# The Performance and Safety of 20Ah Secondary Lithium cells; testing with the Accelerating Rate Calorimeter (ARC$^{TM}$)

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## 1. Introduction

The Accelerating Rate Calorimeter (ARC) gives adiabatic data on electrochemical cells. These tests fall under two main categories: Performance (non-destructive) testing and safety testing.

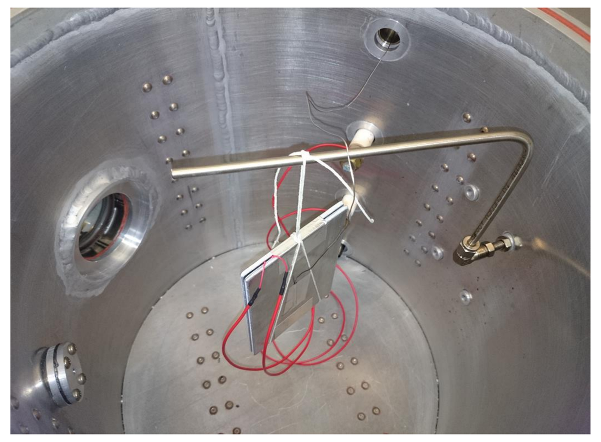
The advantage of the ARC is in its adaptability. An EV or EV+ ARC system with appropriate options can evaluate cells for both performance and safety.

This poster covers a range of tests carried out on two cells from different manufacturers using differing chemistries. Although both cells have the same amp-hour capacity, total stored energy (watt-hours) between the cells varies due to the difference in voltage resulting from the particular chemistries.

The two cells investigated here are both 20Ah. One cell is a 20Ah lithium NMC type manufactured by EIG while the other is a 20Ah lithium iron phosphate type produced by A123. The general industry consensus regarding these two cells is that iron phosphate is a "safer" chemistry than NMC, however the trade-off is a reduction in cell cycling performance.

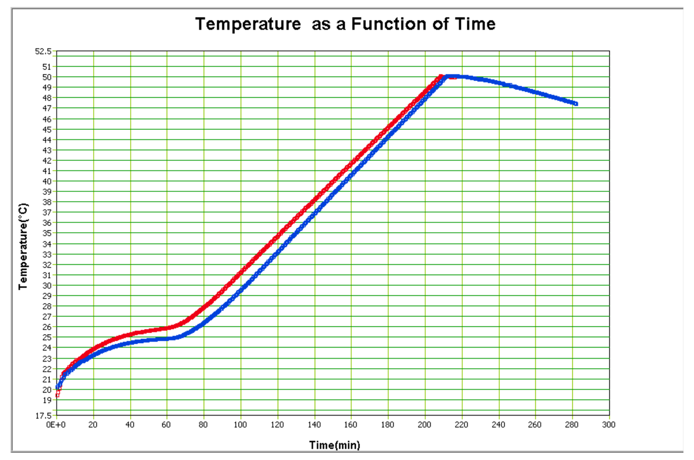
## 2. Heat capacity

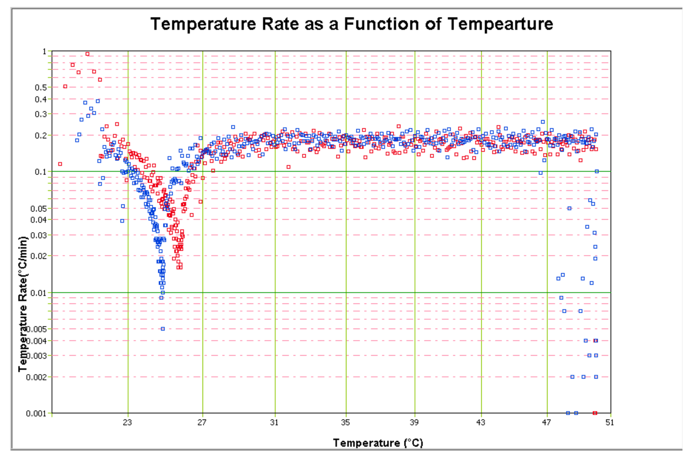
Specific heat capacity is applicable to a homogenous material, however the heat capacity of composites can also be measured. In this case the result is a combination of the specific heat of the materials making up the composite sample. The sample in question is an electrochemical cell. Heat capacity measurements on soft-case pouch cells, used in automotive applications, are simple to carry out in the ARC.



Two cells are placed either side of a thin kapton-insulated heating element. The shape of the heater is rectangular and should approximately match the cell dimensions.

The test protocol is straight forward— The ARC electronics will control the power supply, giving an appropriate power level in order to heat the cells at the specified temperature rate. The calorimeter chamber matches the cell temperature, so all heat from the element heats the cells, and no heat is lost from the cells to the environment. The temperature rise is therefore approximately linear:



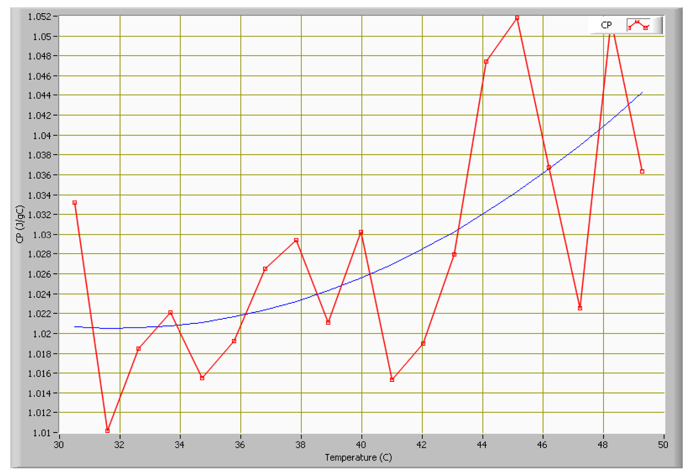




Heat capacity data from the ARC is shown above. Simple visual inspection of the temperature graph is not useful for analyzing the results because the mass of the cells and the input power to the heating element varies. Taking these two parameters into consideration gives results of heat capacity against temperature. The graph then gives a discrete Cp value for data averaged for every 2°C temperature increase. At 35°C the Cp values of the cells are:

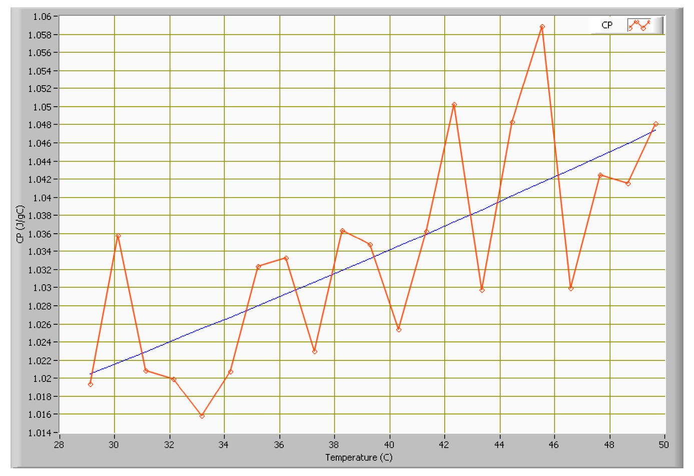
**LiFePO4: 1.03 J/gK** **Li NMC: 1.04 J/gK**

Graphical Cp values versus temperature are shown below:

**LiFePO4:**

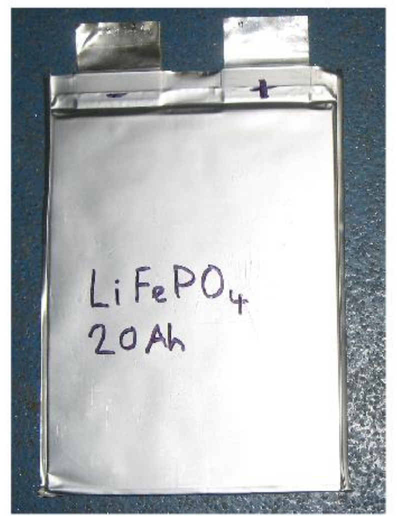


**Li NMC:**



CP Table

| Temperature (C) | CP (J/gC) |
|---|---|
| 30.506000 | 1.033188 |
| 31.573000 | 1.010142 |
| 32.609000 | 1.018475 |
| 33.665000 | 1.022148 |
| 34.709000 | 1.015487 |
| 35.769000 | 1.019201 |
| 36.818000 | 1.026491 |
| 37.835000 | 1.029406 |
| 38.898000 | 1.021062 |
| 39.960000 | 1.030215 |
| 40.987000 | 1.015307 |
| 42.034000 | 1.018954 |
| 43.057000 | 1.027980 |
| 44.121000 | 1.047403 |
| 45.140000 | 1.051835 |
| 46.182000 | 1.036717 |
| 47.214000 | 1.022569 |
| 48.240000 | 1.051595 |
| 49.270000 | 1.036373 |

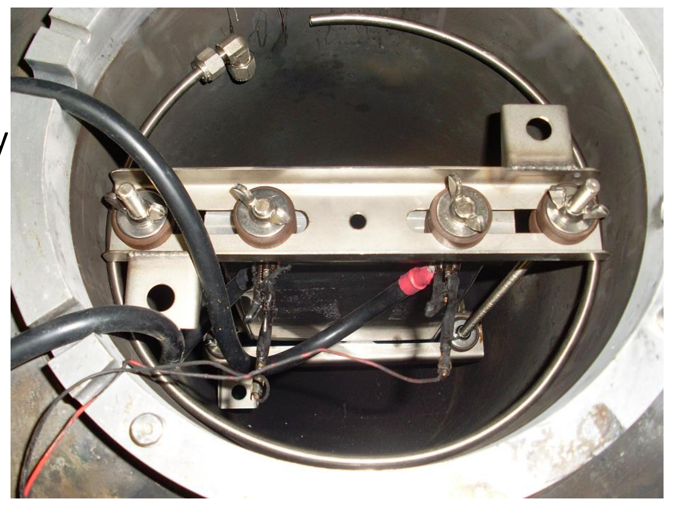



CP Table

| Temperature (C) | CP (J/gC) |
|---|---|
| 29.089000 | 1.019343 |
| 30.111000 | 1.035775 |
| 31.122000 | 1.020865 |
| 32.134000 | 1.019954 |
| 33.175000 | 1.015891 |
| 34.192000 | 1.020783 |
| 35.218000 | 1.032377 |
| 36.230000 | 1.033315 |
| 37.251000 | 1.022968 |
| 38.275000 | 1.036370 |
| 39.279000 | 1.034728 |
| 40.299000 | 1.025428 |
| 41.313000 | 1.036234 |
| 42.326000 | 1.050279 |
| 43.346000 | 1.029770 |
| 44.453000 | 1.048339 |
| 45.553000 | 1.058904 |
| 46.571000 | 1.029949 |
| 47.645000 | 1.042464 |
| 48.656000 | 1.041575 |
| 49.662000 | 1.048106 |

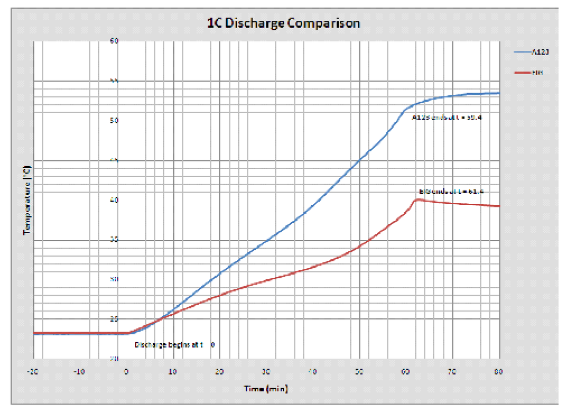

## 3. Performance (cycling) tests

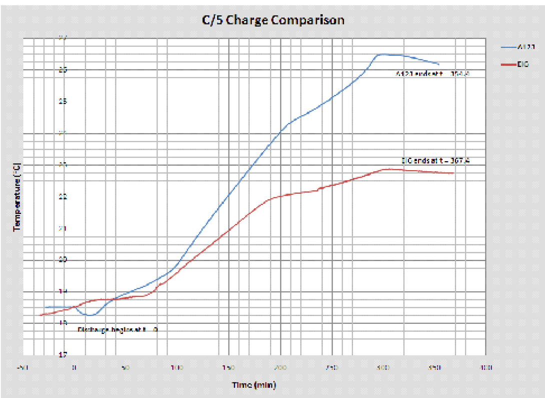
With knowledge of the cell average heat capacity, cycling tests carried out in the ARC become more useful because the heat generation of the cell during charging or discharging can be quantified. For real world applications, lower heat generation is generally preferred. This means a more efficient cell and a reduction in the cooling requirements for the battery system.

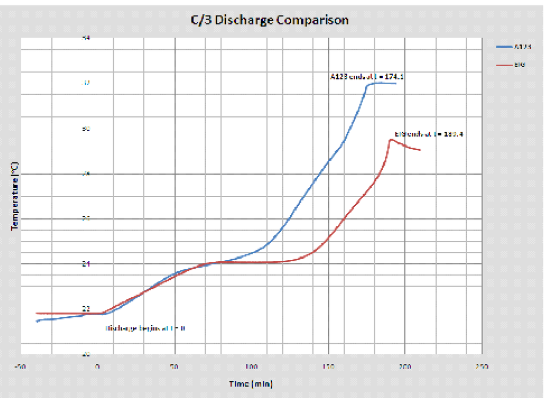


Cycling tests in the ARC are carried out on a single cell. The cell terminals are secured with large aluminium clamps to ensure effective current transfer while the cell is held securely within a metal frame inside the calorimeter chamber.

Cables enter the chamber via a special collar or through current connectors built into the calorimeter. In this case, a simple C/5 (4A) charge (CCCV), 1C (20A) and C/3 (6.7A) discharge (CC) for both cells was compared. Larger currents can be applied using appropriate cables. Integrated cyclers may be provided with the calorimeter system. Any stand-alone cycler can be use in conjunction with ARC but data from the two instruments must be manually synchronized in time. Below is the charging and discharging data from both cells plotted together for comparison. In all cases the lithium iron phosphate cell from A123 produced more heat (greater temperature rise) during the electrical process. The difference in results is examined in greater detail in the tables below.




| Cell | A123 | EIG | A123 | EIG | A123 | EIG |
|---|---|---|---|---|---|---|
| Advertised Capacity | 20Ah | 20Ah | 20Ah | 20Ah | 20Ah | 20Ah |
| Charge Rate | C/5 | C/5 | C/3 | C/3 | 1C | 1C |
| Charged Capacity | 19.56Ah | 20.71Ah | 19.18Ah | 20.85Ah | 19.79Ah | 20.49Ah |
| Charge Time | 354.42 min | 367.38 min | 174.08 min | 189.38 min | 59.37 min | 61.42 min |
| Minimum Voltage | 2.00V | 3.00V | 2.00V | 3.00V | 2.00V | 3.00V |
| Maximum Voltage | 3.60V | 4.15V | 3.60V | 4.15V | 3.60V | 4.15V |
| Av. Charge Power | 11.21W | 12.91W | 20.59W | 23.85W | 58.97W | 71.70W |
| Temperature Increase | 8.39K | 4.36K | 10.26K | 7.74K | 30.21K | 16.84K |
| Maximum Temp Rate | 0.042K/min | 0.028K/min | 0.20K/min | 0.38K/min | 0.91K/min | 1.23K/min |
| Average Temp Rate | 0.032K/min | 0.019K/min | 0.059K/min | 0.041K/min | 0.51K/min | 0.27K/min |
| Battery Mass | 495g | 422g | 495g | 422g | 495g | 422g |
| Heat Capacity Estimate | 1.05 J/gK | 1.05 J/gK | 1.05 J/gK | 1.05 J/gK | 1.05 J/gK | 1.05 J/gK |
| Enthalpy of Discharge | 8.81 J/g | 4.58 J/g | 10.77 J/g | 8.13 J/g | 31.72 J/g | 17.30 J/g |
| Average Heat Power | 0.28W | 0.14W | 0.51W | 0.30W | 4.42W | 1.99W |
| Average Efficiency % | 97.56% | 98.93% | 97.58% | 98.76% | 93.03% | 97.29% |

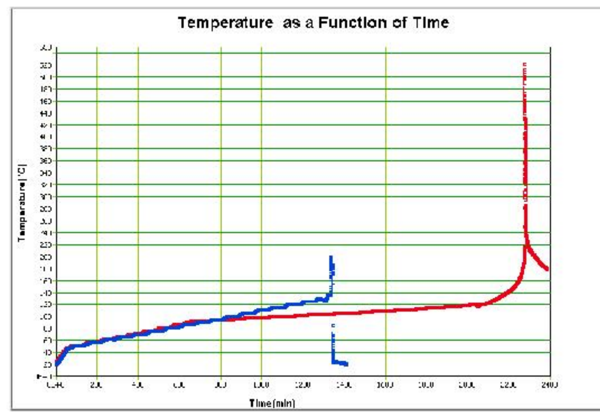
## 4. Cell Safety Testing

The next stage is to use the ARC to carry out safety tests on both cells. These tests can simulate conditions that may occur in real world use if there is a failure in the control systems of the battery pack, or if there is major physical damage to the pack. Heat generated from one cell cannot pass to adjacent cells as there is a uniform temperature throughout the pack. Data obtained is in adiabatic conditions.

The most fundamental ARC safety test is a heat-wait-seek test which establishes the onset of self-heating in the cell by increasing the cell temperature in uniform steps. The various components that make up the cell may begin to react at different temperatures. Different chemistries can have different onset temperatures and "safer" chemistries should have higher onset temperatures, as well as giving out less energy during decomposition. Differences in speed of reaction (kinetics) are also important when evaluating safety.

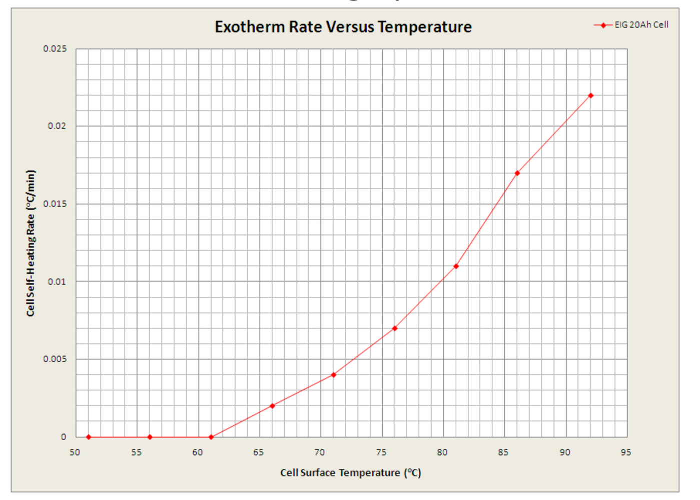
The testing carried out on these two cells used a standard heat-wait-seek methodology. Both cells are charged to 100% SoC. Each cell is heated then held at the starting temperature for around 45 minutes to check for self heating. If self-heating exceeds the sensitivity threshold, the ARC tracks the reaction. If it does not, the temperature is increased again and the process is repeated. The starting temperature was 50°C, the temperature step was 50°C and the exotherm sensitivity was 0.02°C/min.

The cell was held in a steel frame suspended from the calorimeter lid with small diameter wires connected to the cell terminals to monitor the voltage during the test. The test finishes when the decomposition reaction is complete. Below— Iron phosphate cell on the left, NMC in the middle. Comparative data is shown on the right:




There was a considerable difference between the response of the two cells in these tests. Above right is the ARC temperature data of each test plotted together. The LiFePO4 cell is in blue and the Li NMC cell is in red.

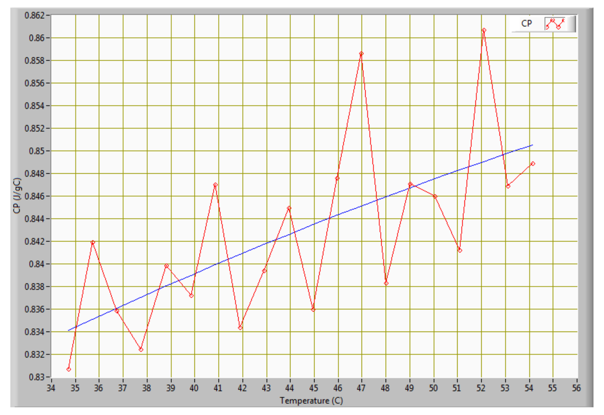
The height of the peak is proportional to the energy released in decomposition. Therefore the NMC cell decomposition is more energetic. Although somewhat difficult to see on the above graph, the NMC cell exceeded the 0.02°C/min sensitivity threshold at 90°C, however slower self-heating (0.002°C/min) was seen from temperatures as low as 65°C. In contrast the Iron Phosphate cell exhibited no self heating until the very rapid decomposition reaction at 135°C. Self-heating rate versus temperature for the NMC cell is plotted to the right.

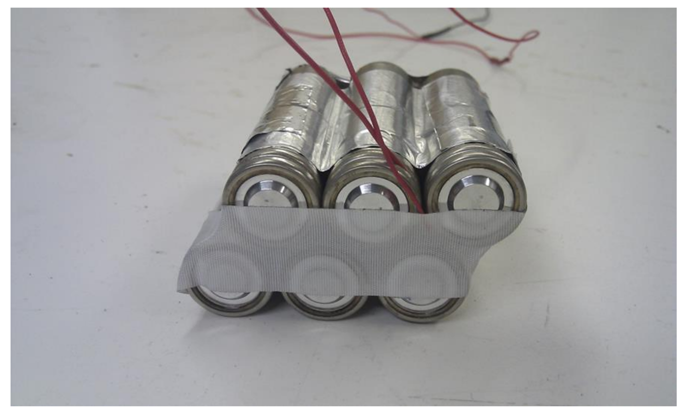



## 5. Further Work – 18650 comparison

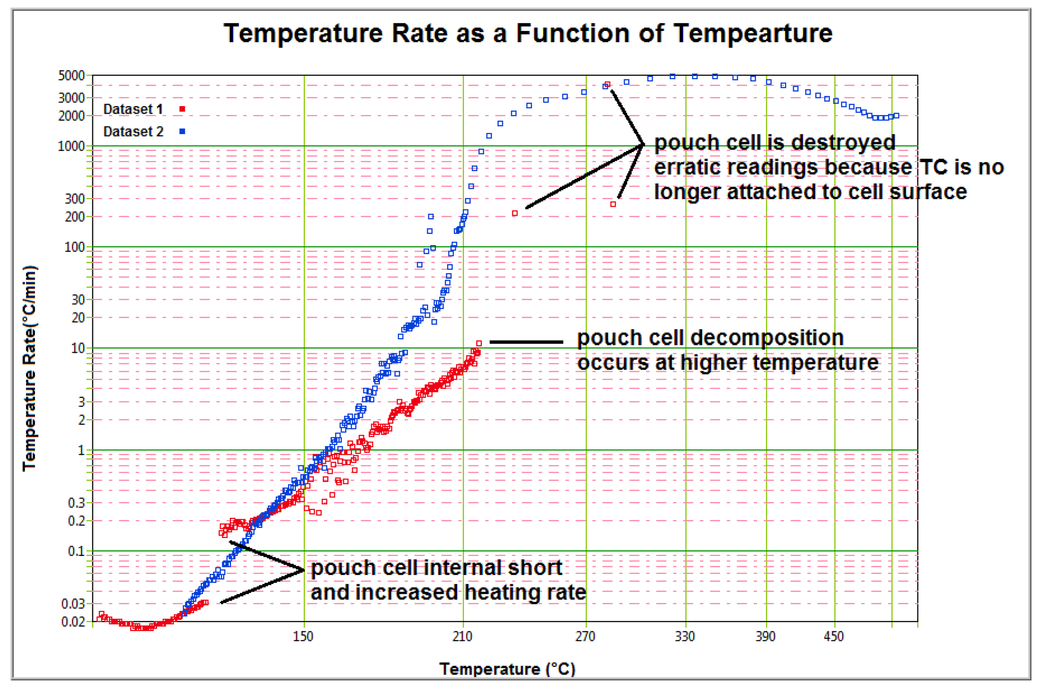
Comparison between cell chemistries is a particular area of study where the ARC can work as a useful evaluation tool, the instrument's sensitivity and accuracy allows the detection of subtle difference between cells. For example, the effect of repeated cycles on a cell's thermal stability may be analysed using the heat-wait-seek protocol to evaluate how stability changes with the age of the cell.

Examining the effect of cell scale-up is also possible. Will an 18650 cell have the same thermal profile as a much larger automotive-size cell? Below is the heat capacity result for metal-oxide 18650 cells. The results from this test and others carried out in the ARC indicate these cells have a 10-20% lower heat capacity value over their operational temperature range compared to pouch cells of the same chemistry. The test on both sizes of cells were carried out in the same calorimeter.





The graph below is a comparison of ARC thermal runaway data from a commercially available high-capacity 18650 cell and the EIG 20Ah pouch cell detailed earlier.




There are several key differences resulting from the variations in cell design. The pouch cell shows a more pronounced internal short when the separator layer melts, however cell decomposition occurs at a higher temperature for the pouch cell.

The 18650 decomposition is linked to the cell venting which is designed to occur through the burst disk when significant pressure builds up inside the cell. The pouch cell has no dedicated vent so the entire cell is blown apart by the decomposition.