

Of the package configurations that were tested, SOCs at 30% (depending on the cell type) and the setup with a pack of water above the cells were the only effective methods to stop propagation.

15. CONCLUSIONS

Lithium-ion cells are susceptible to a hazard called thermal runaway, which produces a rapid increase in internal temperature and pressure, resulting in the contents being expelled or a cell explosion. Cells in thermal runaway produce high temperatures and expel flammable electrolyte and flammable gases. The flammable gases include hydrocarbons and high concentrations of hydrogen.

A single cell failure that results in thermal runaway will transfer enough heat energy to adjacent cells to cause them to go into thermal runaway. Typical bulk cell packaging will not impede the propagation of thermal runaway from cell to cell, box to box, and package to package.

Halon 1301 will suppress vented electrolyte fires; however, Halon 1301 in concentrations currently available will not suppress vented gas explosions.

State of charge (SOC) has an effect on lithium-ion $LiCoO_2$ 18650 cell flammability. A SOC of 30% reduces the intensity of thermal runaway and stops thermal runaway propagation. SOC affects the volume of vent gas generated by a $LiCoO_2$ 18650 cell in thermal runaway. Higher charges yield greater volumes, and lower charges yield decreased volumes.

Fires involving shipments of large quantities of lithium-ion cells exhibit slowed rates of thermal runaway propagation in a Class E cargo compartment due to oxygen depletion. Fires involving shipments of large quantities of lithium-ion $LiCoO_2$ 18650 cells can be partially controlled in a Class C compartment. Open flames are suppressed, but thermal runaway propagation continues and gas explosions are possible.

Cell chemistry and form factor have an effect on flammability. Some chemistries are intrinsically safer than others; they have milder thermal runaway characteristics and reduced likelihood to propagate.

Aqueous fire extinguishing agents are more effective at stopping thermal runaway propagation than gaseous agents. Fire-containment covers are not effective in suppressing fires with large numbers of lithium-ion cells.

In the event of a thermal runaway, cells shipped in confined spaces such as fire-resistant containers or plastic wrapped pallets may trap vent gases and lead to explosive conditions.

Vent gases generated by a lithium-ion cell in thermal runaway contain flammable hydrocarbons and large amounts of hydrogen gas. The volume of vent gases is a strong function of SOC.

The normal Halon 1301 concentration used in Class C cargo compartments is insufficient to suppress an explosion caused by the ignition of lithium-ion vent gases.

A small number of lithium-ion 18650 cells can generate enough gas in thermal runaway that, when confined and ignited, can cause an overpressure in a Class C cargo compartment that will dislodge pressure-relief panels, jeopardizing the benefit of a fire suppression system by allowing for agent leakage and combustion products to spread throughout the aircraft.

Packaging improvements may mitigate some of the hazard in shipping lithium-ion cells.

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