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Aviation Research Division
Atlantic City International Airport
New Jersey 08405

Fire Hazard Analysis for Various Lithium Batteries

March 2017

Final Report

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16. Abstract

Fire tests were conducted on lithium-ion, lithium-pouch, and lithium-metal battery cells of various cathode chemistries and sizes to evaluate their failure effects. First, tests were performed with a single cell in thermal runaway. Next, a thermal runaway propagation test with five cells was conducted. Finally, a vent gas ignition test to determine the flammability of the vent gases was performed. The tests showed a large variation in the fire hazard characteristics of the thermal runaway event. The characteristics depended on cell size, chemistry, construction, and orientation. As a result of the tests, it is recommended that each battery cell be evaluated on an individual basis dependent on its specific application and operating environment.

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LIST OF ACRONYMS

Ah	Ampere-hour
CFx	Carbon monofluoride
THC	Total hydrocarbon concentration
Wh	Watt-hour

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EXECUTIVE SUMMARY

Lithium-metal, lithium-ion, and lithium-ion-pouch batteries offer many advantages over alternative battery technologies. They possess a high energy density (stored electrical energy per unit volume), relatively constant voltage during discharge, relatively low maintenance, good low-temperature performance, and a long shelf life. For these reasons, their use and installation onboard aircraft has become increasingly prevalent. Some of the uses for lithium batteries on today's aircraft include emergency lighting, cockpit voice recorders, flight data recorders, electronic locator transmitters, main batteries, avionics equipment, and emergency medical equipment.

However, there are potential fire hazards associated with the use of these batteries because of their high energy content, flammable hydrocarbon electrolyte solvent, and potential thermal instability. Failure of a lithium battery may cause thermal runaway, which is a self-sustaining uncontrolled increase in temperature within the battery. Thermal runaway often results in fire caused by the ignition of the flammable gases vented from the battery. In addition, any unburnt vented battery gases can be toxic and could accumulate, resulting in the potential for an explosion.

Fire tests were conducted on lithium-ion, lithium-pouch, and lithium-metal battery cells of various cathode chemistries and sizes to evaluate their failure effects. First, tests were performed with a single cell in thermal runaway. Next, a thermal runaway propagation test with five cells was conducted. Finally, a vent gas ignition test to determine the flammability of the vent gasses was performed. The tests showed a large variation in the fire hazard characteristics of the thermal runaway event. The characteristics depended on cell size, chemistry, construction, and orientation. As a result of the tests, it is recommended that each battery cell be evaluated on an individual basis dependent on its specific application and operating environment.

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1. INTRODUCTION

1.1 BACKGROUND AND MOTIVATION

Lithium-metal, lithium-ion, and lithium-ion-pouch batteries offer many advantages over alternative battery technologies. They possess a high energy density, relatively constant voltage during discharge, relatively low maintenance, good low-temperature performance, and a long shelf life. For these reasons, their use and installation onboard aircraft has become increasingly prevalent. Some of the uses for lithium batteries on today's aircraft include emergency lighting, cockpit voice recorders, flight data recorders, electronic locator transmitters, main batteries, avionics equipment, and emergency medical equipment.

However, there are fire hazards associated with the use of these batteries because of their high energy content, flammable electrolyte, and potential thermal instability. Failure of a lithium battery often results in thermal runaway, which is a self-sustaining uncontrolled increase in temperature within the battery. Thermal runaway often results in fire caused by the ignition of the flammable gases vented from the battery. In addition, any unburnt vented battery gases can be toxic and could accumulate, resulting in the potential for an explosion.

Lithium-ion and lithium-metal batteries exist in a variety of chemistries, sizes, and constructions. These variations may all impact the fire characteristics resulting from the failure of a cell.

The chemistry variation involves the cathode material, the anode material, and the electrolyte composition. Table 1 shows the chemical composition of some of the common materials used for several types of lithium batteries.

Table 1. Commonly used materials in lithium battery cell construction

Common Cathode Materials	Common Anode Materials	Common Electrolyte Compositions
Lithium cobalt oxide	Graphite	Ethylene carbonate
Lithium iron phosphate	Lithium titanate	Diethyl carbonate
Lithium nickel manganese cobalt oxide	Tin/cobalt alloy	Dimethyl carbonate
	Silicon/carbon	Propylene carbonate
		Dimethoxyethane
		Gamma-butyrolactone

In addition to the variation of chemistry, the cells may exist in a variety of sizes. Lithium-ion and lithium-metal cells range in size from the more common AA, AAA, C, and D to almost any other possible size for a specific application. Table 2 shows some common sizes of these cells and their respective dimensions.

Table 2. Common cell sizes

Cell Sizes	Cell Dimensions (mm)
CR2025	20(d) x 2.5(h)
CR2032	20(d) x 3.2(h)
CR2450	24.5(d) x 5(h)
CR2	15.6(d) x 27(h)
CR123a	17(d) x 34.5(h)
AAA	10.5(d) x 44.5(h)
AA	14.5(d) x 50.5(h)
½ AA	14.5(d) x 24(h)
A	17(d) x 50(h)
C	26.2(d) x 50(h)
D	34.2(d) x 61.5(h)
DD	32.9(d) x 124.5(h)
18650	18(d) x 65(h)
9-volt	26.5(l) x 17.5(w) x 48.5(h)

Variation in cell construction involves the safety provisions in place within the cell, such as safety vents, current intercept device, shutdown separator, and positive temperature coefficient. Variations of the chemistry, size, and construction contribute to the resulting failure conditions of a cell.

Lithium-pouch cells, also referred to as lithium polymer cells, are available in the same chemistries as lithium-ion; however, rather than being cylindrical in shape with a metal casing, they are typically flat and rectangular in shape with flexible outer casing material. Pouch cells can be more easily formed to the dimensions required for specific applications and are frequently used in cell phones, tablet computers, and other personal electronic devices.

As with the large variation in thermal runaway reactions among cells, the cell surroundings also contribute to the behavior of a cell that is undergoing thermal runaway. For example, a cell that is contained in thick aluminum housing will lose heat more rapidly than a cell that is insulated. In addition to overheating of the cell, thermal runaway may be caused by other conditions, such as external soft short, external hard short, overcharge, crushing, or a manufacturing contaminant. However, when thermal runaway occurs in a single cell, propagation to adjacent cells in a group, such as in a bulk shipment package, is generally caused by overheating of the cells.

1.2 PREVIOUS RESEARCH

The literature contains research and testing to characterize the effect of various lithium battery configurations on the fire hazard characteristics of the thermal runaway reaction. Hyung et al. showed that the addition of additives to a cell electrolyte would reduce heat generation from

reactions between the anode and electrolyte and increase the onset temperature for the initial reaction [1].

Jhu et al. showed that four battery cells of the same cathode material, state-of-charge, and size made by different manufacturers had various thermal runaway characteristics [2]. The thermal runaway onset temperature varied from 116.5°–142.5°C, and the maximum temperature ranged from 654.3°–903°C [2].

Jhu et al. also showed in another study comparing two different lithium-ion cathode materials that $LiCoO_2$ had an onset temperature of 131.5°C for thermal runaway, much lower than the thermal runaway temperature of 175.4°C for LiMnCoNi [3]. The maximum temperature of thermal runaway was 708.8°C for the $LiCoO_2$ cell and 665.6°C for LiMnCoNi [3].

Sandia National Labs performed tests with various lithium-ion chemistries and showed that $LiCoO_2$ had the greatest normalized heating rate followed by nickel cobalt aluminum, nickel manganese cobalt, and finally lithium iron phosphate.

1.3 OBJECTIVE

The objective of this study was to evaluate the fire hazard characteristics during thermal runaway of a variety of lithium-ion, lithium-pouch, and lithium-metal battery cells with various cell cathode materials, sizes, and constructions.

2. SETUP

Tests with the various sizes and chemistries of lithium-metal, lithium-ion, and lithium-ion-pouch batteries were conducted in two test environments. A 10.8 m^3 pressure chamber was used to test lithium-ion, lithium-ion-pouch, and lithium-metal cells (see figure 1). In addition, a 4-ft x 4-ft x 4-ft test chamber with a sealable door was used for testing the lithium-ion-pouch cells (see figure 2). Evaluation of the pouch cells in the smaller chamber allowed for vented gas concentrations to be determined with greater accuracy; however, it was not practical for testing many of the cylindrical Li-ion or Li-metal cells because of safety considerations.

Figure 1. The 10.8 m^3 pressure vessel

Figure 2. The 4-ft x 4-ft x 4-ft test chamber

2.1 BATTERY CELLS

Table 3 shows the battery cell sizes and cathode chemistries that were tested for each of the three types of batteries (ion, pouch, and metal) with their corresponding electrical capacities in watt-hour (Wh). A large variety of commercially available battery cell types and sizes were investigated. The Wh-rating for a cell was calculated by multiplying the ampere-hour (Ah) rating by the nominal voltage of the cell. Multiple entries are shown for some chemistry and size types because multiple models or manufacturers were tested. Figures 3–5 show images of the variety of cells for each battery type.

Table 3. Cells evaluated based on cell type, cathode chemistry, and size

	Li-Ion, Wh				Lithium Metal, Wh						Lithium Polymer, Wh				
Battery size	$LiCoO_2$	$LiFePO_4$	LiMnNi	LiNiMnCO	$LiMnO_2$	$LiFeS_2$	$LiSO_2$	CFx	LiBrCl	$LiSOCl_2$	$LiFePO_4$	LiMnNi	LiNiMnCo	$LiCoO_2$ (std rate discharge)	$LiCoO_2$ (high Rate discharge)
10440 (AAA)	1.8*					1.8									
14500 (AA)	2.88	1.92				4.35				8.82					
14250 (1/2 AA)										3.96, 4.32					
17500 (A)								5.4							
15270 (CR2)					2.25										
16340 (CR123A)	2.7*	2.4			4.65										
18650	9.62														
25500 (C)		10.56	14.8	13.14						30.6					
32600 (D)		9.6			33, 33.3		23.25		58.5	46.8, 50.4, 59.4, 61.2, 68.4, 68.4, 68.4					
DD										126					
9V					9									4.5	
2450 (button)	0.43				1.86										
2025 (button)					0.48										
10 Ah											32	37	37	37	37
4.5 Ah														16.65	
0.8 Ah														2.96	

*AAA $LiCoO_2$ cells were only charged to 67% and cr123 LiCoO2 cells were only charged to 50%
CF_x = carbon monofluoride

Figure 3. Photograph showing the lithium-ion cells that were tested

Figure 4. Photograph showing the lithium-ion pouch cells that were tested

Figure 5. Photograph showing the lithium-metal cells that were tested

Three main types of tests were conducted. Tests were first performed with a single cell driven into thermal runaway by a strapped cartridge heater. Tests were also performed with a cartridge heater to ignite the gasses that vented from the cell if it had not auto-ignited in the previous test. Finally, tests were performed with five cells in a row to determine if thermal runaway would propagate to adjacent cells.

A 100-watt cartridge heater was used to initiate thermal runaway for the tests with cylindrical cells, and a 240-watt heat plate was used to initiate thermal runaway for the lithium-ion-pouch cells and button cells. The cartridge heater and heat plate setup for a single-cell thermal runaway test for a cylindrical and pouch cell, respectively, are shown in figures 6 and 7.

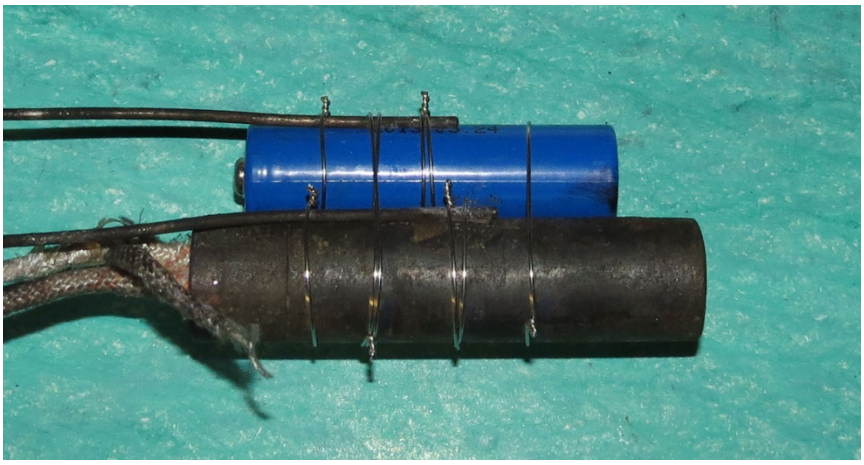


Figure 6. Single-cell thermal runaway setup for cylindrical cell types

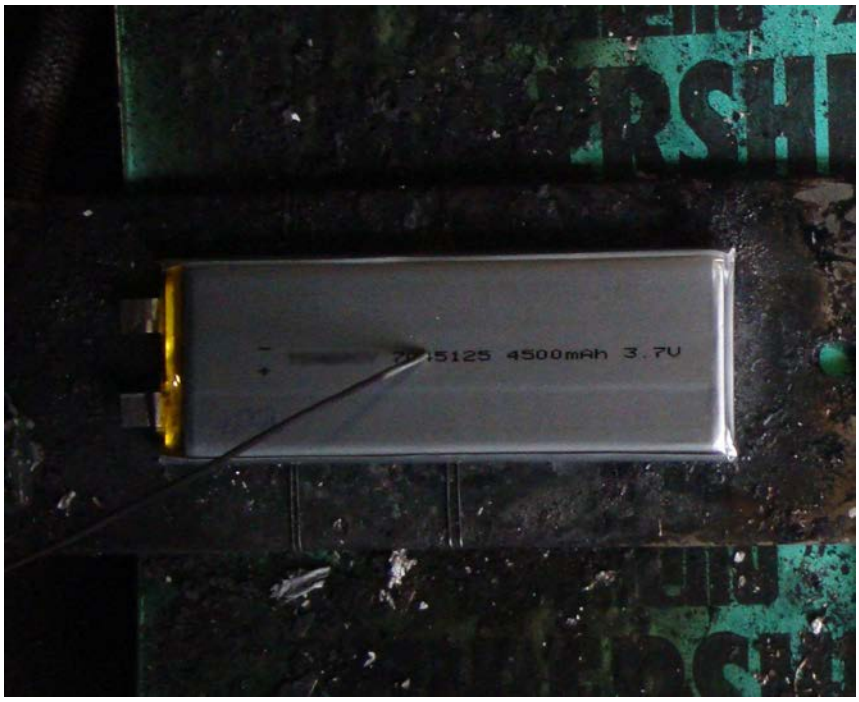


Figure 7. Single-cell thermal runaway setup for pouch cell types

The propagation tests were performed with five cells aligned parallel to each other in a side-by-side orientation (see figure 8). The group was wired together with 18-gauge safety wire.

Figure 8. Cylindrical-cell propagation test setup

The temperature of the cartridge heater, ambient conditions, and of the cell adjacent to the heater was measured with 1/16th-inch type-K inconel thermocouples. A second thermocouple was used in the single-cell tests to measure the surface temperature of the cell. In the propagation tests, the temperature of the outermost cell was also measured. The cell thermocouple for the heater plate setup in the lithium-pouch and button tests was bent in a way that caused it to be pushed up against the cell without any mechanical fasteners (see figure 7). An additional thermocouple was also strapped to the bottom of the heater plate.

Hydrocarbon concentrations were measured with a Signal Instruments 3000HM total hydrocarbon concentration (THC) analyzer. In addition, a Sensotec 50 psia pressure transducer was used to measure the pressure increase in the pressure chamber.

In some of the propagation tests with lithium-pouch and button cells, a holder was required to prevent the stack of cells from falling over once thermal runaway was initiated.

In other tests of button- and pouch-cell thermal runaway propagation, the cells were strapped together tightly to replicate a battery housing that remained rigid as the cells tried to expand (see figure 9).

Figure 9. Pouch-cell propagation test setup

A fan was placed within the 10.8 m^3 pressure chamber to adequately mix the gaseous hydrocarbons ejected from the batteries so that the hydrocarbon analyzer would provide a representative concentration measurement. However, in some of the tests in which a sufficient temperature for thermal runaway was not reached, the fan was turned off to prevent any cooling effect the fan may have had on the battery cells.

All data were collected with the Personal Daq/56 data collection hardware/software system. Data samples were collected and recorded every second. However, in the tests with explosions, pressure data were collected at 1000 Hz with a separate data collection board in an attempt to fully capture the resulting rapid pressure rise.

3. TEST PROCEDURE

Every test was recorded with a digital video recorder, and pre- and post-test photographs were taken to document the test setup and the resulting effects of the thermal runaway event.

3.1 SINGLE CELL TEST

A single cell of each battery type was forced into thermal runaway by overheating. Cylindrical cells were strapped to a 100-watt cartridge heater with safety wire and heated, and button cells and lithium-ion-pouch cells were strapped to and heated by a 240-watt hot plate. Type-K thermocouples recorded the temperatures of the heater and the outer casing of the battery cell. The heater remained on until the battery reached the point of thermal runaway. The battery cell casing temperature at which thermal runaway occurred was recorded, and the effects (i.e., venting, sparking, flaming, and explosion) of the thermal runaway event were also noted. In addition, hydrocarbon concentrations were recorded in each test. The pressure rise was also recorded for tests conducted in the 10.8 m^3 chamber.

3.2 IGNITER TEST

The igniter tests were conducted in the 10.8 m^3 pressure vessel with cells that did not self-ignite the vented gases during the single-cell tests. A single cell was heated into thermal runaway with a heater. For cylindrical cells, heating was provided by a 100-watt cartridge heater strapped to the cell with safety wire. Button cells and lithium-ion-pouch cells were heated with a 240-watt hot plate. Type-K thermocouples were used to record the temperatures of the heater and the outer casing of the cell. A spark gap, powered by an oil burner transformer, was placed approximately 1 inch above and 1 inch away from the battery cell vent location. During certain tests, the location of the spark gap was adjusted to provide the highest probability of ignition because of the venting provisions of the cell. The heater was initiated and remained on until the battery reached the point of thermal runaway. At the first sign of cell venting (i.e., vapors emitting from the cell), the igniter was initiated and remained on for the remainder of the test. The battery cell casing temperature at which thermal runaway occurred was recorded, and the effects (i.e., venting, sparking, flaming, and explosion) of the thermal runaway event were also noted. In addition, hydrocarbon concentration and pressure within the test chamber were recorded.

3.3 PROPAGATION TEST

Five cells were connected, with the surface of longest dimension touching to provide the most surface-to-surface contact of the cells (see figures 8 and 9). An outer cell was forced into thermal runaway through heating. For cylindrical cells, heating was provided by a 100-watt cartridge heater strapped to the cell with safety wire. Button cells and lithium-ion-pouch cells were heated with a 240-watt heater plate. The heater and battery cells were strapped together with safety wire. Type-K thermocouples were used to record the temperature of the heater and the casing of the two outermost cells. The heater was initiated and remained on until the adjacent battery cell reached thermal runaway. At this time, power to the heater was terminated. The battery cell casing temperature at which thermal runaway occurred, the effects (i.e., venting, sparking, flaming, and explosion) of the thermal runaway event, and the number of cells to which thermal runaway propagated were recorded. In addition, THC was recorded in each test. The pressure rise was also recorded for tests conducted in the 10.8 m^3 chamber.

3.4 ADDITIONAL TESTS

In some of the tests, the orientation of the cell was varied. All of the test procedures were the same as the single-cell test except the cell orientation was varied from horizontal to vertical.

4. DISCUSSION OF RESULTS

The tests were performed for the various types of batteries. The results were divided into four sections: cylindrical lithium-ion, lithium-ion pouch, cylindrical lithium-metal, and button cells. For each type of battery, the results are given for the single-cell test, the propagation test, and the single-cell test with an external spark ignition source. Each test determined the thermal runaway onset temperature, maximum temperature rise resulting from thermal runaway, and number of battery cells that propagated. Thermal runaway onset temperature was determined by reviewing the data and finding the temperature at the point at which the battery cell begins to experience a

rapid, uncontrolled rise in temperature. Figure 10 shows an example of a plot used to determine the thermal runaway onset temperature.

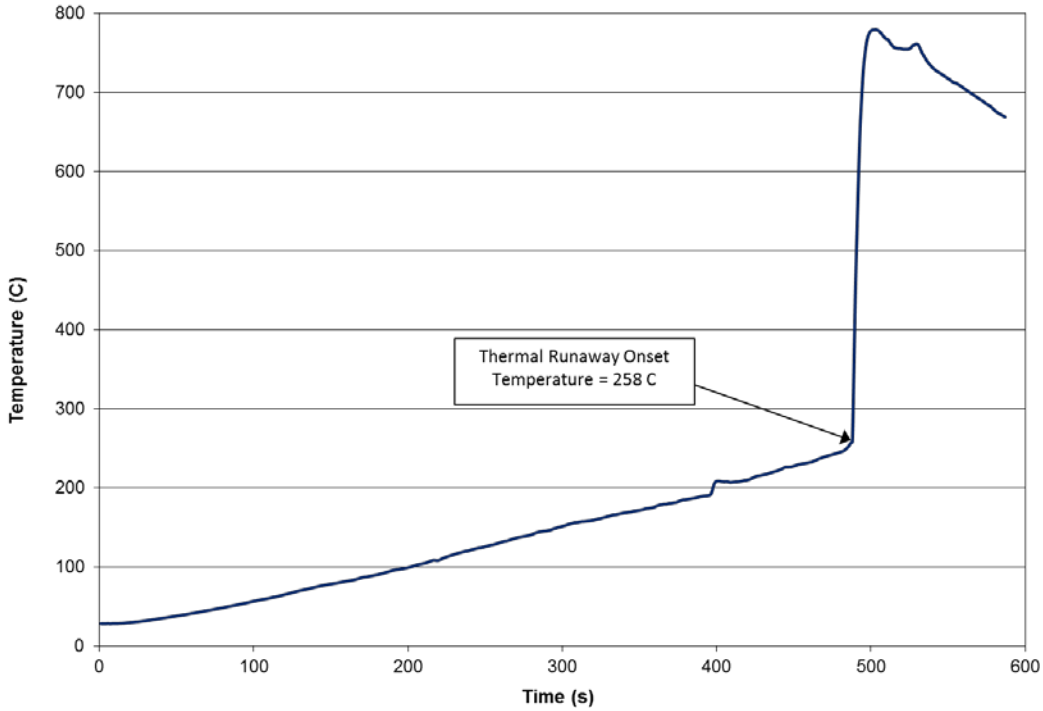


Figure 10. Sample plot showing how thermal runaway onset temperature was determined

4.1 CYLINDRICAL LITHIUM-ION TEST RESULTS

The temperature rise of the cells varied among chemistries (see figure 11). The temperature rise of the $LiFePO_4$ cells was significantly less than the $LiCoO_2$ and LiMnNi cell chemistries. The average temperature rise of all of the $LiFePO_4$ cells was 122°C, whereas the average temperature rise of the $LiCoO_2$ and LiMnNi cells were 372.75°C and 552°C, respectively.

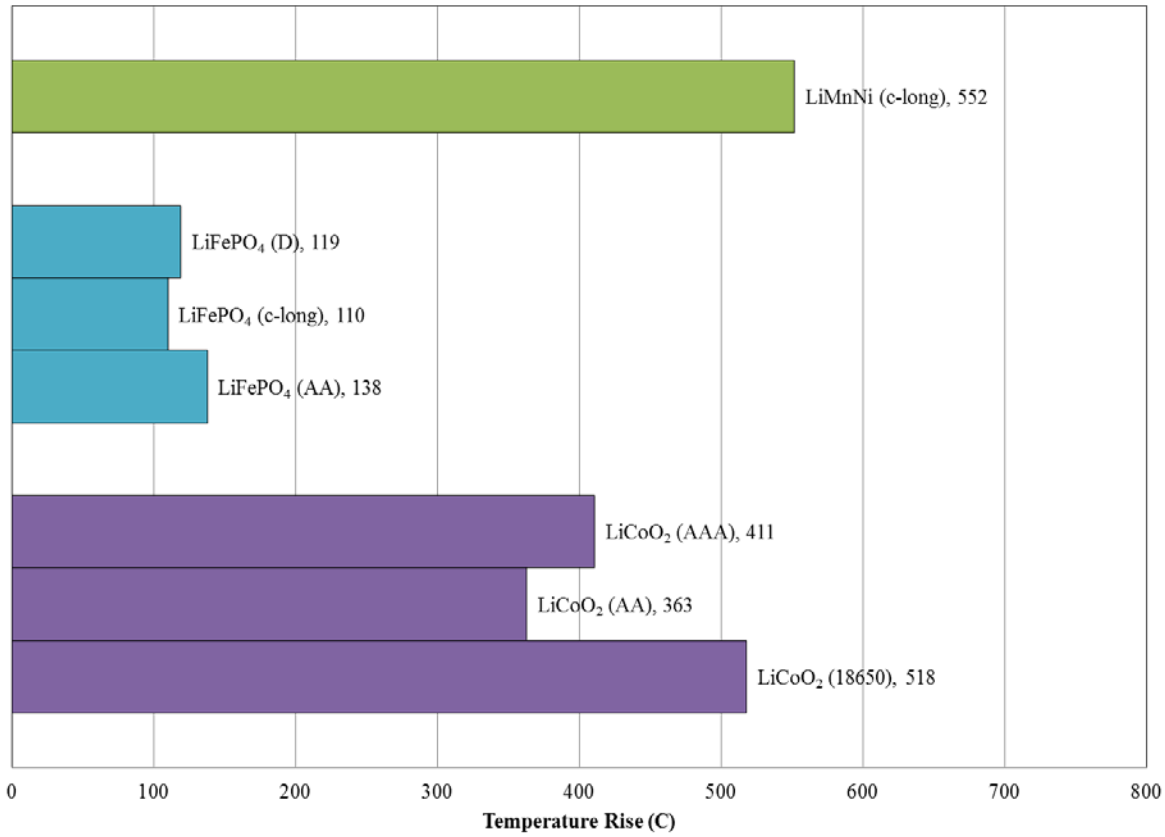


Figure 11. Temperature rise occurring from thermal runaway of Li-ion cells (the LiNiMnCO c-long cell, the LiFePO4 CR123 cell, and the LiCoO2 CR123 cell are not shown in the plot because they ejected their contents)

The average temperature rise for each of the lithium-ion chemistries was plotted against the Wh density of each cell (Wh/g; see figure 12). The figure shows that the mean cell temperature increased with Wh density, among the various cell chemistries.

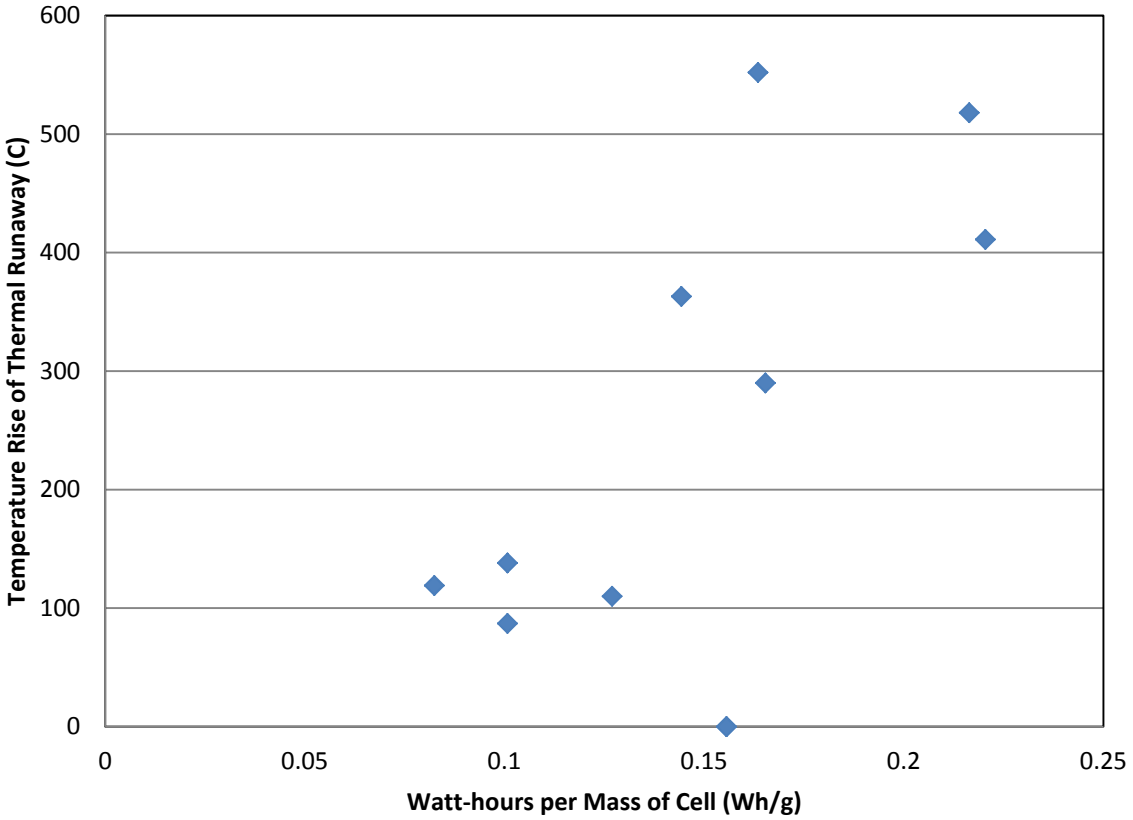


Figure 12. Temperature rise versus the watt-hour density of a Li-ion cell

The temperature rise for the LiNiMnCo cell was not recorded because the cell ejected all of its internal contents through one of the cell's endcaps. Once the contents of the cell were ejected, the outer casing of the cell cooled rapidly, which prevented obtaining accurate temperature measurements.

The onset temperatures of all of the lithium-ion cells tested were in the 200-250°C range (see figure 13). However, the onset temperature of the LiNiMnCo cell was highest followed by $LiFePO_4$, $LiCoO_2$, and LiMnNi. The average onset temperature of all of the lithium-ion cells was 234°C.

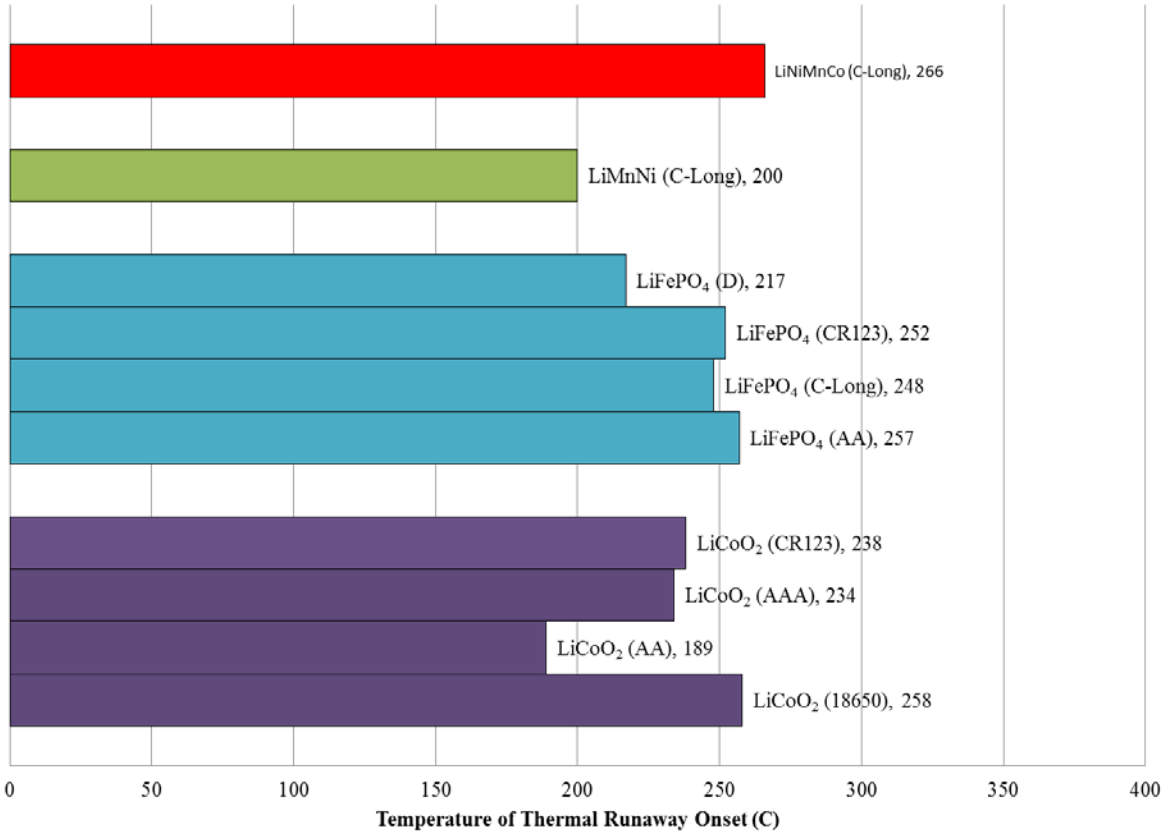


Figure 13. Onset temperature of thermal runaway from Li-ion cells

All of the lithium-ion cells tested had flammable electrolytes that either self-ignited or were ignited with the use of the external igniter. The reason that some of the cells self-ignited and others did not may have been because of a slight deviation in the test fixture or because of the differences in the temperature rises of the cells.

Cells were tested to determine the possibility of propagation of thermal runaway from one cell to the next. Figure 14 shows the number of cells that experienced thermal runaway out of the five that were physically connected together. The initial cell in all of these tests experienced thermal runaway because it was in direct contact with the heater and sufficient time was allowed. The number of the remaining cells that went into thermal runaway provided a measure of the likelihood of propagation for that size and chemistry cell.

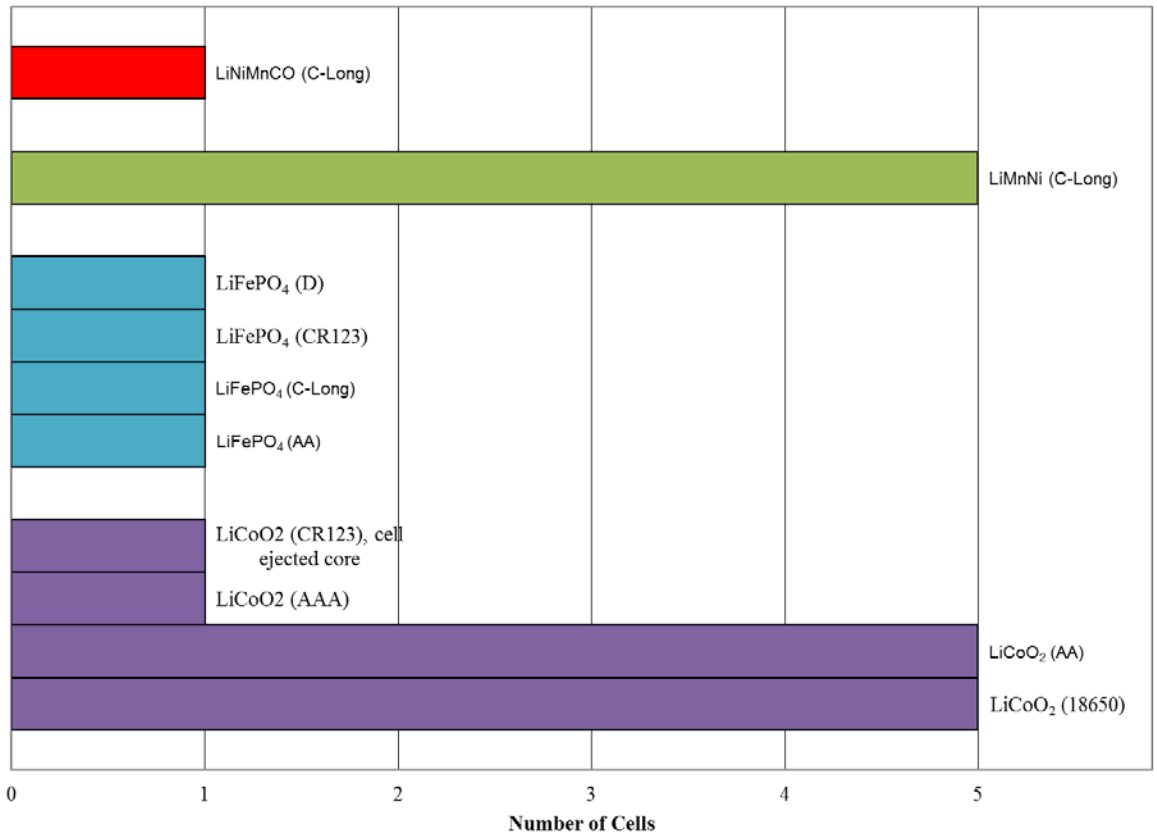


Figure 14. Number of Li-ion cells to have runaway in 5-cell propagation test

The propagation tests with the C-long-sized LiMnNi, and the AA- and 18650-sized $LiCoO_2$ cells were the only tests in which thermal runaway propagated to all five cells. The CR123- and AAA-sized $LiCoO_2$ cells did not propagate to any of the adjacent cells. Similarly, the C-long-sized LiNiMNCO cell and all of the $LiFePO_4$ cells also did not propagate to any of the adjacent cells. The LiNiMnCO cell did not propagate because the heated contents of the cell consistently ejected from the cell casing. The result of ejection was a rapid decrease in cell case temperature, which prevented heating to sufficiently initiate thermal runaway in the adjacent cell. However, in a battery package, the LiNiMnCo would be more likely to propagate because the hot contents would remain in the package, therefore, providing heat input to the remaining battery cells. The $LiFePO_4$ cells did not propagate because of the low temperature rise during thermal runaway (see figure 11).

The smaller-sized cells of similar chemistries may have been less likely to propagate because of a lower energy density.

4.2 LITHIUM-ION-POUCH TEST RESULTS

The temperature rise observed during the thermal runaway event of the lithium-ion pouch cells was similar to that of the lithium-ion cells (see figure 15). The $LiFePO_4$ pouch cells had the

lowest observed temperature rise at 168°C. The $LiCoO_2$ 4.5-Ah cell achieved the highest temperature rise of 437°C, and the average of all of the pouch cells was 310°C.

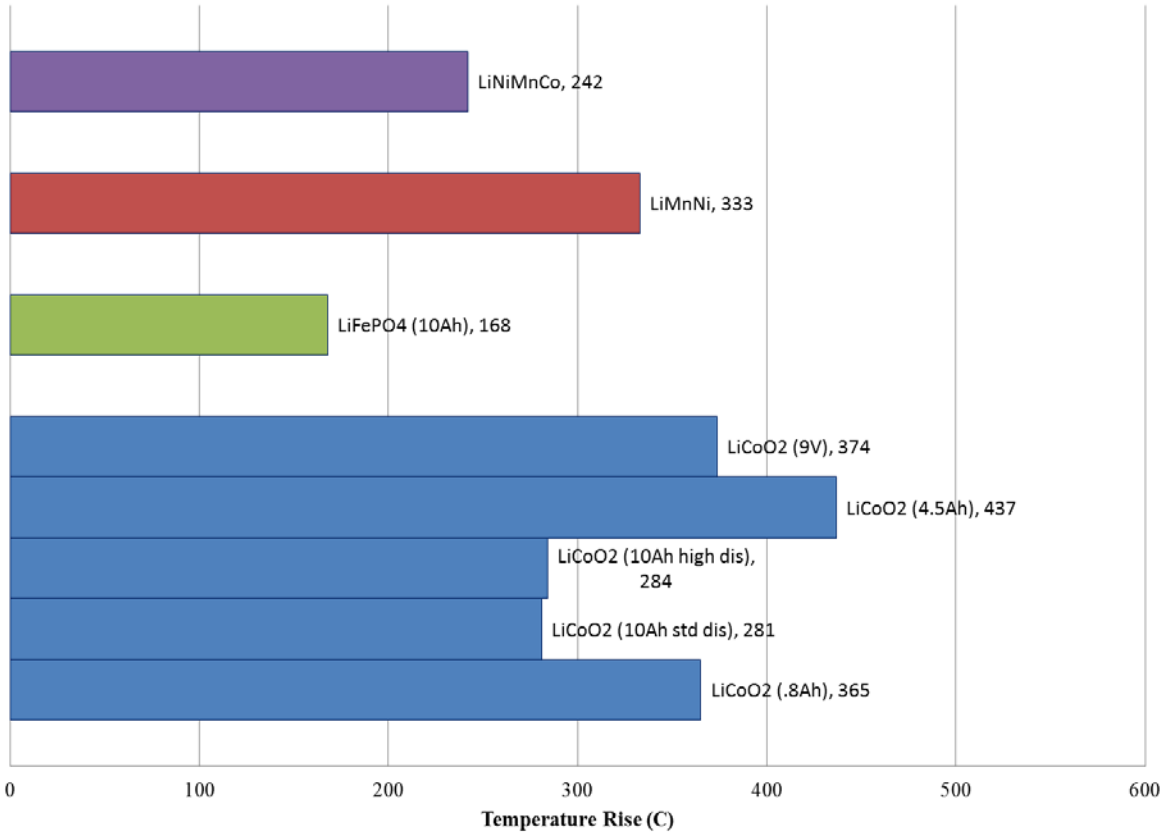


Figure 15. Temperature rise occurring from thermal runaway of Li-ion-pouch cells

The average measured onset temperature of all of the lithium-ion pouch cells was 68°C (see figure 16). The pouch cells conducted heat differently, and the thermal runaway onset temperature was, therefore, not compared directly with the onset temperature of the cylindrical cells. The lowest occurring onset temperature of 42°C was observed with the LiNiMnCo cells, whereas the highest onset temperature of 105°C was observed with the 4.5-Ah $LiCoO_2$ cells.

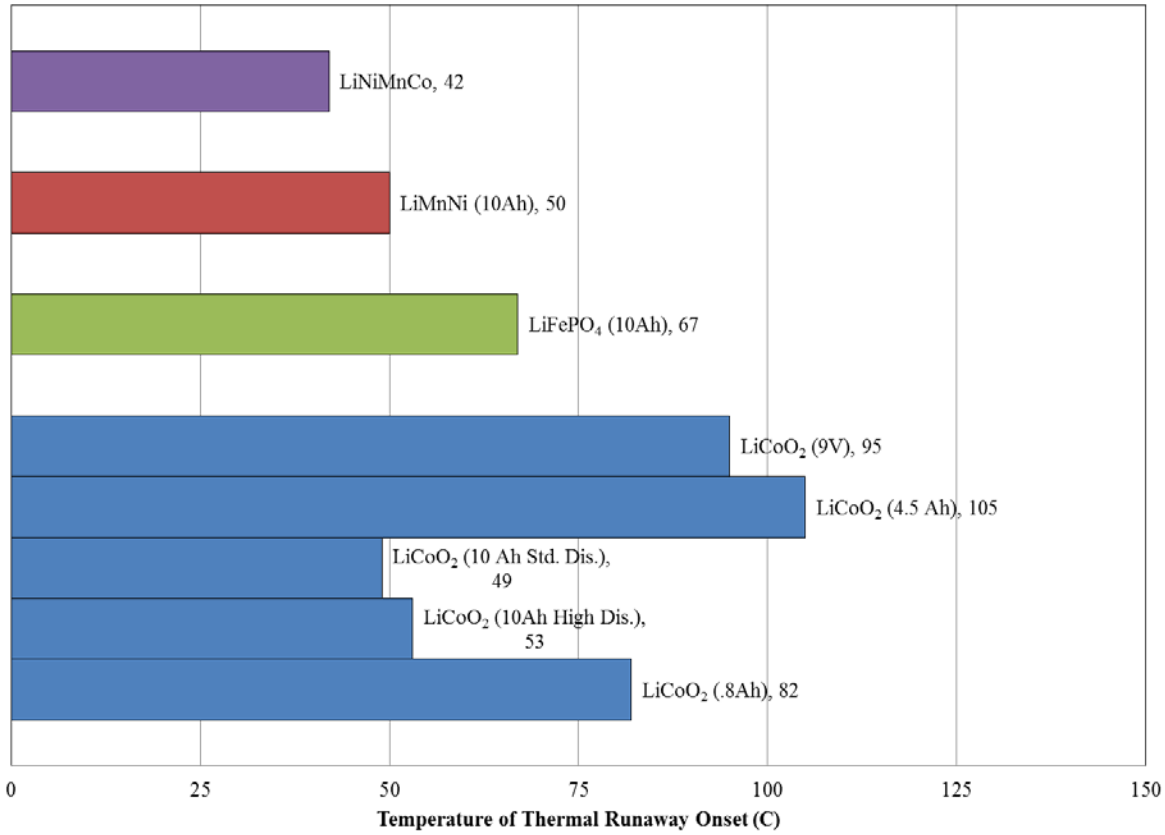


Figure 16. Onset temperature of thermal runaway from Li-ion-pouch cells

All of the cells that were tested off-gassed flammable vapors during thermal runaway that either self-ignited or ignited with the aid of the spark igniter. Self-ignition of the flammable gasses from the pouch cells was more common than for the Li-ion cylindrical cells. Figure 17 shows the results of the Li-ion pouch cell propagation tests. This figure shows the number of cells, out of the five that were physically connected together, that experienced thermal runaway. All of the cells, except for the $LiFePO_4$, achieved full propagation to all five cells. Thermal runaway of the $LiFePO_4$ cell did not propagate to any of the cells beyond the initial one that was in direct contact with the heater.

Though many of the pouch cells self-ignited in the tests, they may not do so in an installed aircraft application. If the pouch cells vented in a battery case, they may be less likely to ignite because the electrolyte content could be above the upper flammability content, preventing sufficient oxygen for combustion. The resulting accumulation of gases could be a greater hazard. The quantity of hydrocarbon gas that exhausted from the pouch cells increased almost linearly with increased capacity independent of the specific chemistries (see figure 18).

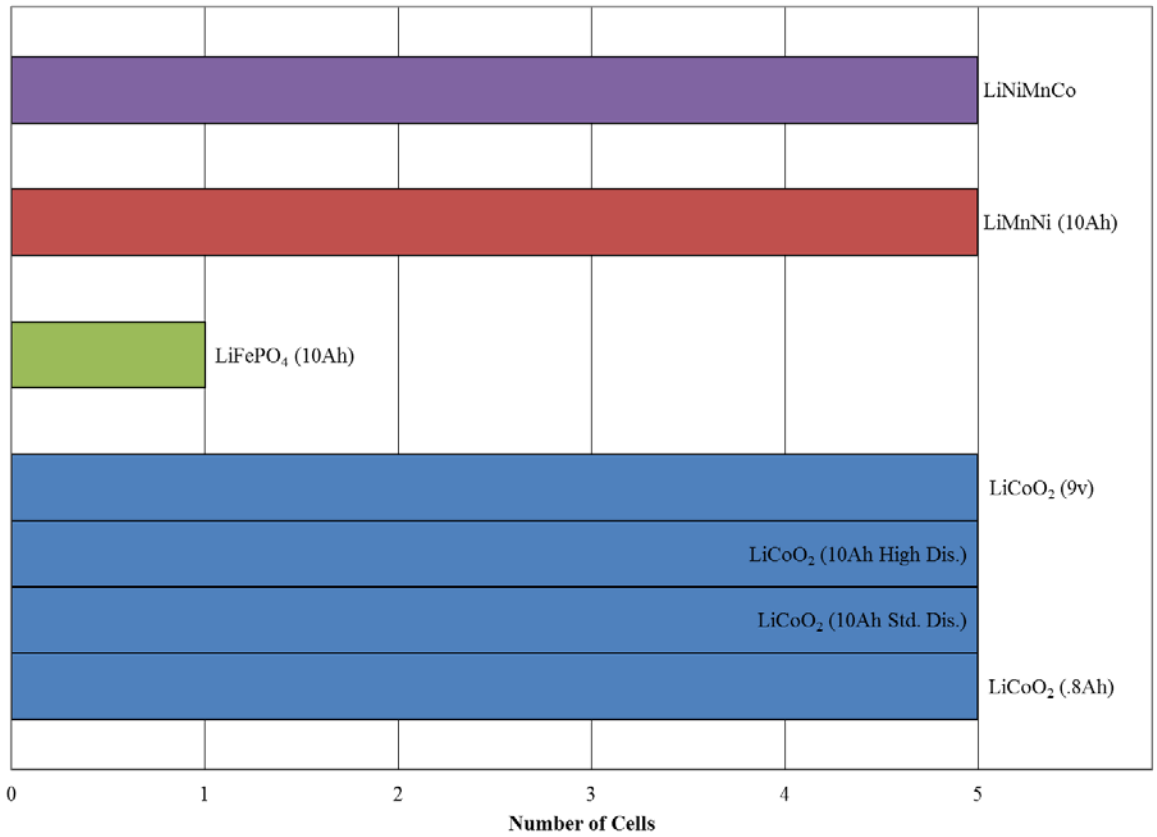


Figure 17. Number of Li-ion-pouch cells to have runaway in 5-cell propagation test (the propagation test was not run for the $LiCoO_2$, 4.5-Ah cells because an insufficient quantity was available)

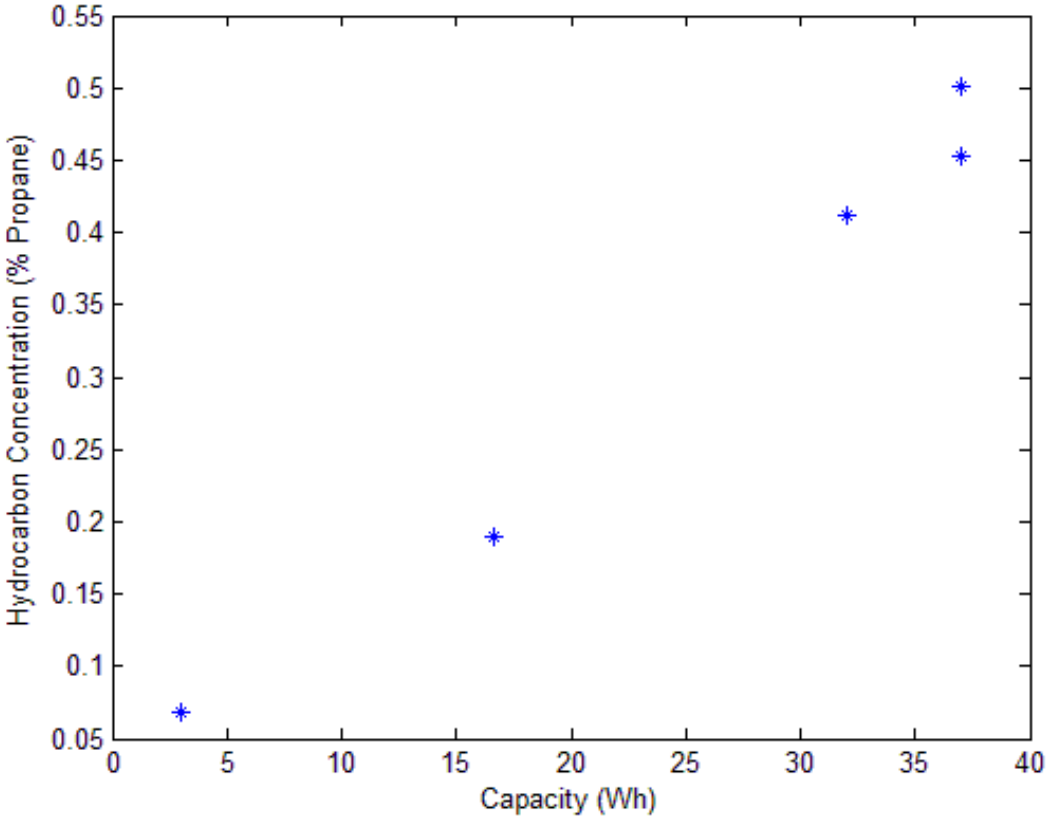


Figure 18. Measured hydrocarbon concentration as a function of Li-ion-pouch cell capacity

4.3 CYLINDRICAL LITHIUM-METAL TEST RESULTS

Figure 19 shows the recorded thermal runaway onset temperatures for the cylindrical lithium-metal cells. The average onset temperature of all of the lithium-metal cells was 212°C. The AA $LiFeS_2$ and the A-sized carbon monofluoride (CFx) cells exhibited the highest onset temperatures of 418°C and 403°C, respectively. The measured onset temperature of the AAA $LiFeS_2$ cell was more than 200°C lower than the AA $LiFeS_2$ cell. This difference in onset temperature points to significant variation within the same chemistry cell. The various $LiMnO_2$ and $LiSO_2$ cells showed some consistency among the onset temperatures, with averages of 182°C and 240°C, respectively.

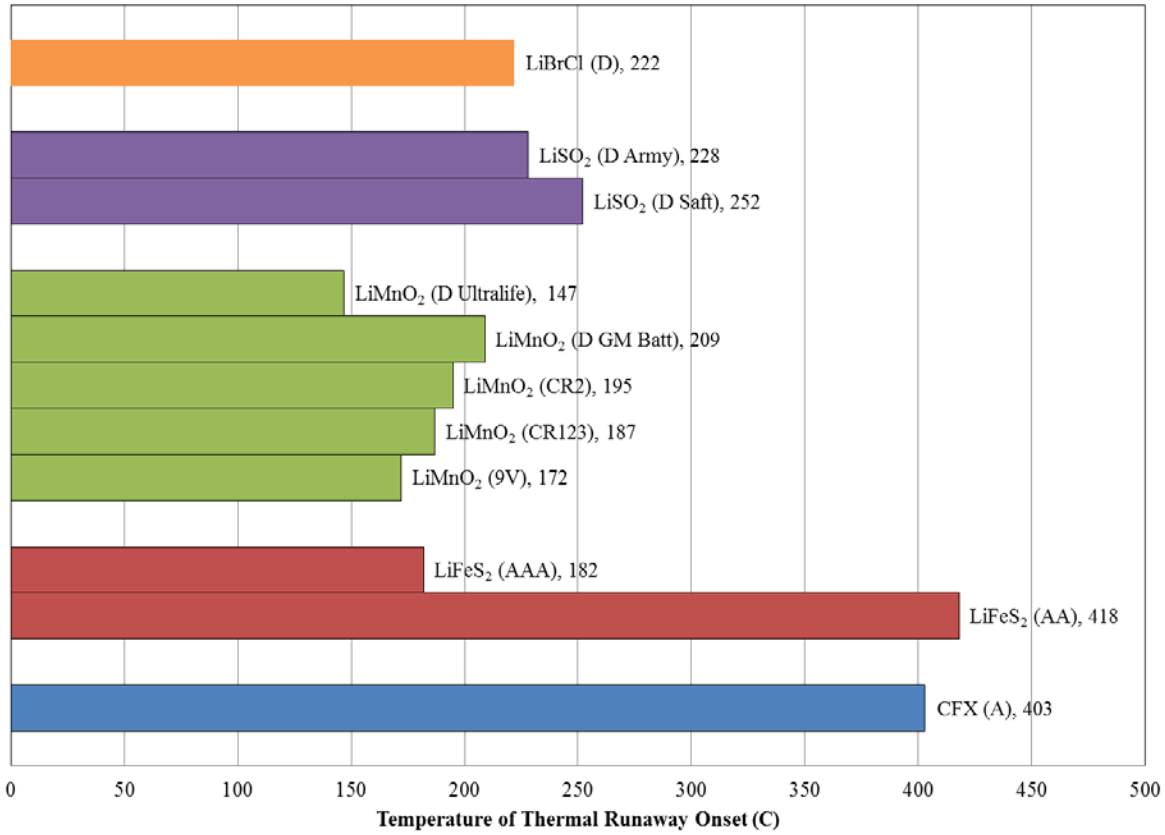
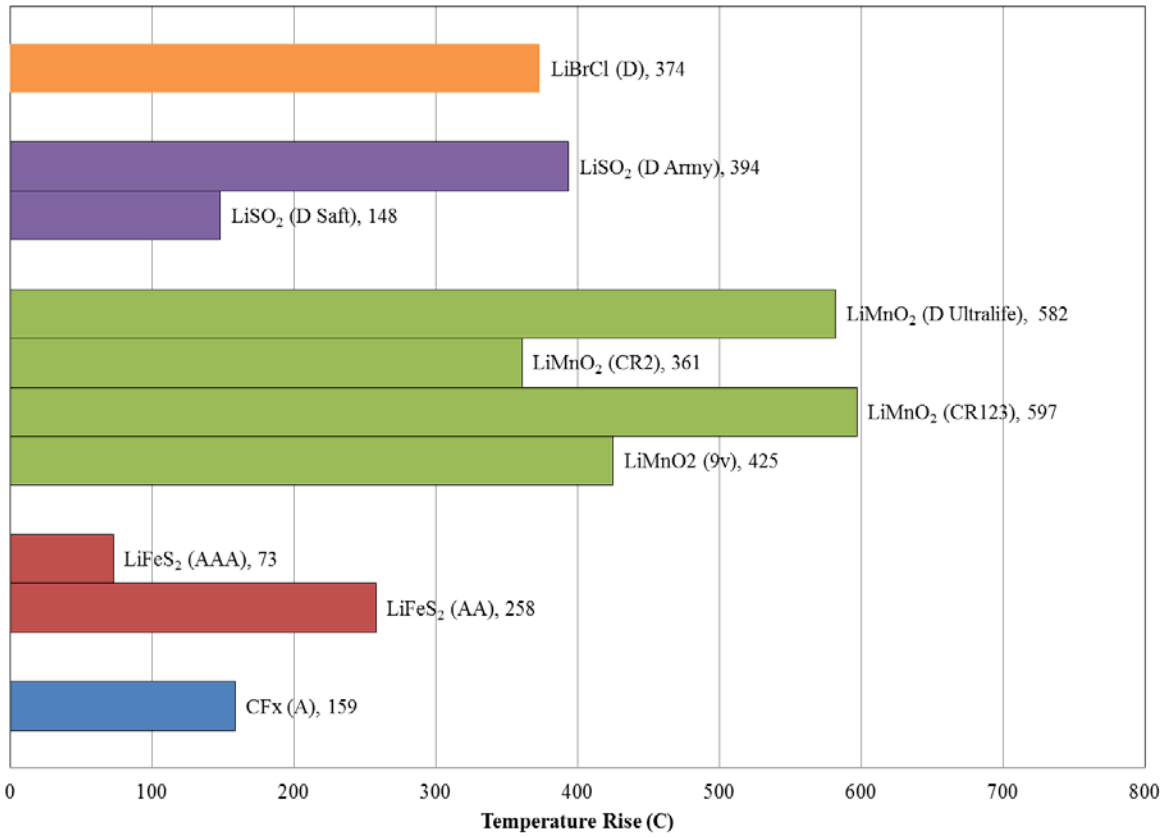


Figure 19. Onset temperature of thermal runaway from lithium-metal cells (all of the $LiSOCl_2$ cells were excluded because there was no thermal runaway event)



Chemistry and Size	Reason for Exclusion in Plot
$LiSOCl_2$, ½ AA	Cell exploded
$LiSOCl_2$, AA	Cell exploded
$LiSOCl_2$, C	Cell exploded
$LiSOCl_2$, D ER34615HD	Vented with no thermal runaway
$LiSOCl_2$, D TL-2300 D STD	Vented with no thermal runaway
$LiSOCl_2$, D LS33600BA	Vented with no thermal runaway
$LiSOCl_2$, D Xeno-XL-205F	Cell exploded
$LiSOCl_2$, DD ER3416125	Cell exploded
$LiMnO_2$, D GM Battery	Cell exploded

Figure 20. Temperature rise occurring from thermal runaway of lithium-metal cells

All of the lithium-metal cells that were tested, except for the $LiSOCl_2$, had flammable electrolytes that self-ignited without the need for an external ignition source. The $LiSOCl_2$ cells vented gas that did not ignite when placed directly under the igniter. Lack of ignition of the $LiSOCl_2$ cell was consistent with general knowledge that the electrolyte is not flammable.

Results of the lithium-metal propagation tests are shown in figure 21. Tests without any cells that experienced thermal runaway were tests in which the first cell exploded. Tests with one cell that experienced thermal runaway were tests in which thermal runaway was initiated but failed to propagate. Furthermore, in some of the tests, thermal runaway began to propagate but could not

sustain itself because of either a lack of sufficient heat or ejection of the core of the cell. When the cell exploded and released all of its internal contents, the outer case temperature dropped rapidly, greatly reducing the possibility of propagation. However, when the $LiSOCl_2$ cell was heated, it did not appear to have produced any of its own heat before it exploded.

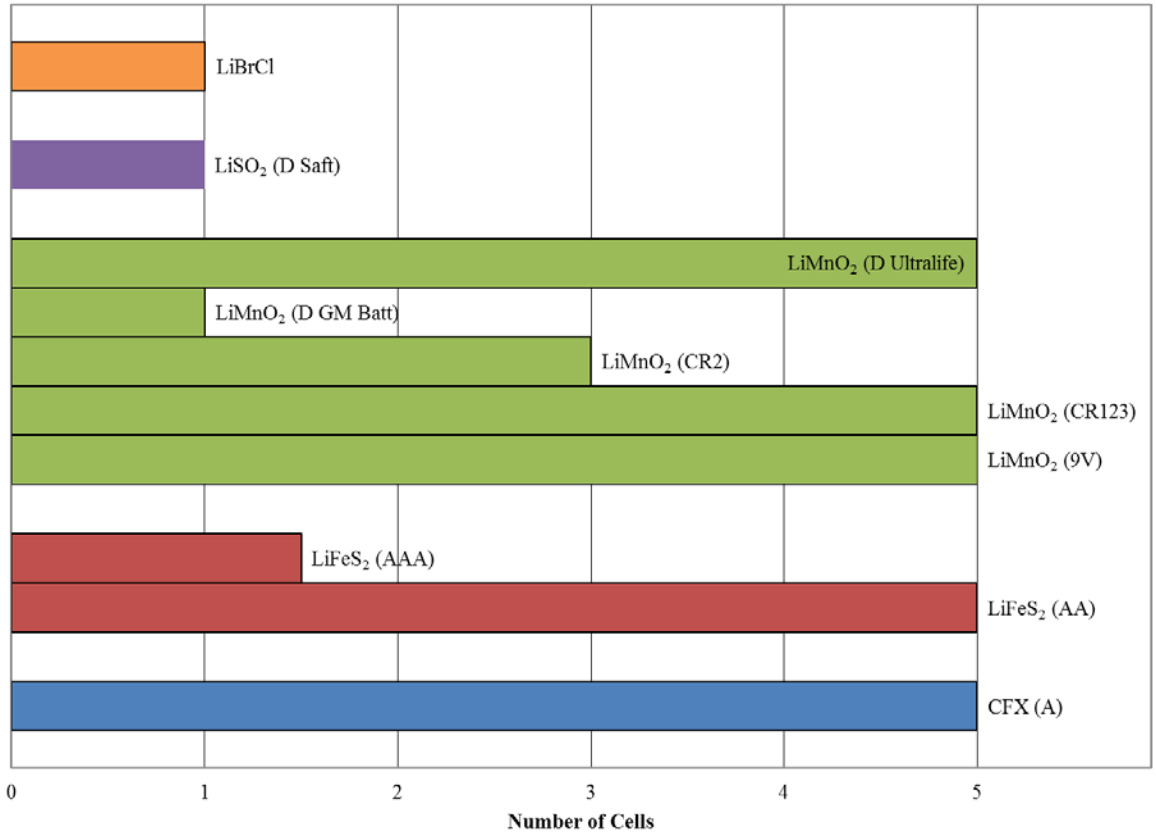


Figure 21. Number of lithium-metal cells to have runaway in 5-cell propagation test

Many batteries of the $LiSOCl_2$ chemistry were tested from a variety of manufacturers. Not all of the $LiSOCl_2$ cells exploded, and many slowly vented through designed vent ports. However, all of the cells without designed venting ports resulted in cell explosions. In addition, the $LiSOCl_2$ cells that gently vented did not show any indication of self-heating. However, for those that did explode, the increase in the internal cell temperature resulted in an increase of internal cell pressure. The internal pressure would rise to a point at which the cell case could no longer contain it, therefore, resulting in an explosion. This explosion was severe and resulted in a large release of toxic, though nonflammable, smoke. Explosion of a single D-sized cell resulted in a pressure rise of approximately 2.2 psi within the 10.8 m^3 chamber.

The LiBrCl cells also exploded in some of the tests. However, the LiBrCl cells showed a greater tendency to explode when oriented in a horizontal position than when they were positioned vertically. In four tests with a vertical orientation, three vented, and all three cells exploded in three tests with a horizontal orientation. This result may be because of the process of internal battery materials melting and clogging the vent ports.

The $LiFeS_2$ cells released flammable gas when heated, but a temperature increase to the ignition temperature of lithium (approximately 400°C) was often required before thermal runaway was achieved [4].

In general, the lithium-metal cells showed the greatest variability among the groups that were tested.

4.4 BUTTON CELL TEST RESULTS

Results of all of the button cell tests are summarized in table 4. In general, the button cells were much less energetic than the cylindrical cells. The only button cell that propagated was the 2025 $LiMnO_2$ cell, which propagated to two additional cells beyond the initial one that was placed into thermal runaway. Some of the cells resulted in flames/sparks during the thermal runaway event, but these were momentary in nature and did not appear to pose a significant safety concern.

Table 4. Summary of lithium button cell results

	Approximate Onset Temperature (°C)	Smoke during Runaway?	Flame/Sparks During Runaway?	External Ignition of Fumes/ Smoke?	Visible Swelling of Cells Prior to Runaway?	Propagation to how many cells?	General Observations
2450 LiMnO2 (Metal)	125	Yes	Flame and sparks	No	Yes	1	These were by far the most energetic, with a large (albeit very fast) flame/flash at the occurrence of event, and some sparking at times
2032 LiMnO2 (Metal)	80	Yes	Sparks	Yes	No	1	Flaming after event (at times sustained) occurred during some tests, but was very minor in nature
2025 LiMnO2 (Metal)	90	Yes	No	No	No	3	
2450 LiCoO2 (Ion)	135	Yes	No	Yes	Yes	1	Smoke was substantial at times

5. SUMMARY OF RESULTS

Testing was conducted to evaluate the fire hazards during attempted induced thermal runaway by overheating of a variety of lithium-ion, lithium-pouch, and lithium-metal battery cells with various cell cathode materials, sizes, and constructions. The results showed that the majority of cells had the potential to undergo thermal runaway. A major safety concern is 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 toxic gases and would have the potential to result in a dangerous situation, specifically in an aircraft. However, failure of cells that exploded was less likely to propagate to adjacent cells due to the fact that post-explosion there was no further heat being conducted 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 battery cells.

The relative safety of a lithium-metal cell may depend on the application. If, in a specific application, an explosion without fire would be a greater hazard, then a hermetically sealed cell without a safety vent, such as some of the $LiSOCl_2$ cells, would be the most hazardous case. However, if a fire would be more hazardous than an explosion, then $LiMnO_2$ would be the most hazardous chemistry. A $LiSOCl_2$ cell with a safety vent may be the safest cell for explosion and fire hazards, but $SOCl_2$ gas that could be released from the cell is also known to be dangerous to breathe. Otherwise, the $LiSO_2$ and $LiFeS_2$ chemistries were also relatively safe compared with $LiMnO_2$.

The button cells were much less energetic than the cylindrical or pouch cells. None of the button cells 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 present a fire safety concern.

Aside from the generalizations that were made, there was a large variability among tests. In addition, the hazard of cells in a specific aircraft application may be different than the hazards presented in this study. In addition to the cell chemistry, the resulting hazard would also depend on the materials that surrounded the battery pack, the spacing between the cells, the wiring of the battery pack, 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. There may, however, be exceptions such as button cells or some of the less reactive chemistries, constructions, and orientations.

6. REFERENCES

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