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Passive Protection of Lithium Battery Shipments

February 2016

Final Report

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16. Abstract Changes in the technology and chemistry of voltaic cells have increased the energy density within the cells. The increased energy density and heightened consumer demand for lithium batteries have both contributed to an increased risk of fire and smoke incidents in transport aircraft. The objective of this study was to evaluate the effectiveness of various types of shipping materials and configurations to prevent or minimize the propagation of thermal runaway in lithium-ion battery shipments. Tests were performed in square cardboard boxes with a capacity of 16 18650-sized cells. A cartridge heater was placed on the outside corner of the cells to initiate thermal runaway, and a thermocouple was attached to each cell for temperature measurement. The state-of-charge (SOC) of the cells and divider material between each cell was varied. The effectiveness of a packet of water placed above the cells was also evaluated. Tests showed that thermal runaway propagated when the cells were at a charge level greater than 30% with typical battery package material. Insulative divider materials 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. The pack of water above the cells prevented thermal runaway propagation at a 50% SOC. Tests were performed to evaluate the effectiveness of intumescent paint as a method to decrease the propagation of thermal runaway. When exposed to a direct flame, intumescent paint was minimally effective on organic materials and significantly effective on aluminum foil. Intumescent paint was slightly effective when tested against a radiative heat source at a low heat flux, but at higher heat fluxes was unable to deflect the heat away from the organic material. In the tests with lithium batteries, the replacement of cardboard dividers with those coated with intumescent paint or aluminum foil only delayed adjacent batteries from being driven into thermal runaway and did not prevent propagation. Of the package configurations that were tested, SOC's at 30% and the setup with a pack of water above the cells were the only effective methods to stop propagation. Insulative separation materials helped to reduce the propagation risk, and conductive materials increased the onset time and decreased the propagation time once thermal runaway occurred.					
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LIST OF ACRONYMS

FAA	Federal Aviation Administration
PTC	Positive temperature coefficient
SOC	State-of-charge

EXECUTIVE SUMMARY

Changes in the technology and chemistry of voltaic cells have increased the energy density within the cells. The increased energy density and a heightened consumer demand for lithium batteries have both contributed to an increased risk of fire and smoke incidents in transport aircraft.

Tests were previously performed by the Federal Aviation Administration to demonstrate the effectiveness of various shipping configurations at containing a lithium battery fire initiated by a simulated single cell in thermal runaway. The configurations included an oxygen overpack box, a steel drum, and a decrease in cell packaging density in standard cardboard boxes. The tests demonstrated that the overpack box failed in most cases, 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, and the setup with decreased cell packaging density (half the cells removed) failed to prevent thermal runaway 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 battery shipments.

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. The state-of-charge (SOC) and material between each cell was varied. An additional test evaluated the effectiveness of a packet of water placed above the cells.

Tests showed that thermal runaway propagated at charge levels greater than 30% with typical battery package material. Insulative divider materials 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. The pack of water above the cells prevented thermal runaway propagation at a 50% SOC.

The effectiveness of intumescent paint as a method to decrease the propagation of thermal runaway was also tested. When exposed 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 battery 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 and did not prevent thermal runaway propagation.

The insulative separation materials helped to reduce the propagation risk. Conductive materials increased the onset time and decreased the propagation time once thermal runaway was initiated. Of the package configurations that were tested, SOCs at 30% and the setup with a pack of water above the cells were the only effective methods to stop propagation. Future tests are proposed for other cells and configurations.

1. INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Changes in the technology and chemistry of voltaic cells have increased energy density within the cells. The increased energy density and heightened consumer demand for lithium batteries have both contributed to an increased risk of fire and smoke incidents in transport aircraft. Since 1991, approximately 83 U.S. aviation incidents involving lithium metal or lithium-ion batteries have occurred [1]. Most of the incidents did not result in fatalities.

In 2011, an ASIANA Airlines cargo flight crashed near the coast of South Korea after declaring an emergency due to a cargo fire. It was suspected that lithium batteries were involved in the fire [2]. Shortly after an indication to the crew of a fire on the main deck, the aircraft flight controls and systems began failing [3].

In 2010, a UPS flight departed from Dubai and, shortly after takeoff, reported a main deck smoke detector alarm. After a series of events within the aircraft (including the search for an oxygen supply by the pilot and changes in the autopilot status) and radio messages, the aircraft crashed. Wreckage from this crash is shown in figure 1. Later investigations revealed that the likely cause of the incident was heat from an uncontrolled main deck cargo fire, which caused slack in the flight control cables, and smoke from the fire decreased visibility in the cockpit. The likely ignition source of the fire was thermal runaway of lithium ion or lithium metal batteries. [4].



Figure 1. Wreckage from Dubai flight accident [5]

In February 2006, a UPS DC-8 experienced an inflight main deck cargo fire. The aircraft safely landed and the crew evacuated with minimal injuries. The fire could not be extinguished and led to the destruction of the aircraft. The cause of the fire could not be determined. Shipments of lithium batteries were present on the main deck, and this incident encouraged further research into battery fires.



Figure 2. Fire in a DC-8 Freighter [6]

There have been many lithium battery fire incidents unrelated to the aviation industry that could also occur on an aircraft, such as an incident that occurred in 2011 with a lithium-ion-powered Chevy Volt that created a fire and destroyed several other vehicles after it was crash-tested [7].

A series of tests were performed previously at the Federal Aviation Administration (FAA) to better understand the effect the variation of cell packaging had on thermal runaway propagation and containment. The tests addressed three questions:

1. Would a decrease in the cell packaging density by 50% prevent propagation?
2. Would an oxygen over-pack box used to ship oxygen generators be suitable to contain a lithium battery fire?
3. Would a 30-gallon steel drum contain a relatively small quantity of cells in thermal runaway?

In the first test, thermal runaway continued to propagate when every other cell was removed from a box with a capacity of 100 18650-sized lithium-ion cells. All cells were consumed in that test.

In the second series of tests, 100 18650-sized lithium-ion cells were driven into thermal runaway by a cartridge heater in an oxygen over-pack box. In the first test, the packaging tape failed and the box opened. In the second test the box was fastened with wire, which contained the thermal runaway event. This test was repeated with 100 123a-sized lithium metal cells in an oxygen over-pack box. The flammable vapors ignited as they exited the box and caused the outer cardboard packaging to catch fire. In the last test a flame arrestor was attached to the box, which prevented flaming of the vented gases.

In the initial test with the 30-gallon drum, six 123a-sized cells were driven into thermal runaway, and the vented gases caused an explosion, which launched the drum lid approximately 75 feet into the air. The test was repeated three times using 6, 18, and 99 cells with a flame arrester attached. Thermal runaway was contained in all three tests.

1.2 LITHIUM AND LITHIUM-ION CELL OVERVIEW

Voltaic cells are often called batteries; however, the strict definition of a battery is two or more voltaic cells in series. In this report, the term battery will be used interchangeably with voltaic cell.

Lithium metal batteries, also called primary lithium batteries, are discharged once and then discarded. Lithium-ion and lithium-ion-pouch (also commonly called lithium-ion-polymer) batteries are called secondary batteries and have the capability of being recharged after discharge.

1.2.1 Geometries

Lithium batteries exist in many geometries, each of which is determined by the end-use application. A larger device, such as a power tool, would require a larger battery than a wristwatch. Many batteries are sold and transported in plastic molds, such as an electric drill battery, or may be built-in or pre-installed in products. Fire tests were performed with shipping pallets of lithium-ion power tool batteries in plastic molds by FM Global, which resulted in a large and difficult to control fire after approximately two and a half minutes [8]. The tests showed that cells electrically connected in a pack can present a danger if thermal runaway occurs during shipment.

A common lithium-ion geometry used for many industrial purposes is a cylindrical cell called an 18650, for which 18 represents the approximate diameter of 18mm and 65 represents the approximate length of 65mm. Because of their relatively small size, thousands of these cells may be on a single shipping pallet.

A common cylindrical lithium metal cell is the 3 volt 123a, which has a diameter of 16.5mm and a length of 34.3mm. As with the 18650, thousands of these may fit onto a shipping pallet.

Lithium-ion-pouch cells exist in an assortment of geometries; the shape of these batteries is largely determined by the desired application. They are similar to the lithium-ion batteries except for their geometry and outer case material. A lithium-ion cell is generally cylindrical and has a hard metal outer case. A lithium-ion-pouch cell may exist in a variety of shapes and generally has a thinner outer case.

Lithium-polymer cells (often times confused with lithium-ion-pouch) are similar to lithium-ion cells, but use a polymer for the electrolyte. This type of cell is still under development and, therefore, is rarely shipped in bulk.

Lithium metal, lithium-ion, and lithium-ion-pouch batteries are made with two electrodes, an electrolyte, and a plastic separator between the two electrodes.

In a lithium-ion cell, the negative electrode is generally made of graphite, the positive electrode is generally made of a metal oxide, and the plastic separator is generally made of polyethylene and/or polypropylene [9]. The electrolyte is a salt, such as:

- Lithium hexafluorophosphate
- Lithium tetrafluoroborate
- Lithium perchlorate
- Lithium hexafluoroarsenate monohydrate [10]
- Lithium triflate [10]

The electrolyte salt is dissolved in an organic solvent, such as:

- Ethylene carbonate
- Diethyl carbonate
- Dimethyl carbonate
- Propylene carbonate
- Dimethoxyethane
- Gamma-butyrolactone

The contents of a lithium metal battery are similar to the contents of a lithium-ion battery except for the anode material. They have an anode that is typically made of lithium and a cathode that is typically made of a metal oxide such as manganese dioxide. The cells have separators that are typically made of polypropylene and an electrolyte that is typically a lithium salt dissolved in an organic solvent.

1.2.2 Additional Battery Components

The design features that make a battery safer and increase its usable life varies among manufacturers. Many manufacturers include circuitry in each cell to prevent over-discharge and over-charge. Many also include a thin piece of material at the positive terminal called a positive temperature coefficient (PTC) device. If the current draw from the battery gets too high, the temperature of the PTC device increases, which increases its resistance and limits the draw of power from the cell. However, these devices may not make the battery safer during transport and may add a relatively small amount of combustion heat.

The plastic separator within each cell may be designed so that if an internal short exists because of an impurity within the layers of coiled material, it can melt and isolate the adjacent anode and cathode materials in that portion of the cell. This technology primarily affects the safety of a cell that is being discharged or charged and, to a lesser degree, helps with the safety of the cell during shipment. The plastic will also contribute to the heat of combustion of the cell.

Lithium-ion cells generally have a burst disk (also called safety vent) built into their outer metal shells that ruptures if the internal pressure, caused by a temperature increase, exceeds a certain threshold. The disk decreases the likelihood of a cell explosion or ejection of the cell. Finally,

many cells contain a metal tube in the center that allows pressure to equalize and decreases the probability of an explosion. Observations from experiments showed that a cell explosion may prevent or reduce the propagation of thermal runaway by moving hot cell materials away from adjacent cells that have not yet gone into thermal runaway. Figure 3 shows a typical cell diagram with various components.

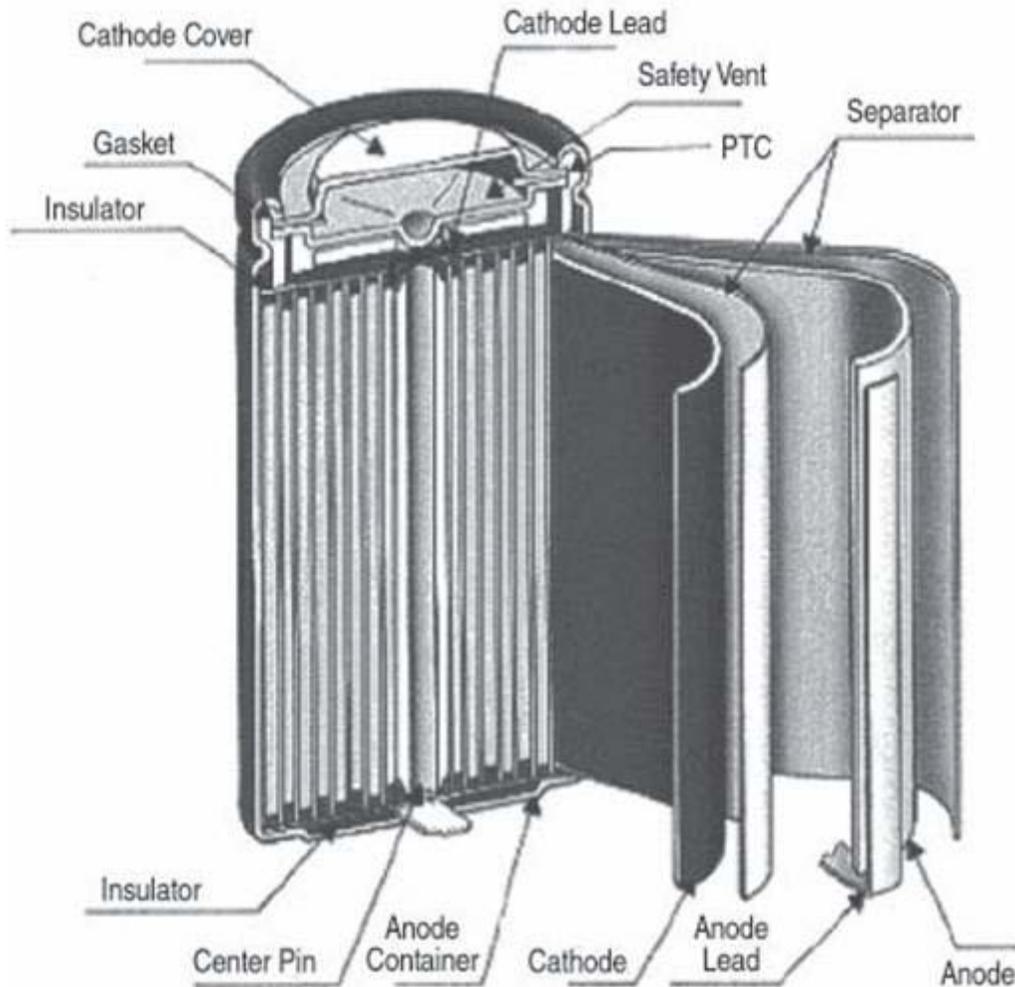


Figure 3. Typical lithium-ion cell [11]

1.3 EXOTHERMIC REACTIONS

Thermal runaway is the term that has been used to describe a cell that self-heats faster than it cools until it reaches a failure temperature. At temperatures in the range of 70°C–90°C, the reaction between the anode and electrolyte begins to rapidly accelerate; in the temperature range of approximately 130°C–250°C, the reaction between the cathode and electrolyte begins to rapidly accelerate [9].

Thermal runaway of a typical cell is a series of chemical reactions and mechanical events. As the temperature increases, chemical reactions begin to take place and the burst disk ruptures. At

higher temperatures, the plastic separator that divides the anode and cathode melts and causes the cell to short circuit internally. The stored electrical energy is converted to thermal energy because of resistance heating and accelerated reactions. With the burst disk already ruptured, the melting of the separator and the increase in the reaction rate causes the electrolyte to jet from the cell. It is frequently hot enough to auto-ignite as it escapes the cell but may also cool below the auto-ignition temperature as it mixes with ambient air. These reactions are what cause the cell to reach unsafe temperatures and compromise battery safety. The graphite electrode, the plastic separator, and the electrolyte solution may be considered flammable at typical battery fire temperatures.

Lithium-ion cells have three major sources of heat release: (1) the heat of combustion of the electrolyte solution, (2) the stored electrical energy that becomes available when the cell is charged, and (3) the energy from chemical reactions within the cell. Table 1 from reference 12 shows approximations for the amount of energy released from each of these heat release components for an 18650 cell with a capacity of 10 Wh. The electrical energy contribution to the heat release of the cell is proportional to the state-of-charge (SOC) and capacity of the cell. There may be additional heat release from the oxidation of battery components, such as the graphite electrode and the plastic separator, but this may be considered small in comparison to the previous three sources.

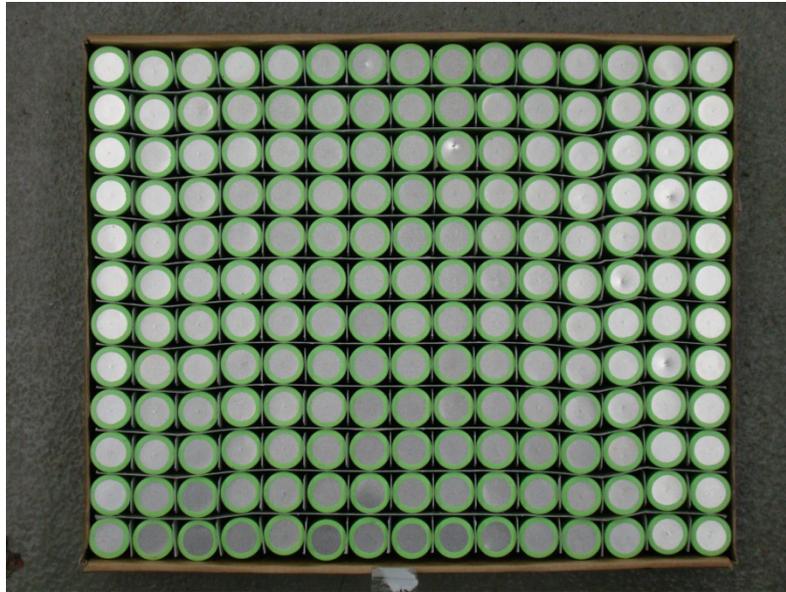
Table 1. Heat release contributions in an 18650 cell [12]

Internal Chemical Reactions	Process	Temperature Range (°C)	Energy Release in a 10Wh 18650 Cell
	Anode decomposition and reaction with electrolyte	80–120 150–300	~11 kJ
	Cathode decomposition and reaction with electrolyte	150–300	~23 kJ
	Self-reaction of salt with solvent	250–400	~4 kJ
	Complete combustion of solvent	Auto-ignition temperature ~450	~110 kJ
	Release of stored electrical energy	~150	≤36 kJ

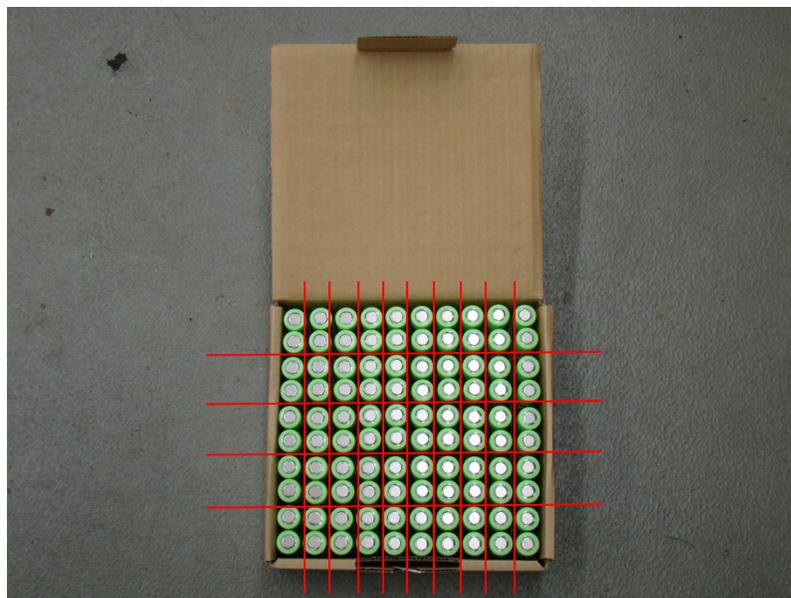
1.4 CELL PACKAGING

1.4.1 18650 Lithium-Ion Cells

18650 cells, when shipped in boxes of 100, are generally separated by 1/16" thick cardboard. Some manufacturers ship their cells in pairs, as shown in figure 4(b), and others separate each individual cell, as shown in figure 4(a).



(a)

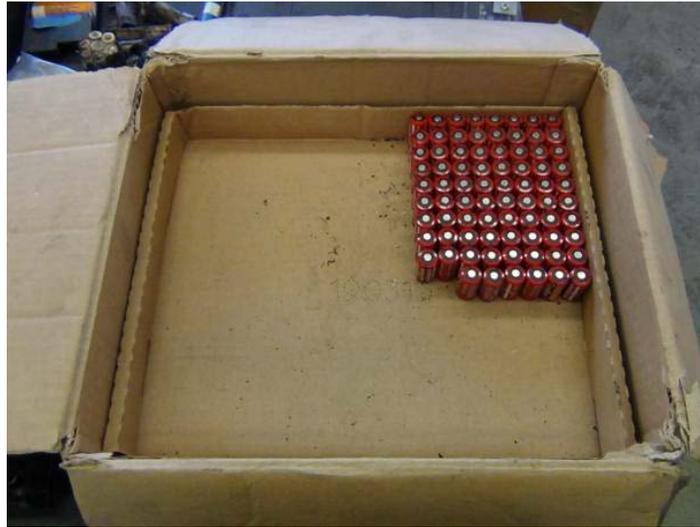


(b)

Figure 4. Lithium-ion 18650 cell packages: (a) 180 cell package and (b) 100 cell package

1.4.2 Lithium Metal Cells

Lithium primary cells are shipped in various configurations. A common configuration is for all of the cells to be grouped together without any separator, as shown in figure 5(a). The cells may also be shipped with several of these groups in a single larger box, as shown in figure 5(b). In both configurations, there are several cells in direct contact with each other.



(a)



(b)

Figure 5. The (a) larger and (b) smaller lithium metal cell packages

1.4.3 Packaging Regulations

International rules require certain quantities and capacities of cells to be transported as dangerous goods. However, a common practice is to ship undeclared cells in an overpack. The overpack consists of many small boxes, each packed with no more than eight cells per box, contained in a larger box. Recently, the ICAO DGP recommended limitations on the quantities of lithium batteries that could be shipped undeclared (i.e., stopping the practice of overpacking).

1.4.4 Damage of Cell Packaging

Cells may become damaged when transported, often when they are moved with machinery such as fork lifts and carts. Once the cells are damaged, there may not be enough time before they are stowed away in an aircraft for a worker to notice smoke and heat emission from the box. If certain conditions exist, such as unsafe packaging or excessive SOC, the entire shipment could go into thermal runaway and destroy the aircraft, possibly during flight. Figure 6 shows an example of a damaged battery shipment that the FAA received. The cells in the image were shipped at a relatively low SOC, which may be the reason why a fire/smoke event did not occur.



Figure 6. Damaged battery packaging as received at the FAA

1.5 INTUMESCENT PAINT

Because of its inherent qualities as a fire retardant, intumescent paint was evaluated as a passive protection approach against lithium battery fires. An intumescent coating swells when heated by a flame and acts as a thermal insulation barrier that protects the underlying material against rapid increases in temperature. Intumescent coatings are composed of three components that are bound together by a binder. The three components most commonly used are an acid source (normally ammonium polyphosphate or a mineral acid), a carbon source (to form chars), and a blowing agent. The formation of the carbonaceous char is a complex process. First, the acid source breaks down to form a mineral acid, then it dehydrates the carbonization source to yield the carbon char. The blowing agent then decomposes to generate gaseous products that cause the char to swell and create an insulating multi-cellular protective layer [13].

1.6 OBJECTIVE

The objective of this report was to evaluate the effectiveness of various types of shipping materials and configurations to prevent or minimize the propagation of thermal runaway in lithium-ion battery shipments.

2. EXPERIMENTAL SETUP

The experimental setup was divided into two parts: Section 2.1 describes the setup for the 4 x 4 battery box configurations, and section 2.2 describes the various test setups for the experiments with intumescent paint.

2.1 4 x 4 BATTERY BOXES—TEST SETUP

Each test had cells placed in a 4 x 4 array, as shown in figure 7. One of the 16 cell positions was occupied by a heater and another by an aluminum dummy cell. 18650-sized cells filled the remaining 14 slots. The array was enclosed in a cardboard box without a lid and with cell separators between each cell. Each cell and box component had a 1/16th" type-K ungrounded thermocouple attached with nichrome wire. The boxes were placed on a steel holder and the tests were conducted in a 4' x 4' x 4' steel box with a polycarbonate door for viewing, as shown in figure 8.

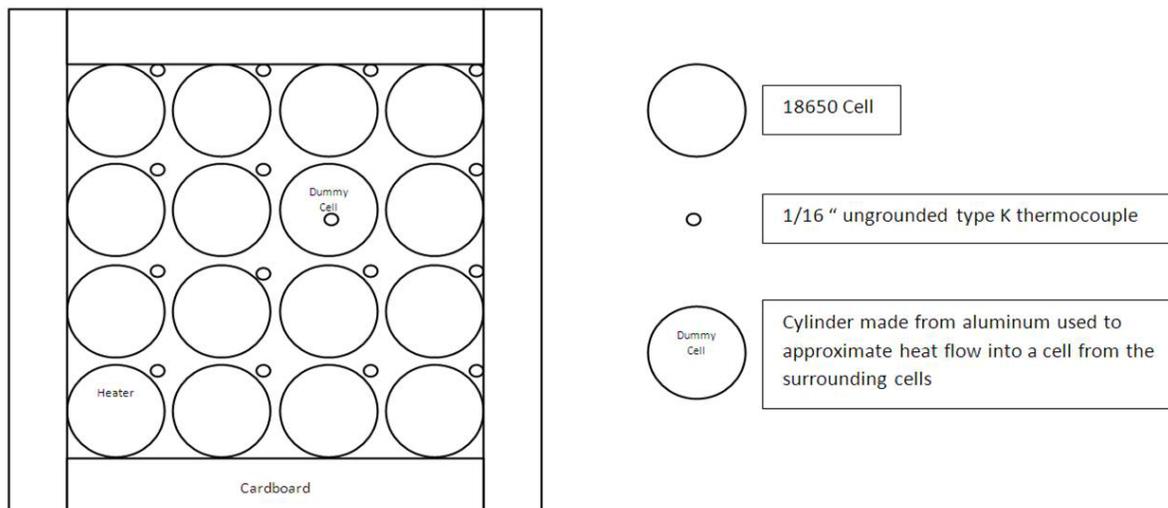


Figure 7. Layout of the 18650 battery box (the separators between each cell are absent from this figure for simplicity)



Figure 8. Test chamber and setup

Tenergy 18650-sized cells with a 2600-mAh rated capacity and a 3.7-volt rated potential were used for these tests. They were brought to various SOCs with an Arbin battery charge and discharge system. The safety technology present within these cells included a PTC material, a burst disk, a plastic shutdown separator, and a pressure relief tube to help prevent explosion.

The cartridge heater, shown in figure 9, was the same size as the 18650 cells and had a rated output of 100 watts.

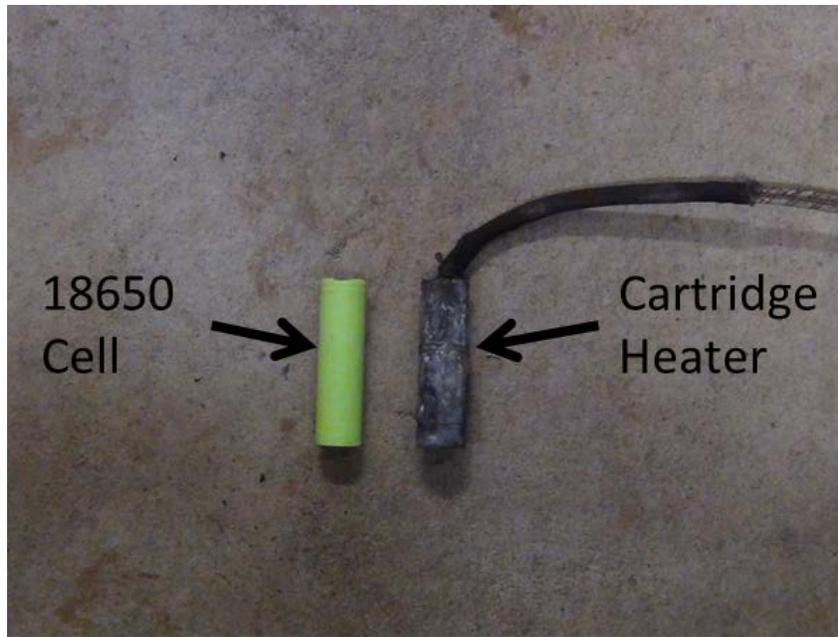


Figure 9. 100-watt cartridge heater and 18650 cell

The cardboard that was used to make the outer box material was approximately 0.15" thick and corrugated. All of the boxes were made from the same source of cardboard. They were held together with annular ring-shank nails.

The various cell packaging dividers that were used in the tests were acrylic, aramid gasket material, cardboard (as shipped), cardboard (as shipped) treated with Flamex fire retardant spray, type 5052 aluminum, two sheets of 0.15" thick cardboard (0.3" total thickness), three sheets of 0.15" thick cardboard (0.45" total thickness), and five sheets of 0.15" thick cardboard (0.75" total thickness). The materials were 1/16" thick and were cut to fit within the boxes. A typical divider is shown in figure 10. The test with a water pack contained 35 grams of water in a plastic bag that was placed on top of the cells to determine the potential for stopping thermal runaway propagation.

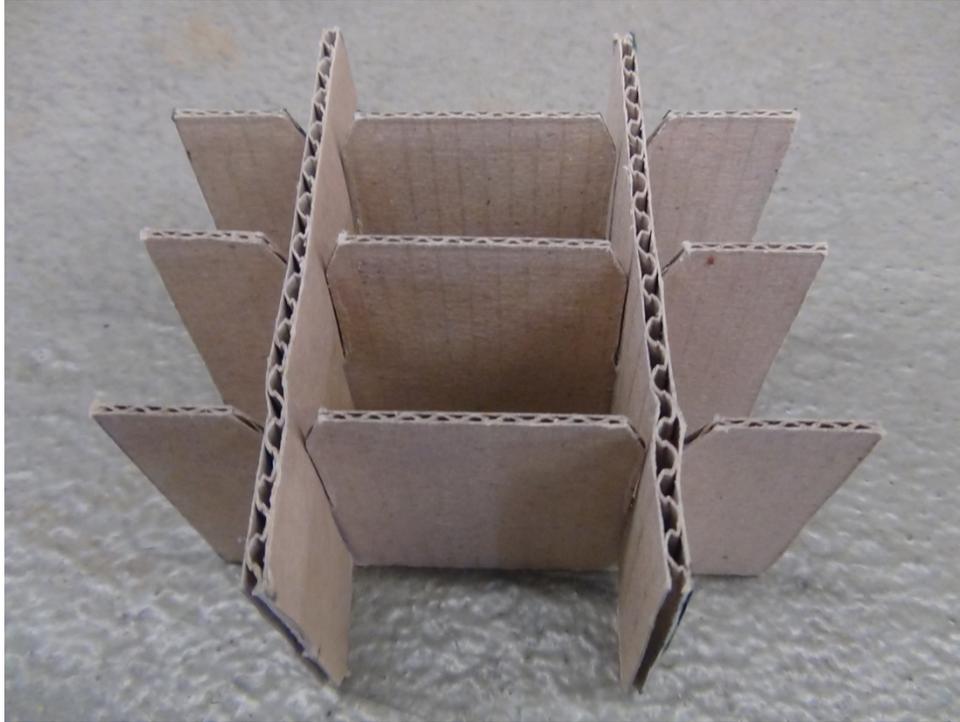


Figure 10. Cardboard cell dividers

Temperature data were collected with PDAQ 56 collection hardware and software created on site. The data collection interval was approximately every second. After each test, the data were processed in MATLAB[®] and the following test parameters were identified: the maximum cell temperature, the length of the test, and the mean maximum temperature of each cell.

The maximum cell temperature was the greatest temperature achieved by a particular cell. The length of the test was the time from the first rapid increase in temperature ($dT/dt \gg 1$) to the last temperature peak. Finally, the mean maximum temperature was the average of the temperature peaks of the 14 cells.

2.2 INTUMESCENT PAINT—TEST SETUP

Three types of tests were conducted with intumescent paint. In the first setup, samples were exposed to a propane burner. In the second setup, samples were exposed to a radiant heat source. In the third setup, packaging with intumescent paint-coated dividers was evaluated against lithium batteries driven into thermal runaway via a cartridge heater.

2.2.1 Propane Burner Test

To examine the effectiveness of intumescent paint when exposed directly to a flame source, 5" x 5" samples were placed 1" in front of an open flame, as shown in figure 11. The samples were coated with a water-based acrylic paint via a paintbrush. The paint was allowed to dry before the next coat was applied. The samples were then cured in an oven at 200°F for 30 minutes. The aluminum samples were 1/8" thick and the cardboard samples were made out of

standard corrugated sheets from boxes commonly used in the shipping industry. A propane burner was used as the flame source. The samples were placed so that the flame impinged directly at the center of the samples. The samples were unpainted or otherwise coated with varying layers of intumescent paint. They were then exposed to the flame until it burnt through the sample or for a maximum of 5 minutes.

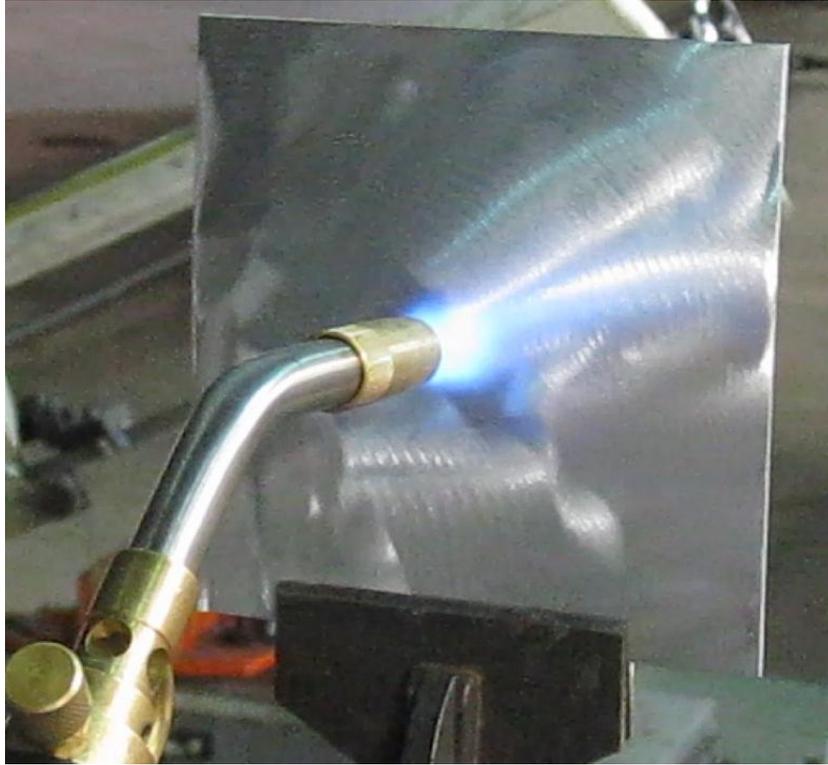


Figure 11. Setup of a propane burner test

Another set of experiments was conducted with a 10" x 10" cardboard sample. The samples were covered with intumescent paint and exposed to the open flame. The number of coats of paint on the sample was varied from zero to eight coats at two-coat intervals.

2.2.2 Radiant Heat Source Test

To examine the effectiveness of intumescent paint when exposed to a source of radiant heat, 5" x 5" samples were placed 2" underneath a cone heater, as shown in figure 12. The samples were coated with a water-based acrylic paint via a paintbrush. The paint was allowed to dry before the next coat could be applied. The samples were then cured in an oven at 200°F for 30 minutes. A thermocouple was placed above the sample to determine the approximate temperature at which the cardboard sample ignited. The radiant heater was adjusted to specific heat flux settings via a voltage regulator. The sample was placed under the heater 5 minutes after the heater was adjusted to the desired heat flux setting. The samples were unpainted or coated with varying layers of intumescent paint and were exposed to the flame until it burnt through the sample or for a maximum of 5 minutes.



Figure 12. Setup of a radiant heat source test

2.2.3 Lithium Battery Fire Source

To examine the effectiveness of the intumescent paint when exposed to a lithium battery fire, a test configuration was constructed, as shown in figure 13. It consisted of a corrugated cardboard box without a top and dividers made out of aluminum, cardboard, or cardboard coated with intumescent paint placed inside the box to separate the cells. A 100-watt cartridge heater was placed in the center of the box and surrounded by four lithium-ion 18650 cells. Thermocouples were attached to the cartridge heater and the cells. The objective of this test was to get a cell to achieve thermal runaway via the cartridge heater and observe the effectiveness of the intumescent paint.

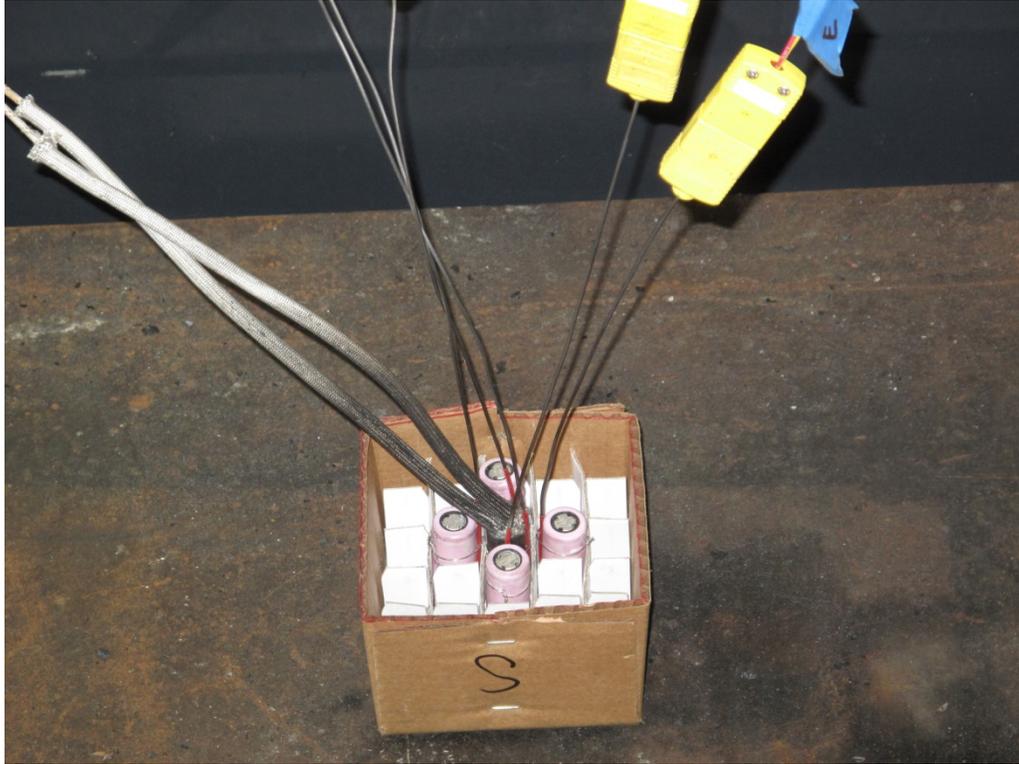


Figure 13. Setup of a lithium-ion battery fire source test

3. EXPERIMENTS

The experiments were divided into two parts: Section 3.1 describes the tests involving the 4 x 4 battery boxes, and section 3.2 describes the tests involving intumescent paint.

3.1 4 X 4 Battery Boxes

The parameters that were varied throughout the tests were the SOC of each cell, the type of material separating each cell, the thickness of the cardboard between the cells, and the effect of a water pack on the top of the cells. The tests performed are shown as the shaded regions in table 2. The variation of the separation materials altered the heat transfer between adjacent cells. The bag of water above the cells melted and released the water content when the first cell experienced thermal runaway and absorbed heat by internal energy change and phase change of the water.

Table 2. Tests performed

SOC	Cardboard Separators (as shipped)	Aluminum Separators	Fire Retardant Cardboard	Water Pack Above the Cells	Acrylic	Cardboard 0.3" thick	Cardboard 0.45" thick	Cardboard 0.75" thick
30%								
40%								
50%	x2							
60%								
70%								
80%								
90%								
100%								

3.1.1 Procedure: 4 x 4 Battery Box Tests

The battery boxes were assembled with cells each having an attached thermocouple. The assembly was then placed into the 64 ft³ steel box. The video camera, data collection software, and cartridge heater were then turned on. The amount of time that it took for visible smoke to be observed was recorded. Once a cell reached the temperature at which the internal plastic cell separator melted and the electrolyte solution was ejected (indicating that the first cell experienced thermal runaway), the heater was turned off. Other events that were recorded were fire, explosion, and the temperature for the initial pressure relief venting. The temperature history of a typical test is shown in figure 14.

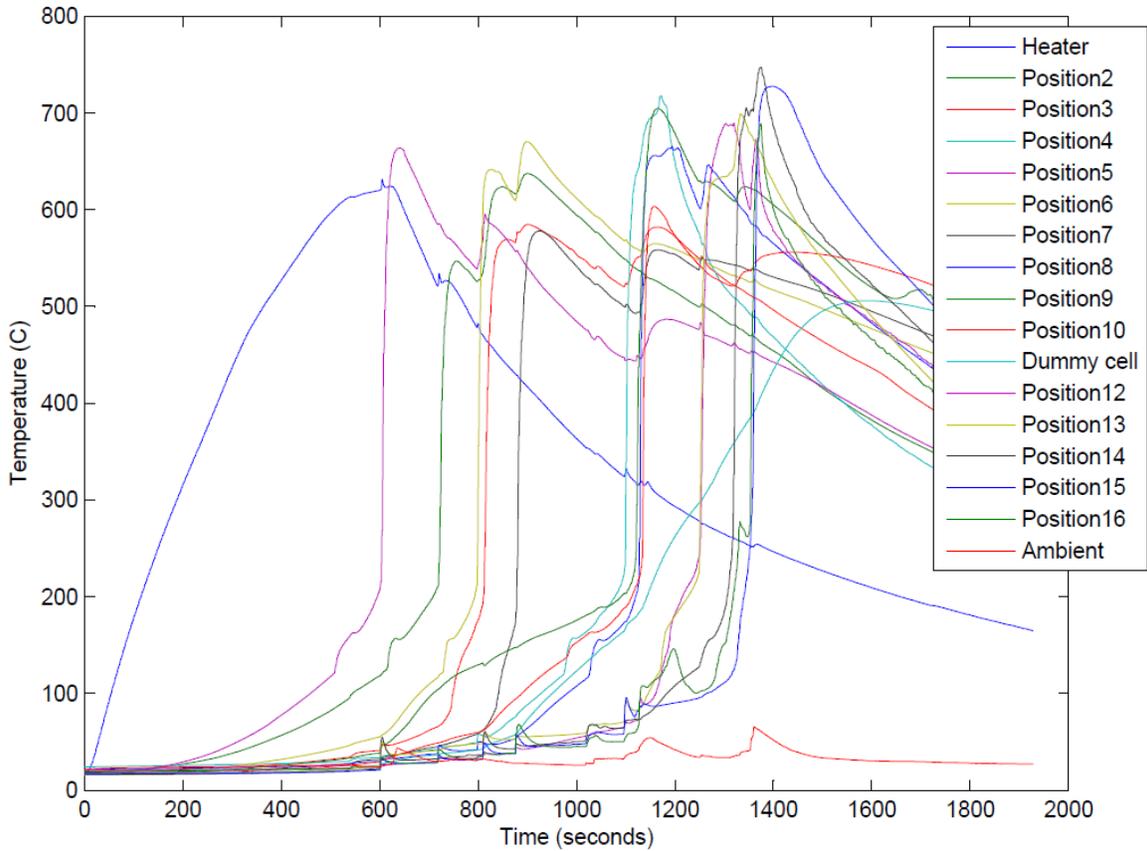


Figure 14. Typical 4 x 4 battery box test (50% SOC)

3.1.2 Variation of Parameters: 4 x 4 Battery Box Tests

The two main parameters that were varied were the package separation material and the SOC of the cells, as shown in table 2.

A pouch of water was used in a test at 50% SOC (1300 mAh) to absorb heat and potentially stop the propagation of thermal runaway. The pouch was placed on the cells so that the plastic was not in contact with the heater.

For another test, the cardboard box material and separator material were treated with Flamex flame-retardant spray. This test was intended to show how much the fire from the cardboard contributed to propagation of thermal runaway of the cells.

3.1.3 Discussion of Results: 4 x 4 Battery Box Tests

The maximum of the individual cell temperatures achieved for each test with the various cell divider materials as a function of SOC are shown in figure 15, and the average of the peak temperatures of the cells are shown in figure 16. The test times are shown in figure 17. Cells exploded in the 100% test, 80% test, and 60% test. Fire was observed in all of the tests except for

the 40% SOC test with fire-retardant cardboard. The pressure relief disk typically burst at a case temperature of 160°C, and the cells' internal polyethylene separator generally melted at a case temperature of approximately 190°C. Smoke was usually observed approximately 4 minutes after the heater was activated.

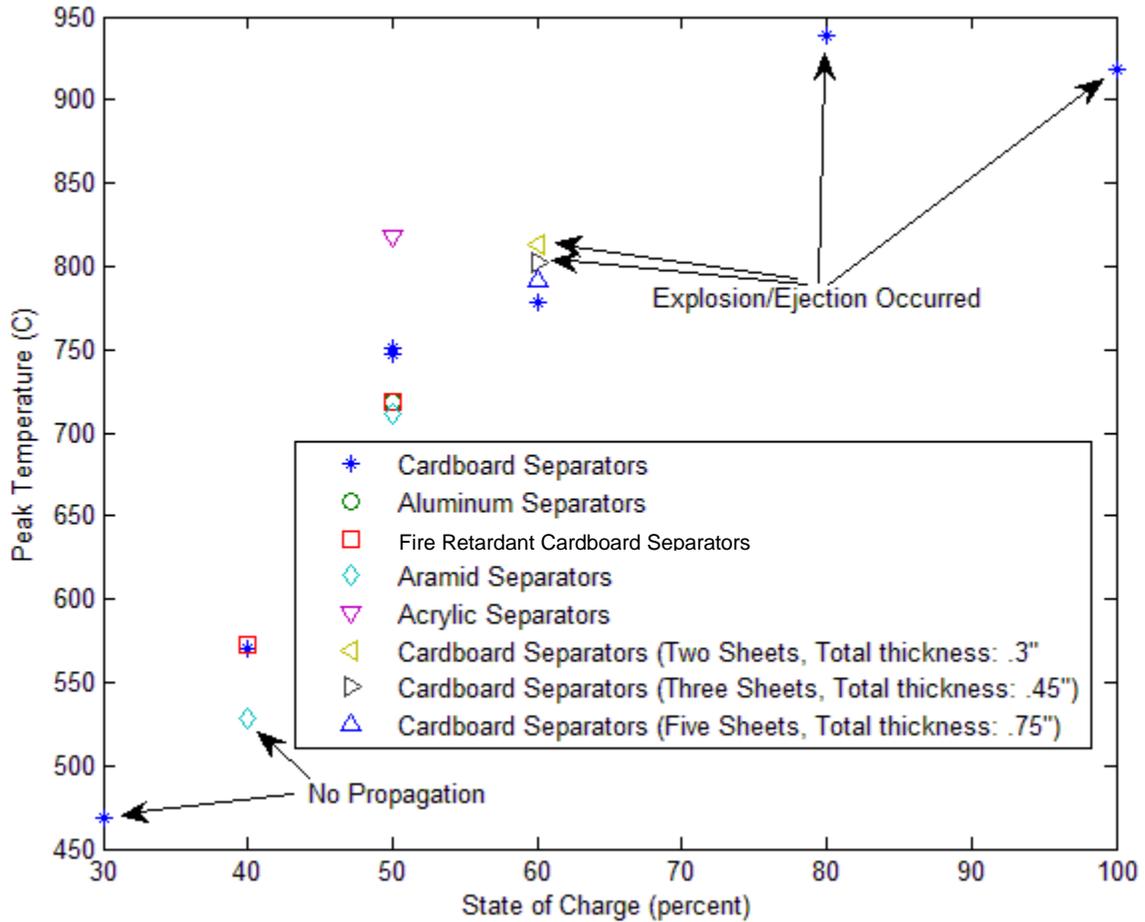


Figure 15. Peak temperatures during 4 x 4 battery box tests

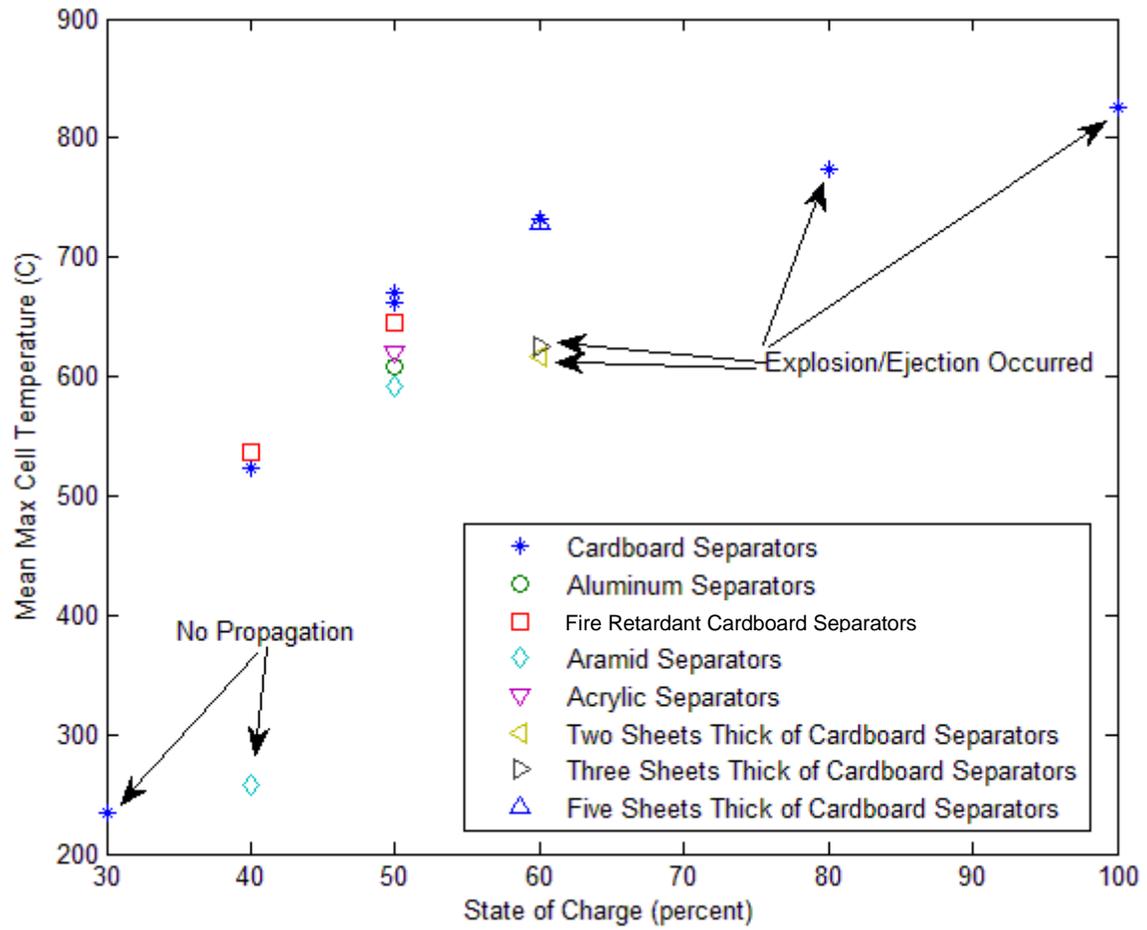


Figure 16. Average of the maximum temperatures of the cells in the 4 x 4 battery box tests

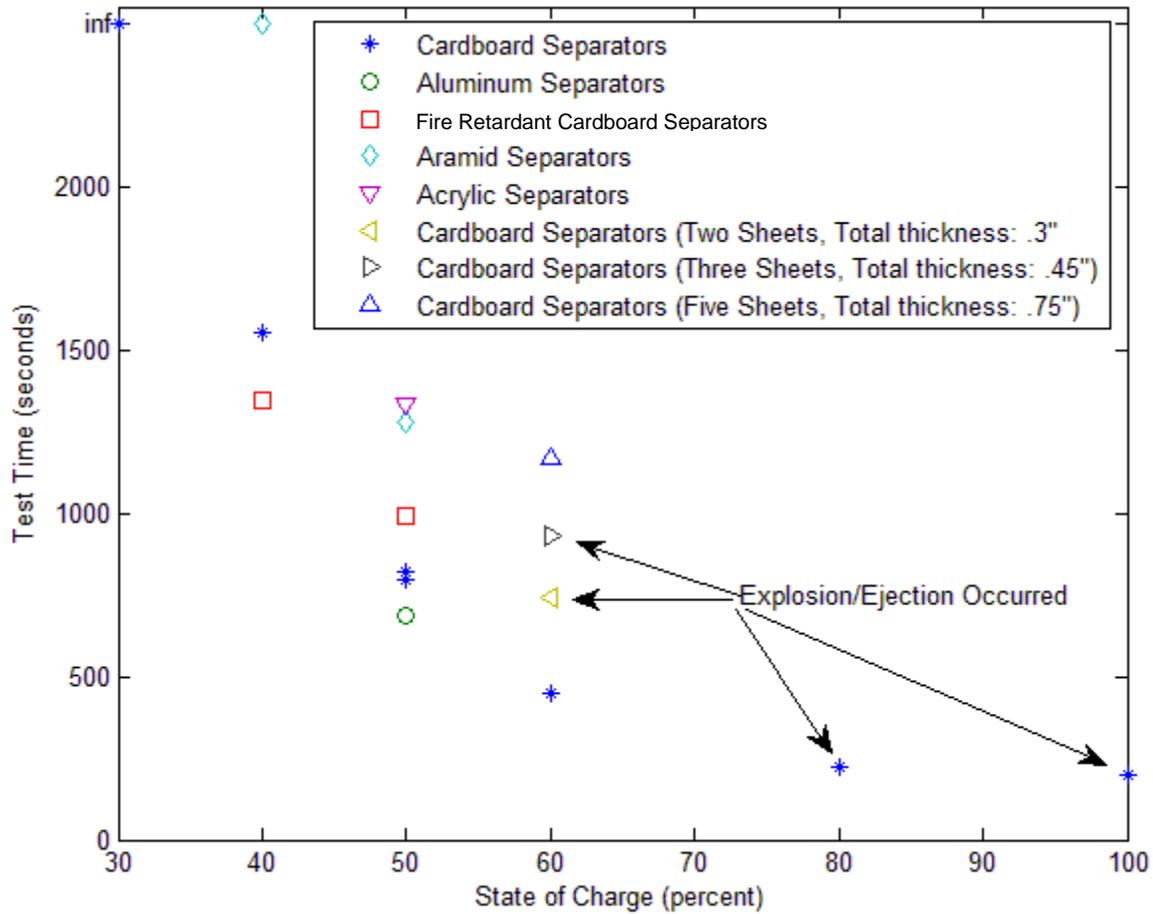


Figure 17. Test time for various configurations of the 4 x 4 battery box tests

The two sources that contributed the greatest thermal energy were the internal short circuit of the cells and the burning of the electrolyte solution. The internal short circuit had the greatest effect on the adjacent cell temperature. When the cells vented, the electrolyte would eject and sometimes ignite. Though the electrolyte solution had the potential to contribute more heat to the cell temperature as it burned, most of that heat was dissipated to the surrounding air.

As the test time decreased during tests with higher SOC, the power released by the cells during a test increased. The insulative materials, such as plastic, aramid, and extra thick cardboard, allowed less heat transfer than the standard cardboard separators, causing the first cell to experience thermal runaway earlier, but conversely showed a more prolonged propagation time. The tests showed that the amount of time necessary for a package to burn decreased with an exponential trend as SOC increased and, as the SOC decreased to 30% or 780 mAh, the thermal energy caused by thermal runaway was insufficient to sustain propagation. The amount of time required for the first cell to vent is shown in table 3 and was a function of the conductivity of the divider material.

Table 3. Time to vent of first cell for various configurations

Test	Time for first cell to vent from melting of its internal separator (seconds)
Cardboard, Average of Tests	616
Aluminum, 50%	1047
Aramid, Average of Tests	681
Acrylic, 50%	689
Pouch of Water Above Cells, 50%	2147

The results of the water-pouch test did not have thermocouple readings. Figure 18 shows before and after images of the battery box. The pouch material melted during the test and the water prevented cell propagation. Additionally, the time required for the first cell to vent was three and a half times more than for the similar configuration without water.



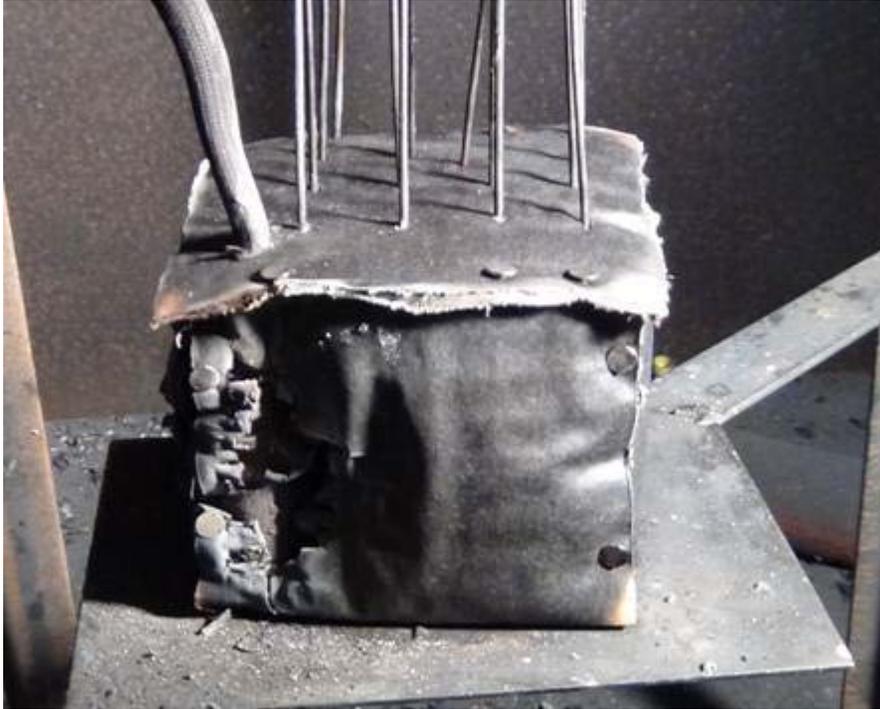
(a)



(b)

Figure 18. Result of the test with water above the cells: (a) before and (b) after

Images for the results of tests with cardboard that was treated with Flamex are shown in figure 19 for 40% and 50% SOCs. Figures 20(a) and (b) show post-test images of fire retardant cardboard and untreated cardboard, respectively, from 50% SOC tests.

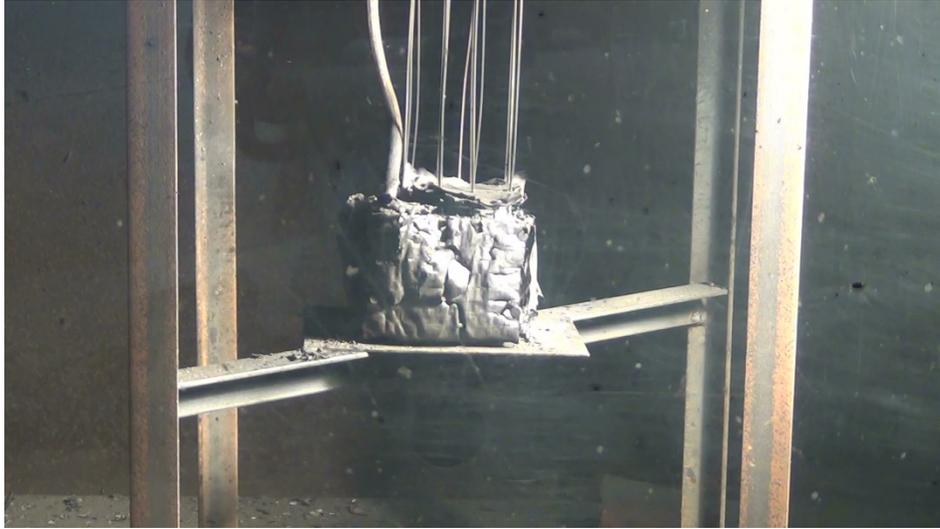


(a)

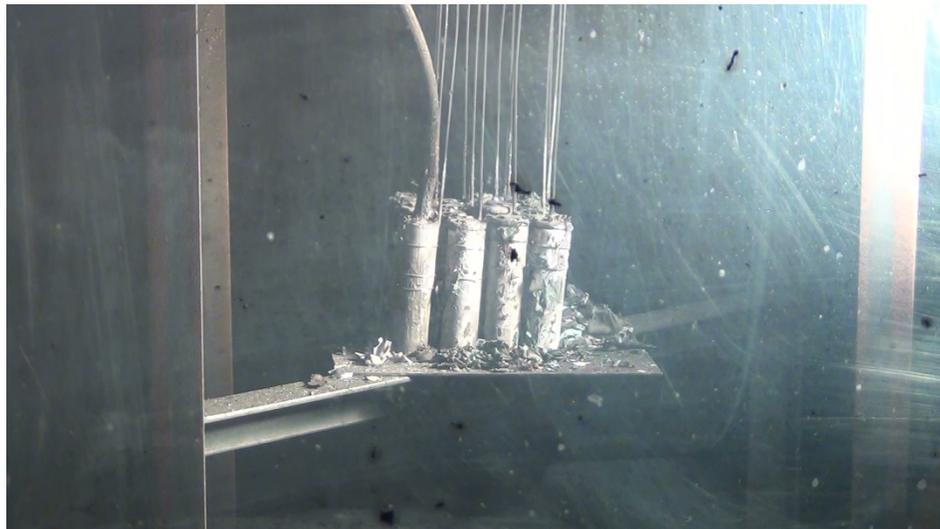


(b)

Figure 19. Treated cardboard at (a) 40% SOC and at (b) 50% SOC



(a)



(b)

Figure 20. The (a) treated cardboard and (b) untreated cardboard

The fire-retardant cardboard reduced burning compared to the untreated cardboard, as expected. As the treated cardboard remained present throughout the test, it remained as an insulator for the cells. Insulative divider cardboard caused the cells to take longer to propagate throughout the box. Insulative outer package cardboard had the effect of trapping much of the generated heat within the box.

3.2 INTUMESCENT PAINT TESTS

3.2.1 Propane Burner Test

Table 4 shows the experiments that were run to examine the effectiveness of intumescent paint for preventing burnthrough of a sample when exposed directly to a flame source.

Table 4. Set of experiments for the propane burner test

Coats of Intumescent Paint	Aluminum	Cardboard
10	X	X
15	X	X
20	X	X
25	X	X

The results from the propane burner test are shown in figure 21. The burnthrough time was measured when the center of the sample was breached. The results showed that the application of 10 coats of intumescent paint improved the resistance to the fire by approximately 30 seconds when compared with the bare cardboard. The subsequent application of 5 coats showed an approximate improvement of 3 seconds per application. It was observed that when the paint started to intumesce, the flame was diverted away from the center of the sample and ignited the edges of the sample, because the edges of the sample were not coated. This phenomenon is shown in figure 22. The samples could have otherwise performed better if the flames did not reach the edges.

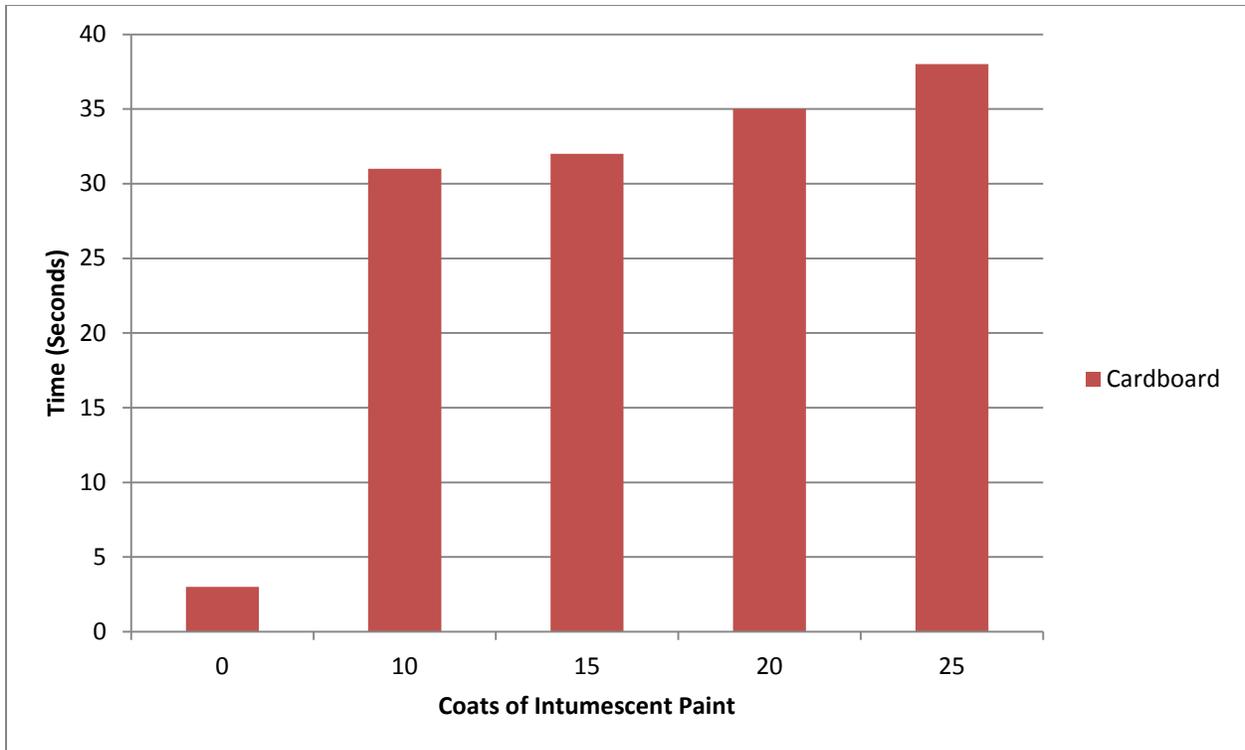


Figure 21. Burnthrough times of a 5'' x 5'' cardboard sample exposed to a direct flame source

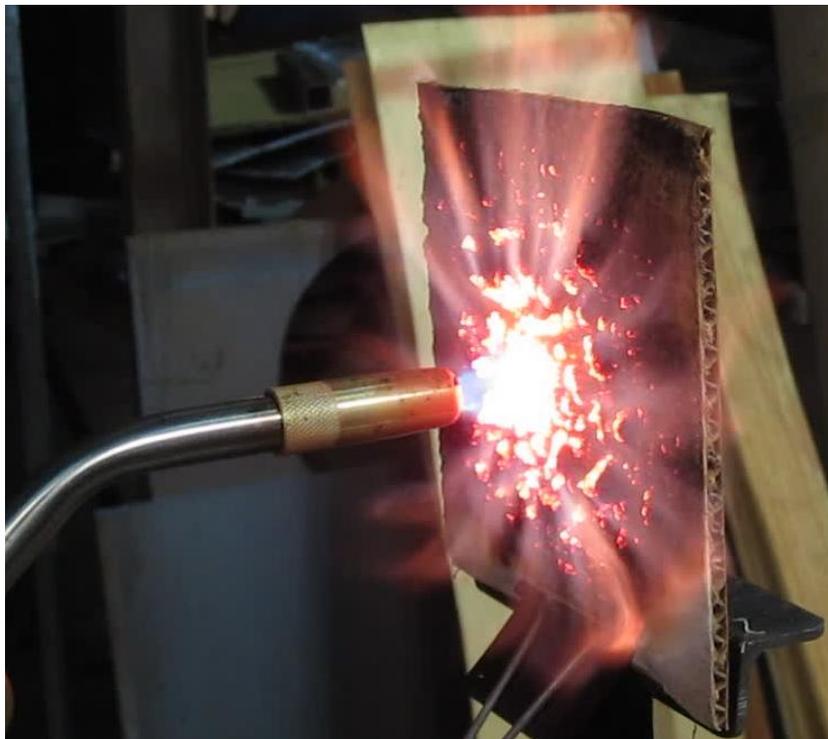


Figure 22. Flame spread reaching the edges of the sample

To verify the effectiveness of intumescent paint, the sample size was increased to 10" x 10" to eliminate the flame wrapping around the edges. The results are shown in figure 23. Fewer coats of intumescent paint were applied to the samples to replicate a realistic scenario. The results showed a dramatic change in the amount of protection time the intumescent paint provided against the fire source. This showed that the intumescent paint was effective on cardboard until the heat flux reached the auto-ignition temperature of the cardboard.

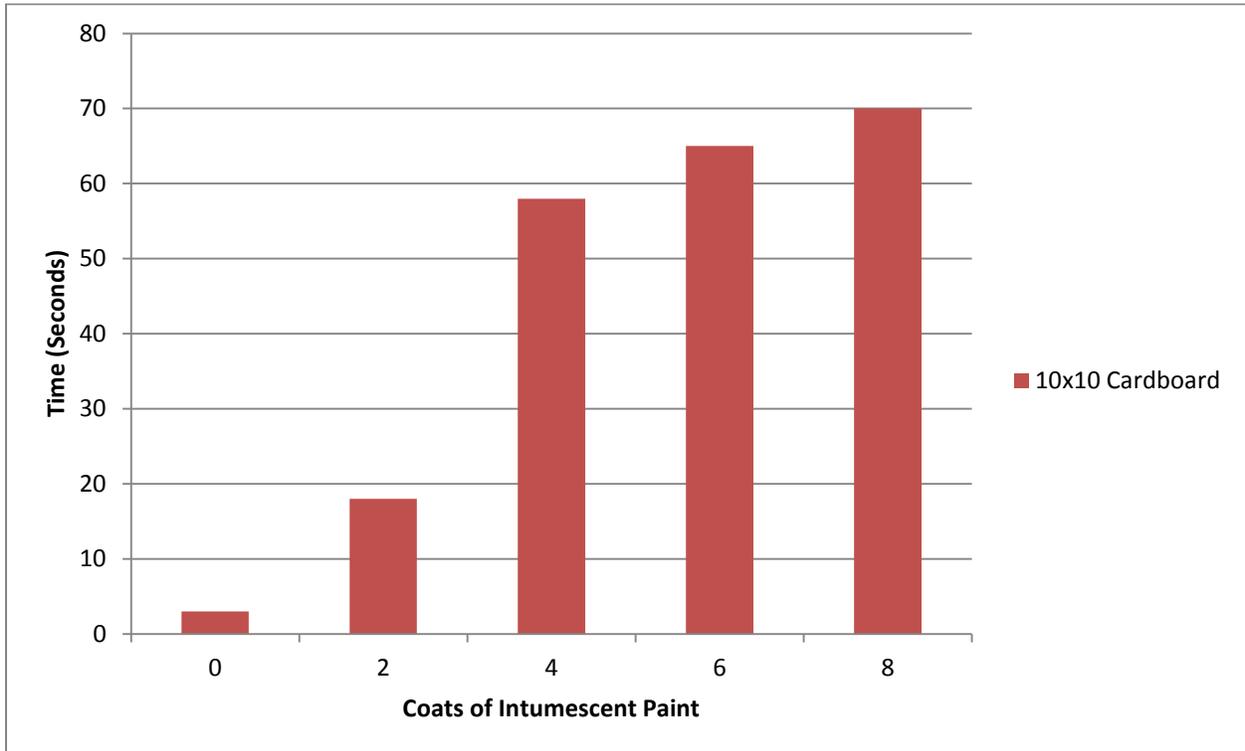


Figure 23. Burnthrough times of a 10" x 10" cardboard sample exposed to a direct flame

While subjecting the 5" x 5" aluminum samples to the propane burner, it was observed that without the protection of the intumescent paint, the flame was able to penetrate the sample within 100 seconds. Multiple applications of intumescent paint showed that the paint was very effective in diverting the heat flux from the flame source away from the sample. The flame was not able to penetrate the sample, as shown in figure 24. It can be inferred that intumescent paint works well when applied on materials with high conductivity, which helps in transferring the heat away from the sample.

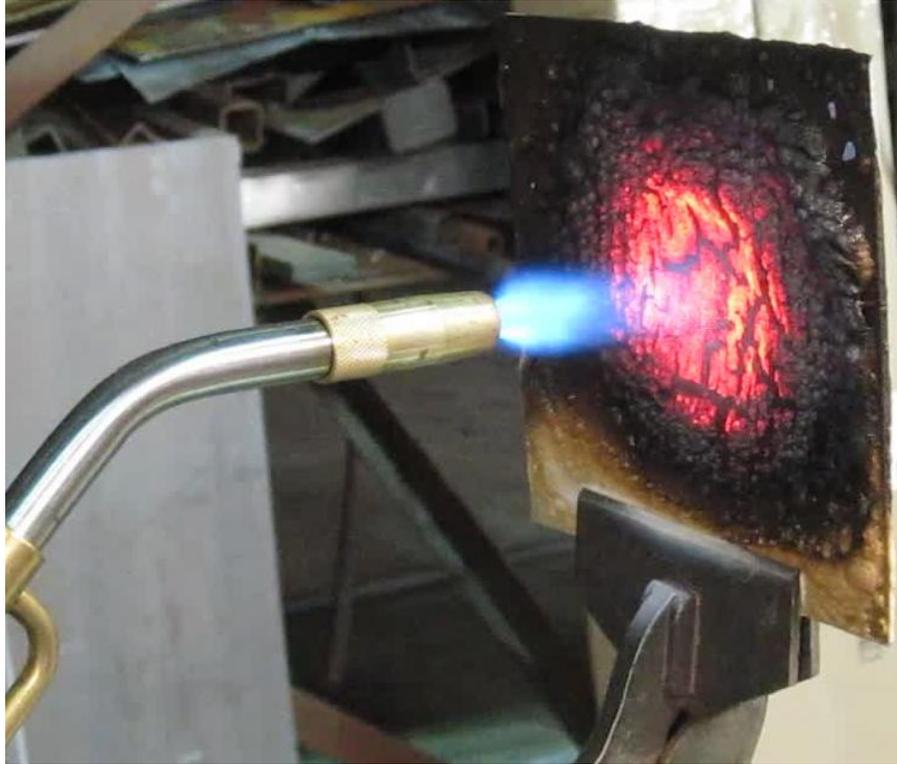


Figure 24. A 5" x 5" aluminum sample covered with 10 coats of intumescent paint

3.2.2 Radiant Heat Source Test

Table 5 shows the experiments that were conducted to examine the effectiveness of intumescent paint when exposed directly to a radiant heat source. The samples were made out of corrugated cardboard most commonly used in the shipping industry.

Table 5. Set of experiments for the radiant heat source test

Heat Flux (Btu/sq.ft-sec)	Coats of Intumescent Paint				
	0	2	4	6	8
3.5	X	X	X	X	X
5	X	X	X	X	X
6.6	X	X	X	X	X

The results from the radiant heat source test are shown in figure 25. At a lower radiant heat flux setting and with an increased number of paint coats, the intumescent paint provided a linear increase in protection against the radiant heat source. As the heat flux increased, the effective protection that was provided by the intumescent paint decreased. Once the cardboard reached its auto-ignition temperature, the cardboard samples ignited and the intumescent paint could not protect the sample from the subjected heat flux.

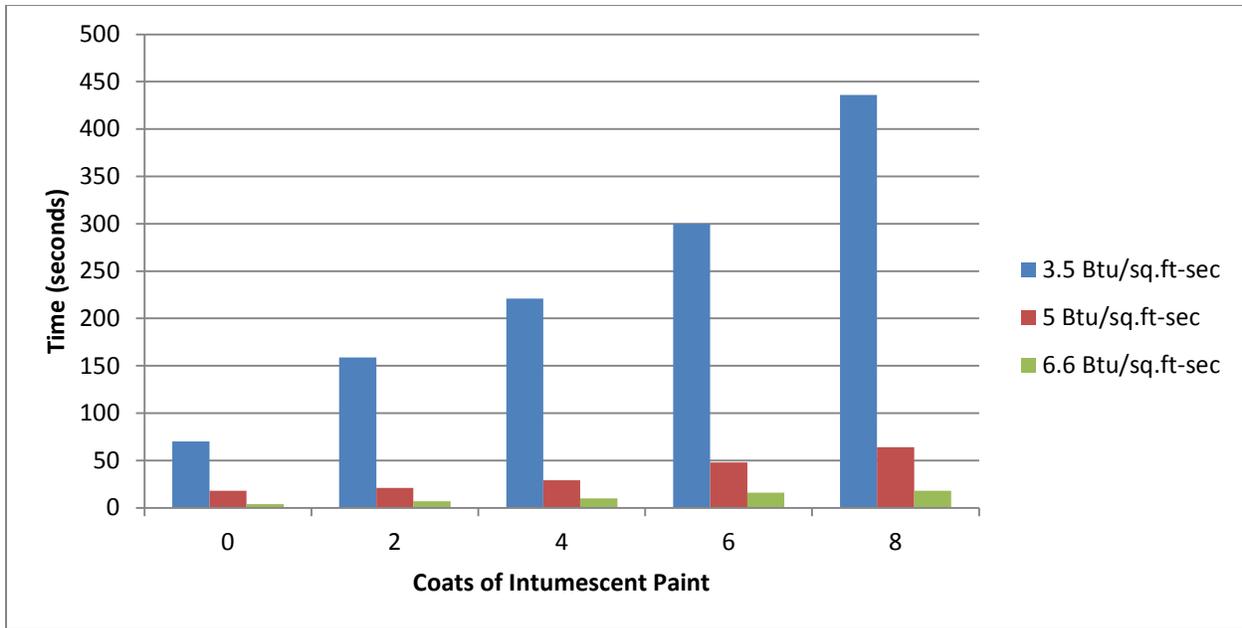


Figure 25. Burnthrough times of a 5'' x 5'' cardboard sample exposed to a radiant heat source

3.2.3 Lithium Battery Fire Source

Table 6 shows the tests that were run with cardboard dividers to examine the effectiveness of intumescent paint exposed to a lithium battery fire.

Table 6. Set of experiments for the lithium battery fire source

Coated with Intumescent Paint	1	2	3	4	5
Box	-	-	-	X	X
Dividers	-	X	-	X	X
Batteries	-	-	X	-	X

The results from the lithium battery fire tests are shown in figure 26. The amount of time required for thermal runaway to propagate from the first cell to the second cell was approximately 5 minutes. In the remainder of the tests with intumescent paint, all the methods that were used to prevent adjacent cells from going into thermal runaway failed. The data demonstrated that the methods used only delayed the adjacent batteries from going into thermal runaway. As the adjacent cells went into thermal runaway, it was observed that the cardboard would ignite from within the protective coatings. The heating rate was not fast enough to activate the intumescent paint and insulate the heat conducted from the heater or the cells in thermal runaway. Additionally, once the cardboard packaging caught on fire, it also became a heat source and accelerated the propagation of other cells into thermal runaway. The packaging with the dividers only that were painted with intumescent paint and the packaging with the dividers that were replaced with an aluminum foil showed the most resistance to heat transfer from the cartridge heater to an adjacent battery. The amount of time it took for the second cell to go into

thermal runaway while using an aluminum foil divider or dividers painted with intumescent paint was three times greater than the time required for cardboard alone.

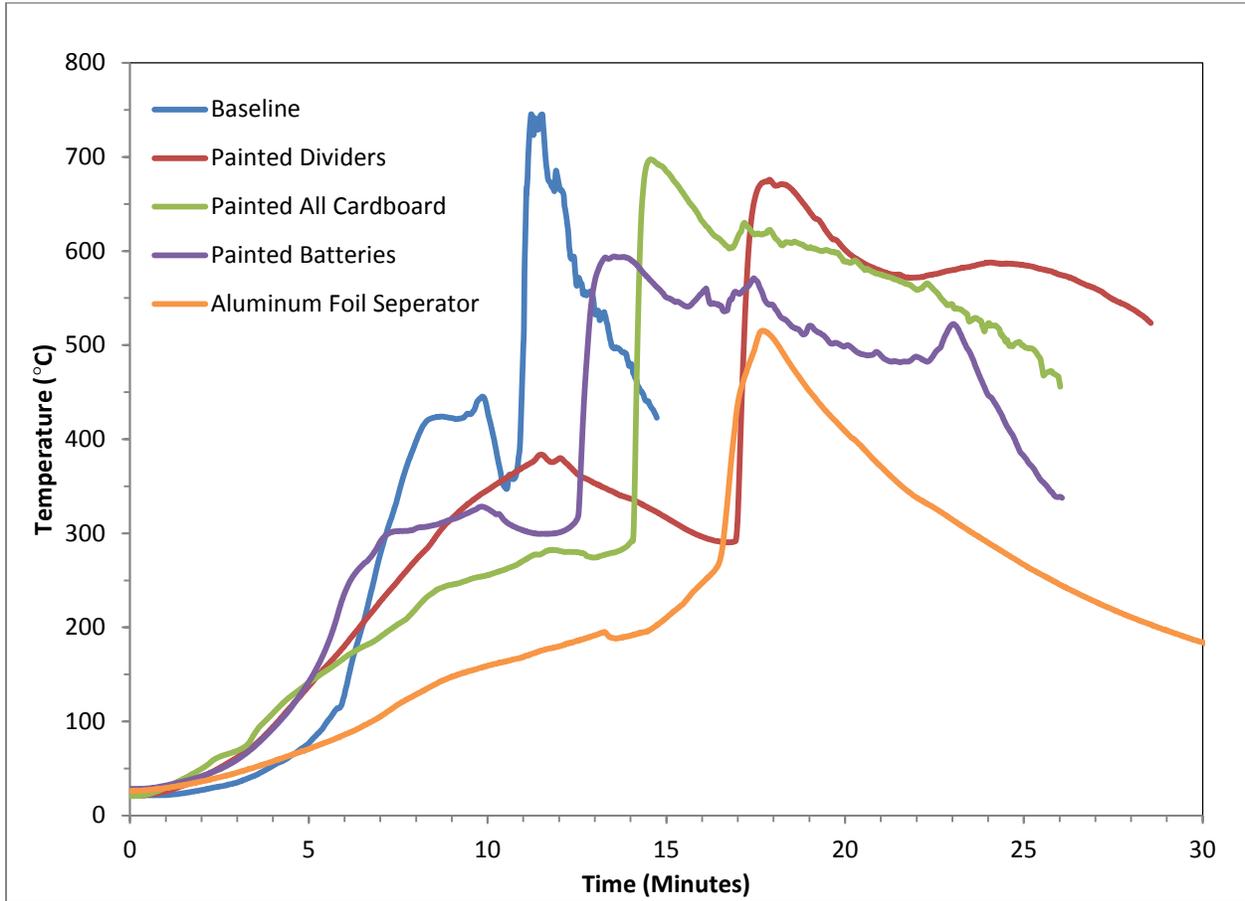


Figure 26. Temperature timelines for first battery to enter thermal runaway

3.3 ADDITIONAL OBSERVATIONS

3.3.1 Cell Ejection of Contents and Explosions

When a cell ejected its contents, the packaging would often be disturbed and other cells would separate from the package. Ejections and explosions delocalized the heat source. Therefore, they were sometimes effective at stopping cell propagation. Figure 27 shows a cell that ejected alongside a cell that exploded. Note that the cell in the figure had a pressure relief tube to decrease the likelihood of ejection and explosion.



Figure 27. 18650 cell with ejected inner materials

3.3.2 MATERIALS EJECTED.

In the thermal runaway process, the electrolyte and internal cell materials would be ejected from the cell. Initially, the burst disk would rupture and the electrolyte would evaporate from within the cell. Next, when the cell separator melted, internal temperature and pressure rise would cause the electrolyte to rapidly exit the cell. A short time later (approximately 1 second), other materials, such as plastic, lithium compounds, graphite, and aluminum attempted to exit the cell through the vent hole. It was at this moment that the vent may have become clogged and the entire upper surface of the cell case could have detached because of pressure and caused an ejection or an explosion of the cell.

4. SUMMARY OF RESULTS

The net rate of heat absorbed into the cells was the factor that determined if thermal runaway would propagate. If the power released by thermal runaway was low enough, then heat was dissipated fast enough to prevent the adjacent cells from reaching the thermal runaway onset temperature.

The pack of water above the cells prevented thermal runaway propagation at a 50% SOC. Of the package configurations that were tested, SOC at 30% and the setup with a pack of water above the cells were the only effective methods to stop propagation. The insulative separation materials helped to extend the time for thermal runaway to propagate throughout the box, and conductive materials increased the onset time but decreased the propagation time once thermal runaway had begun.

Intumescent paint exhibits some fire resistive capabilities against a direct flame until the heat flux exceeds the auto-ignition temperatures of organic materials, whereas it shows significant fire resistive capabilities against conductive materials, such as aluminum.

The lithium battery fire tests showed that using intumescent paint or aluminum foil dividers only delayed the adjacent batteries from going into thermal runaway and eventually transferring the heat to all the batteries and setting them into thermal runaway. The temperatures produced by the batteries in thermal runaway exceed the auto-ignition temperatures of cardboard, therefore igniting the cardboard beneath the protective coatings.

4.1 TRANSPORT APPLICATION

The greater propagation times associated with the use of insulative divider materials and lower SOC's may be one layer to a multilayered approach to stop thermal runaway propagation. Other layers could include alternate outer packaging, the effective use of cooling agents, and fire inhibiting materials.

From these tests, aside from a low SOC, the pack of water above the cells was the most effective method for stopping thermal runaway propagation. Packs could also contain water with an additive producing a distinct smell if additional warning signs were desirable for detecting damaged packages.

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