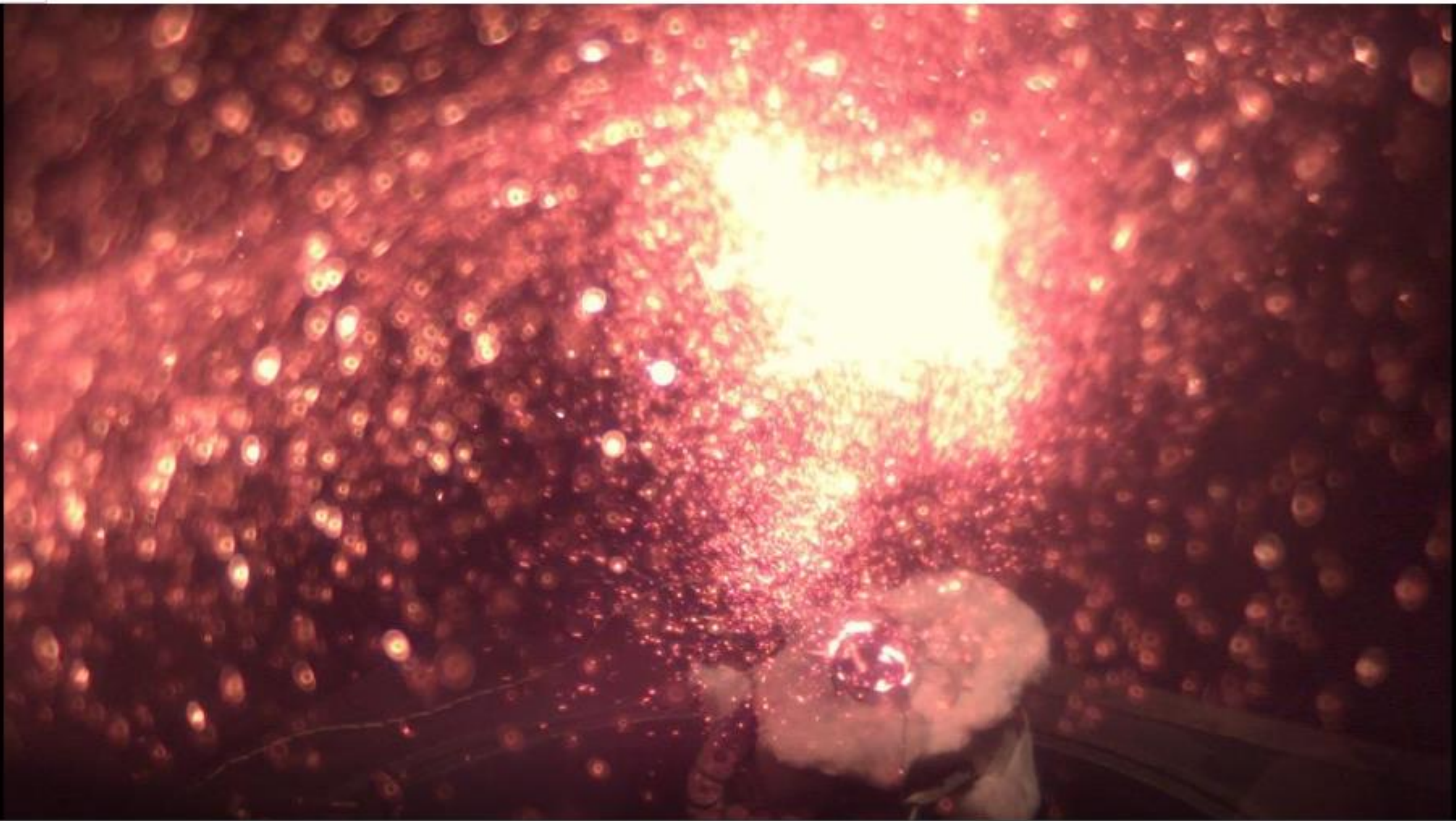
Battery ARC Test Design and Data Analysis



1 North House • Bond Avenue • Bletchley
MK1 1SW • UK Tel +44 1908 646800
Email: danny@thtuk.com • Web www.thtuk.com

Danny Montgomery
Thermal Hazard Technology
October 2020

Lithium Battery Safety & Performance

Thermal Issues With Lithium (and other) Batteries

These can be separated into two main types:

Battery Performance – how the battery operates under intended use conditions

Battery Safety – what happens when the battery is exposed to adverse conditions

Assess the hazardsafely in the lab

To help safe design for normal use

The THT ARC helps to address both these areas. Performance testing ensures in normal use the battery stays within a safe operating window.
Safety testing helps to quantify the hazard so thermal runaway avoided and/or protected against.

Types of ARC Safety Test:

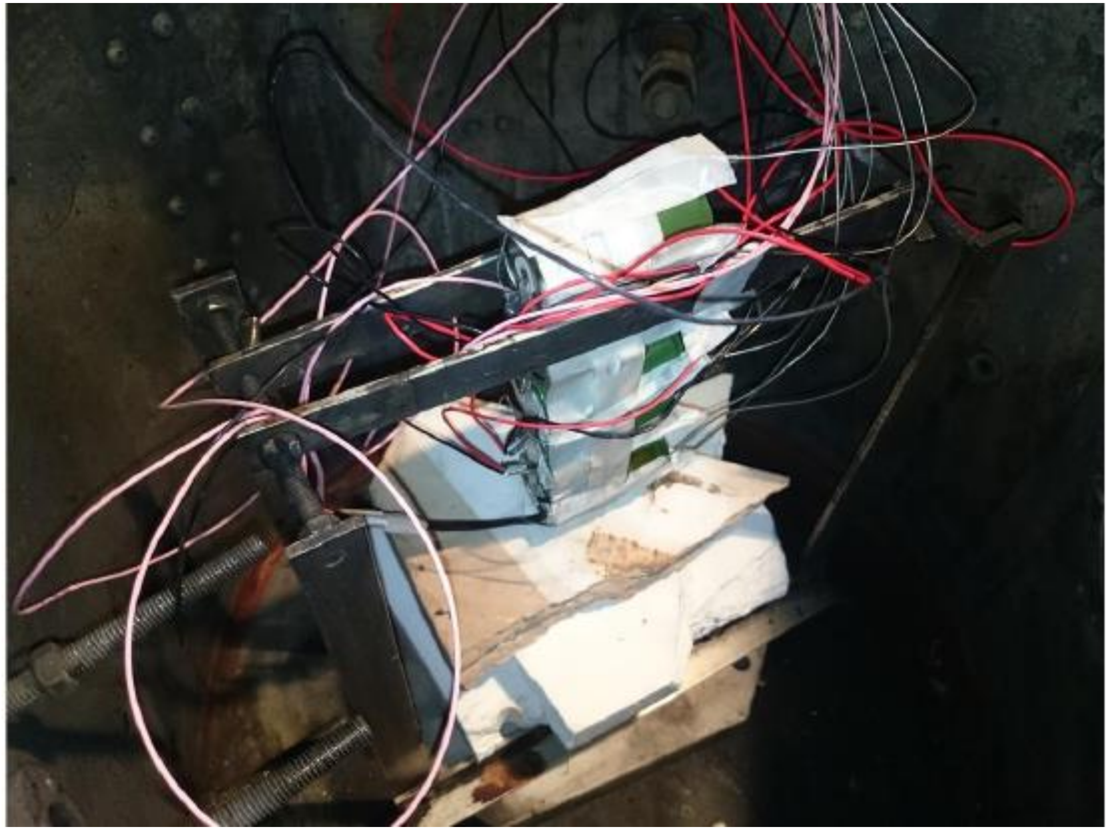
- Ramp heating
- Step heating (heat-wait-seek)
- Hotbox/oven
- Short circuit (external)
- Nail penetration/crush (internal short)
- Overcharge

Additional Measurements:

- Internal cell pressure
- External pressure (pressure vessel)
- Gas collection
- Cell voltage
- Multiple thermocouple
- Overcharge current
- Short-circuit current
- Optical video
- IR video

Types of ARC Performance Test:

- Cycling tests (adiabatic)
- Cycling tests (isothermal)
- Specific heat capacity test
- Thermal stability



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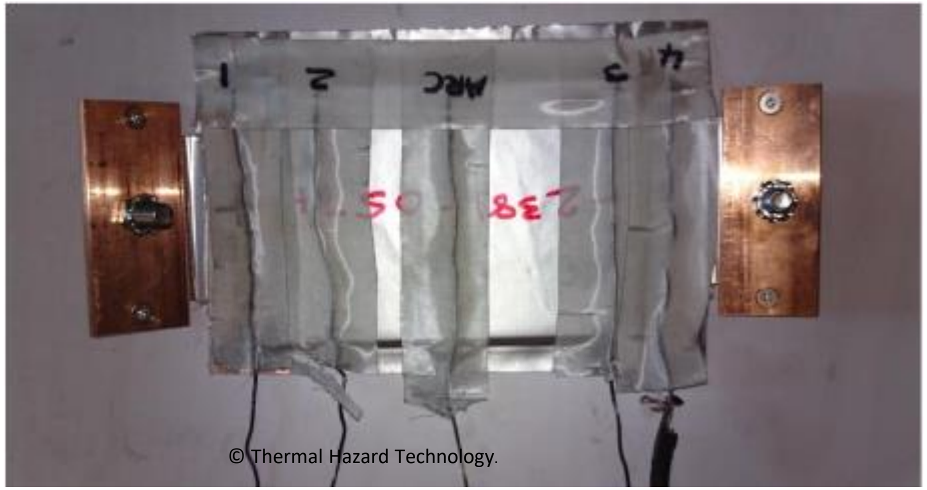
Consider before you start…

Calibration – A good calibration is required if carrying out a Heat-wait-seek tests, or tests where thermal stability is important (for example a cycling test or tests with lower rates of heating).

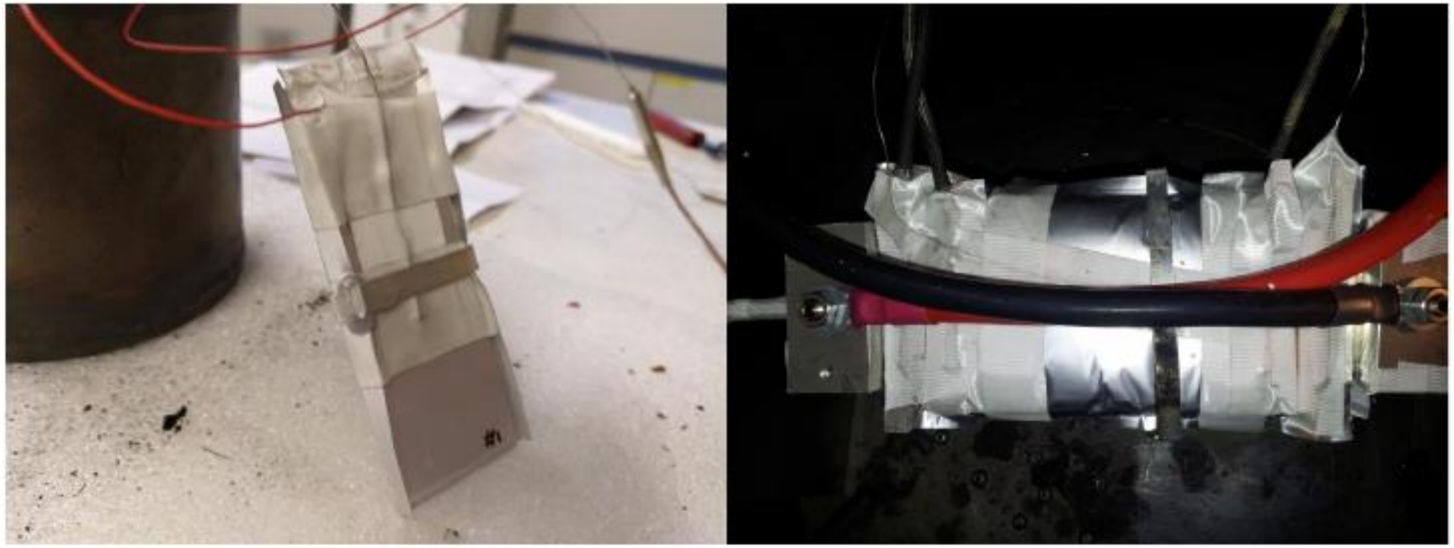
Thermocouple care – Take care when adding/removing the bomb thermocouple. The thermocouples are strong enough to survive thermal runaway but will not survive repeated bending. If it breaks then the system has to be recalibrated.

Attaching thermocouples – A key point. If the thermocouple is not well connected, it can come off the cell during the test and the results will not be representative.

Example of poor thermocouple attachment – tape does not go all around cell diameter so it can simply lift off during the test as the cell expands (but this is ok for cycling tests at lower temps).



Example of good thermocouple attachment – tape combined with aluminium band around cell diameter keeps thermocouple secure even if cell expands

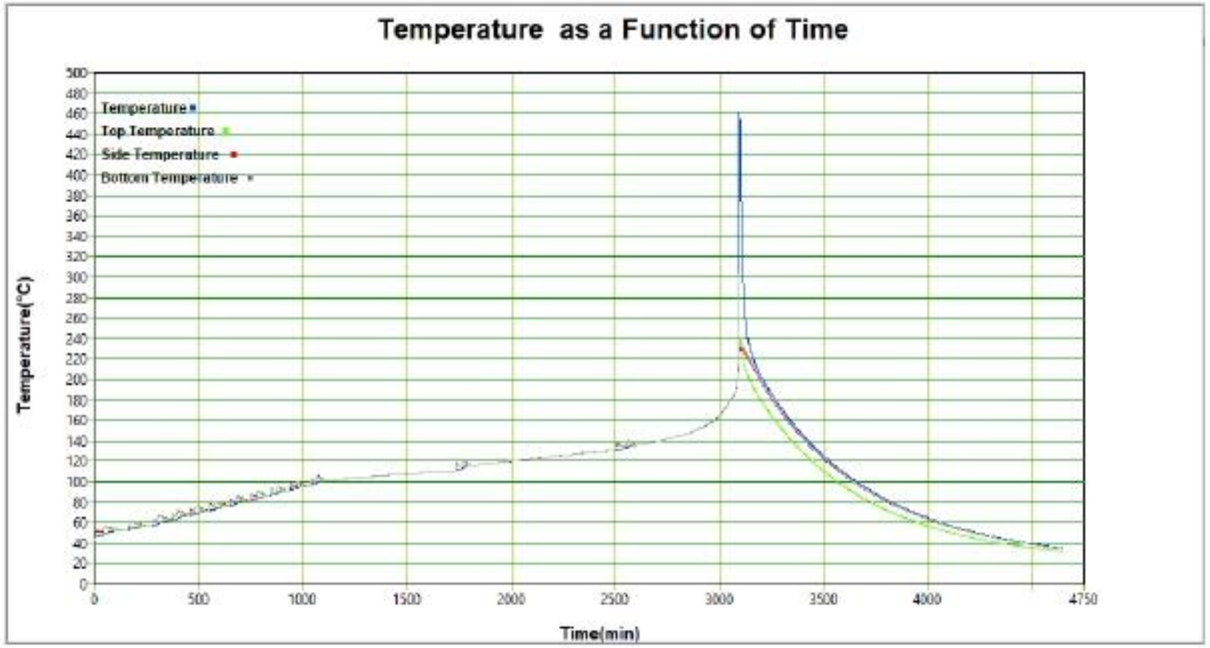


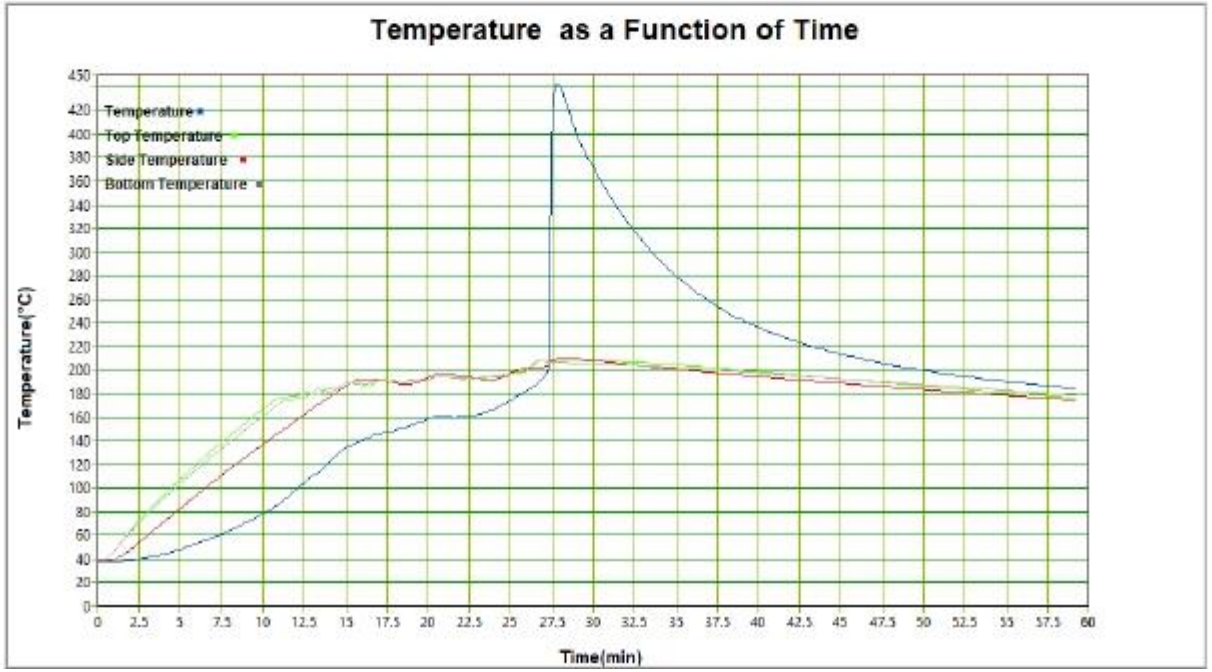
Thermal Safety Testing

Two main methods:

~~1. Step heating or “heat wait seek”~~
This is the classic ARC adiabatic method. It is a slow test, but it allows accurate detection of reaction onset, and complete tracking of the cell reaction
Typical test time: 1-2 days

~~2. Ramp heating~~
This is a much quicker thermal abuse which is designed to achieve thermal runaway in a short time
The cell decomposition can be analysed, but accurate onset temperature cannot be measured. In a ramp heating test, the cell undergoes excess heating. The test is not adiabatic. Typical test time 1-2 hours.



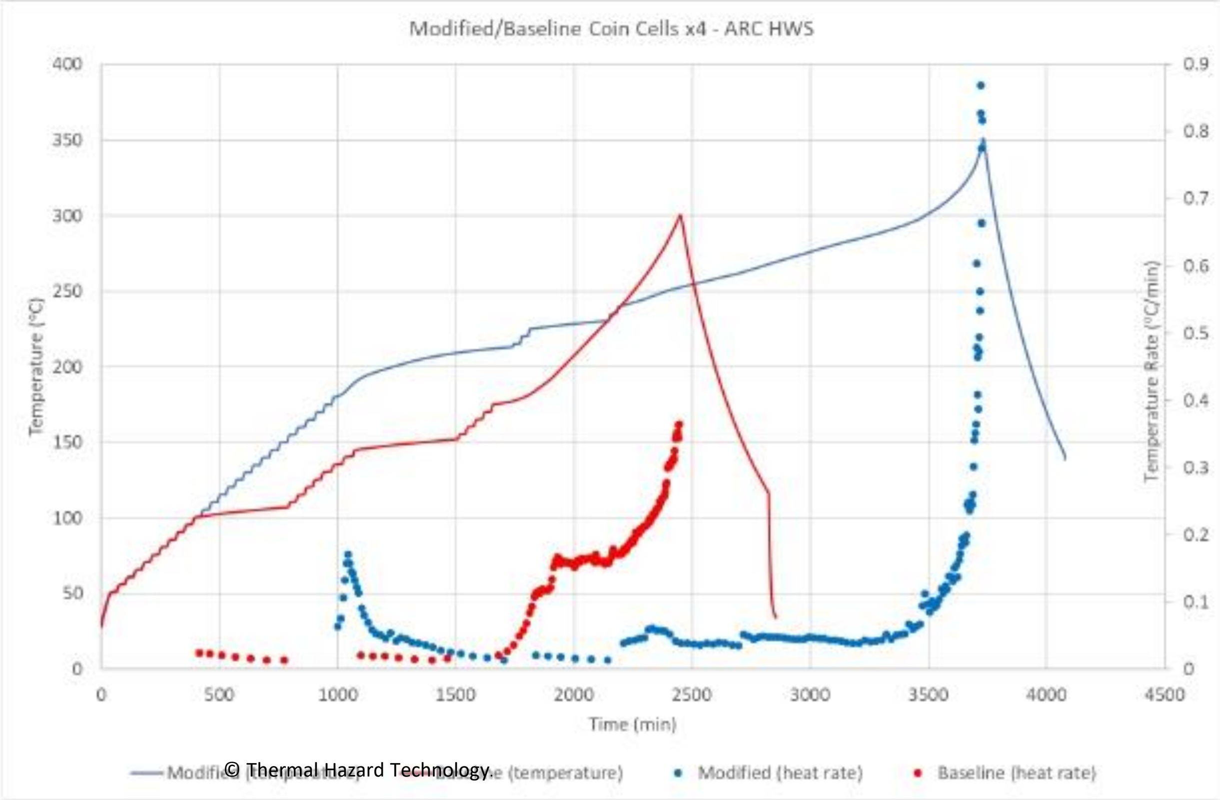


Coin Cell Testing

Coin cells and mono cells (thin cells with a single cathode/anode layer) produce a very small amount of heat from decomposition because they have a small mass of active component.

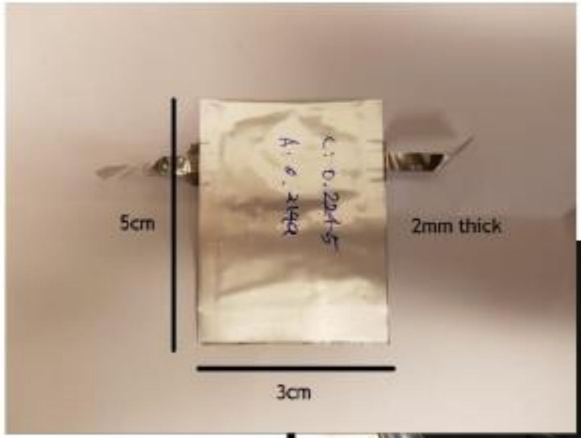
A coin cell has a smaller % mass of active material compared to larger cells. The steel cell case make up a relatively large % of the cell mass. This makes it more difficult to obtain good thermal data.

contain heat and reactive components.

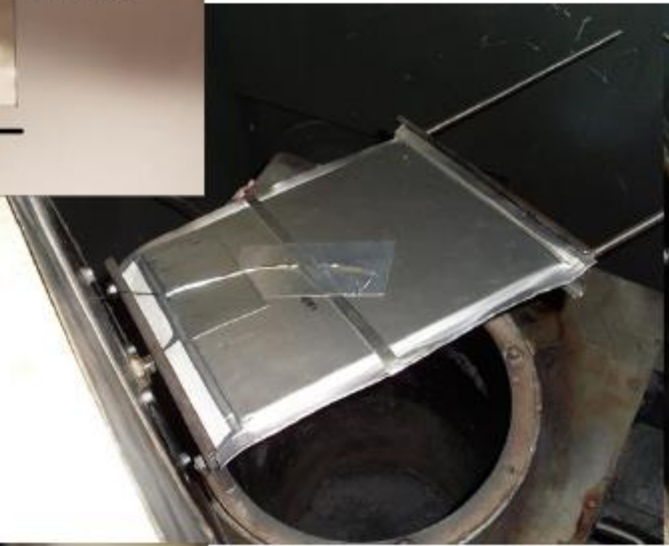


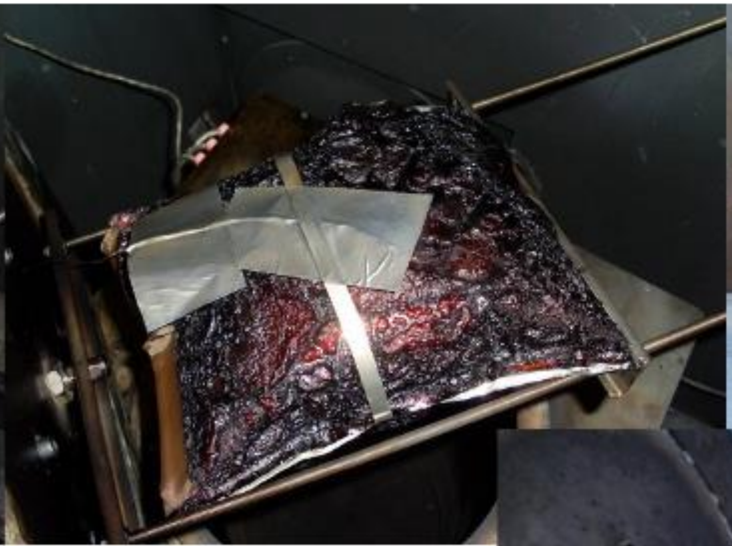
Results can be improved by using two or more cells together for one test with the thermocouple placed between the cells. Using a thinner diameter thermocouple also helps as does wrapping the coin cell stack in insulatingtape to

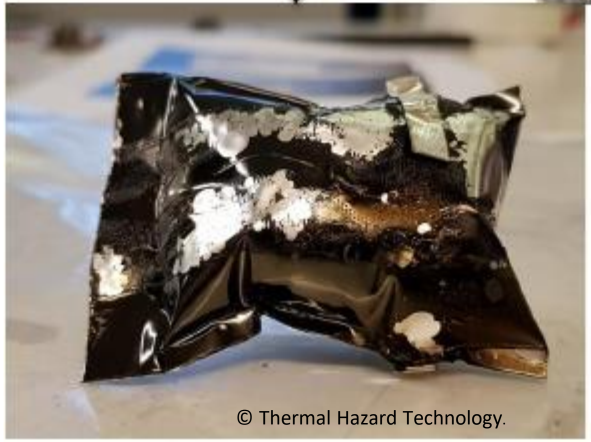
Pouch Cell Testing



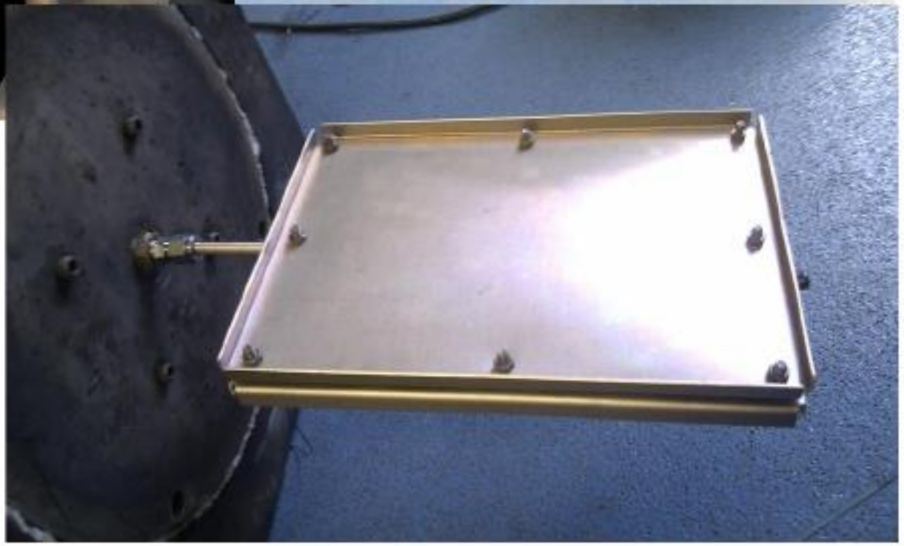
The key consideration when testing pouch cells is whether or not to clamp the cell between two metal plates. A pouch cell has a flexible case which “balloons” due to internal gas generation at higher temperatures. This process can affect the thermal profile as cell layers move apart from each other. Clamping the cell prevents this and generally gives more repeatable results.





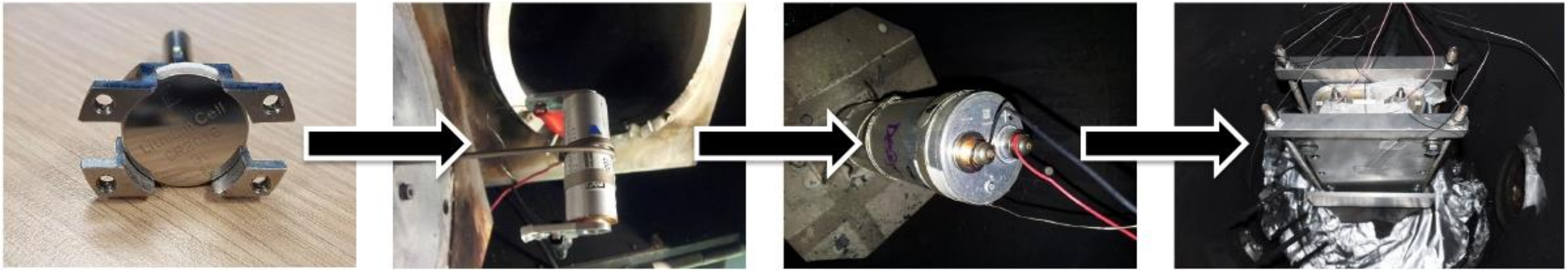


Clamping the cell also simulated the conditions seen in the battery pack where the cell is constrained by adjacent cells. However – the clamps act as a thermal sink and thus the reaction is partially subdued by this heat transfer. Results must be corrected using the **phi-factor**which considers the thermal mass of the plates (more on this later).



Scale-Up

Scaling up the sample in battery testing. If we test a coin cell, can we scale the result to an EV battery? This is not so straightforward, because the sample is heterogeneous, and the cell design will change the thermal response. There will be similarities between thermal profiles for cells of the same chemistry but they may not be directly comparable.



0.1Ah 5Ah 30Ah 130Ah

Some cells have a burst disk for pressure relief, others do not. Pouch cells expand during a reaction which may change the reaction profile. There are many design differences between cells from different manufacturers. Coin cells have a very high ratio of cell case to active material so low temperature reactions will be difficult to detect.

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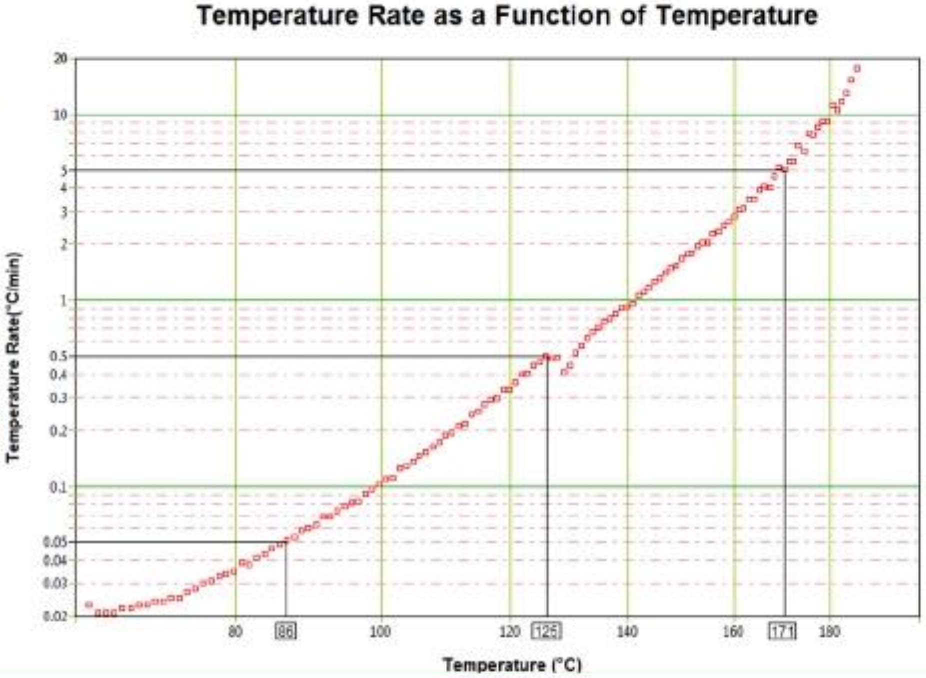
Thermal safety testing

Although the test is takes a long time, it can be sped up in several ways:

1. **Reduce wait time** (the wait time should not be reduced too much or false exotherm can be detected.
2. **Increase temperature step** (default is 5ºC, using 10 instead will reduce test time in the H-W-S phase by 50%). For “QC” type testing, 10ºC is ok.
3. **Decrease sensitivity**. If the ARC detects a reaction at 0.02ºC/min, this rate of reaction will take 50 minutes to increase the sample temperature 1ºC. If you instead choose 0.1degC/min you select a reaction rate 5 times fast, you have missed a lot of the slower, lower temperature reaction and reduced test time (but keep in mind the data from these lower temperature reactions can be useful when comparing cells).
4. **ES-ARC software version 7.0.1** implemented a faster heating algorithm. This considerably speeds up the time taken to reach the start temperature.

Karlsruhe Institute of Technology (KIT) – Calorimetry Lab



0.02ºC/min
Standard onset temperature for ARC tests

0.05ºC/min
Reaction onset avoiding electrolyte reaction in li-ion

5ºC/min
Sometimes considered as a critical point beyond which the reaction cannot be prevented

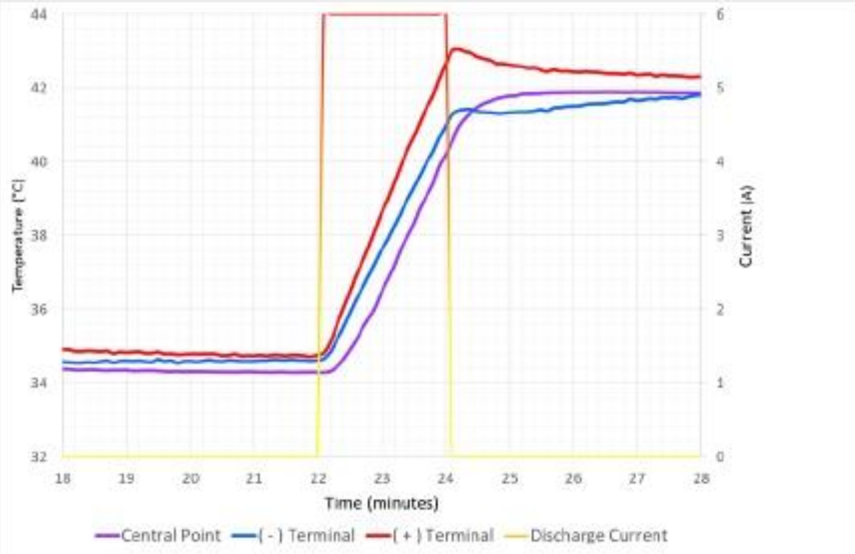
15ºC/min
Maximum tracking rate of EV+ calorimeter

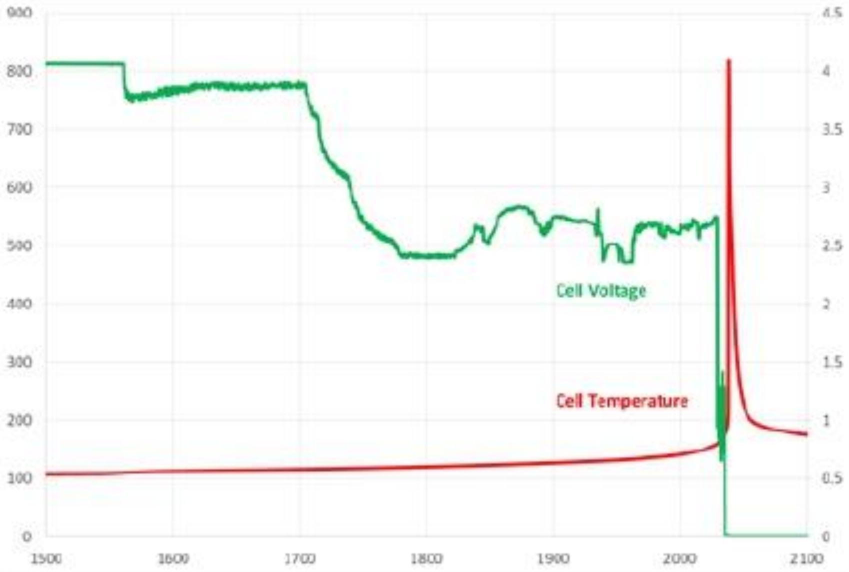
Auxiliary measurements

In any test, when adding **extra thermocouples**, it’s more beneficial to attach thermocouples securely than to add as many as you can. If the thermocouple comes off the cell during the test it isn’t providing any useful information. Also be careful of shorting the cell with the thermocouples

Cell voltage is an easy measurement which can give useful information about the cell throughout the test, it can predict thermal runaway before temperature.

When **videoing the cell in the calorimeter**, the smoke/gas release can often obscure cell. The video is generally used to try identify venting, smoke, fire or explosion rather than providing a very detailed view of the cell. THT have used a high speed camera inside the blast box to film the thermal runaway of small cells.



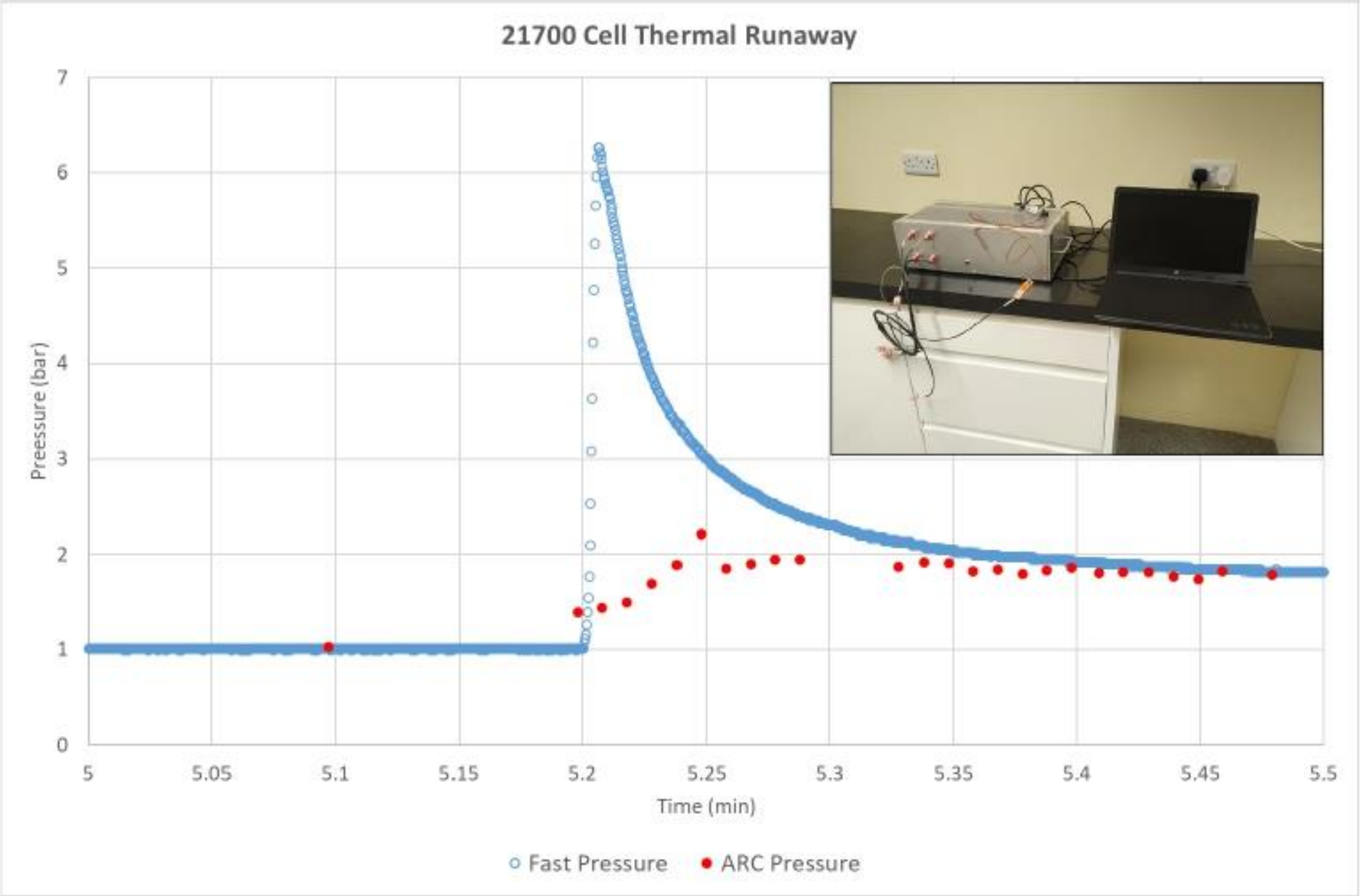


High-speed data collection can be highly beneficial, especially for pressure or voltage measurement, as well as short circuit currents which can last for only seconds.

ARC - Rapid Data Collection

For increased data collection speed, a rapid data logging device (RDCS) connected to a laptop can be triggered from the ARC instrument using a temperature or temperature rate trigger via a network connection. This ensures data size is kept manageable because only the rapid part of the reaction is recorded.

One pressure channel, one voltage channel and four temperature channels can be recorded at logging rates of up to 1kHz. This is useful for thermal runaway pressure measurements. The pressure test can show a pressure wave "spike" during cell decomposition which is not always detectable with slower data logging rates.



Procedure for "non HWS" tests

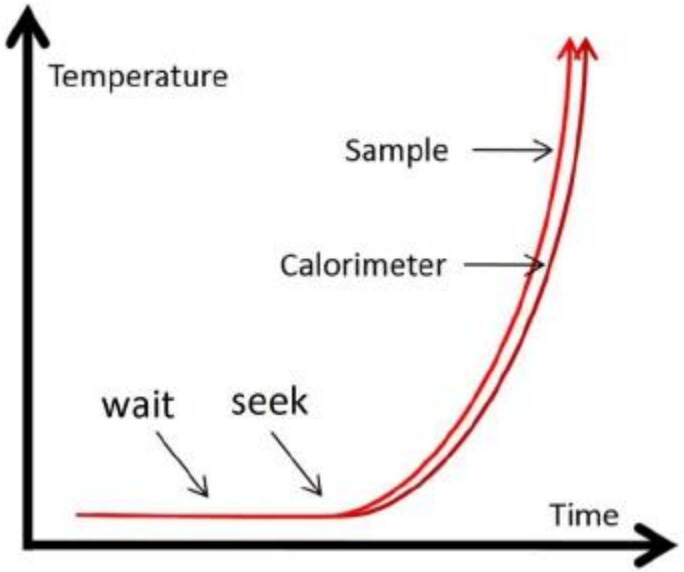
Any other type of test in the ARC which is not using heating as the method to induce thermal runaway follows basically the same procedure:

1. Set start temperature as the temperature which you want to carry out the test. If you wish to carry it out at room temperature, set the start temperature below the cell's current temperature.

2. Set the end temperature as the temperature at which the cell will be well into thermal runaway (for example: 300 ^{o}C).

3. Set a wait time suitable for the sample, or if the test is beginning from room temperature and the calorimeter and sample are already at room temperature, a short 5 minute wait time is fine.

4. The "trigger" which could be user-operated or automatic should occur in seek mode. This happens automatically for a software-integrated option such as nail penetration, but for example if a third-party cycler is applying an overcharge current it should be timed to begin when the ARC enters seek mode.



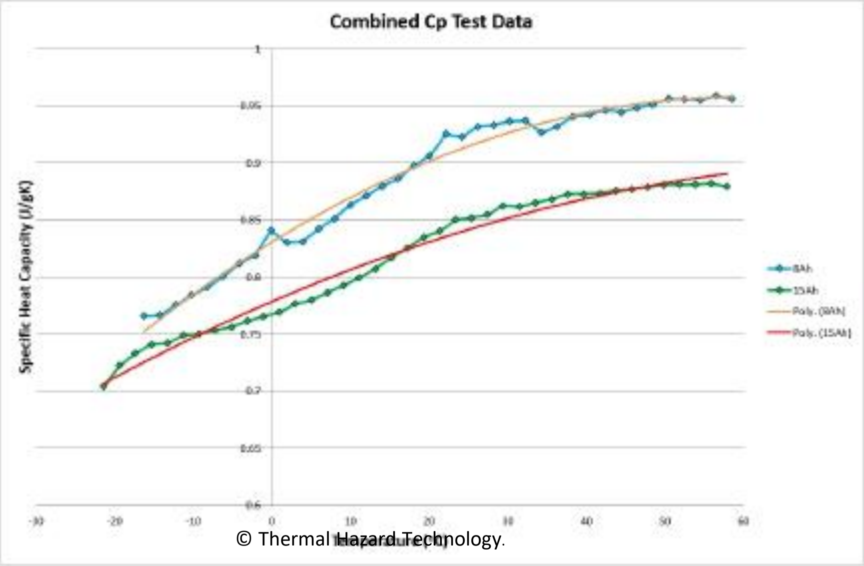
Performance testing in the ARC

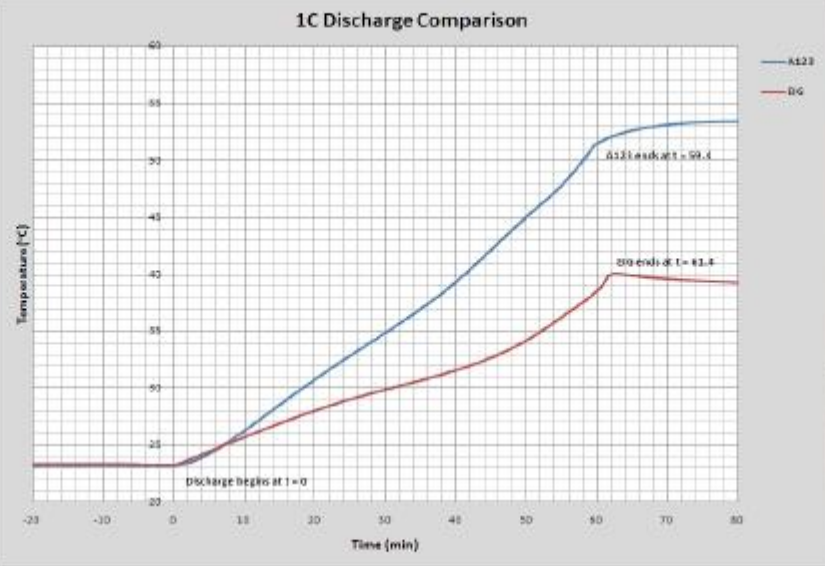
Key points to remember:

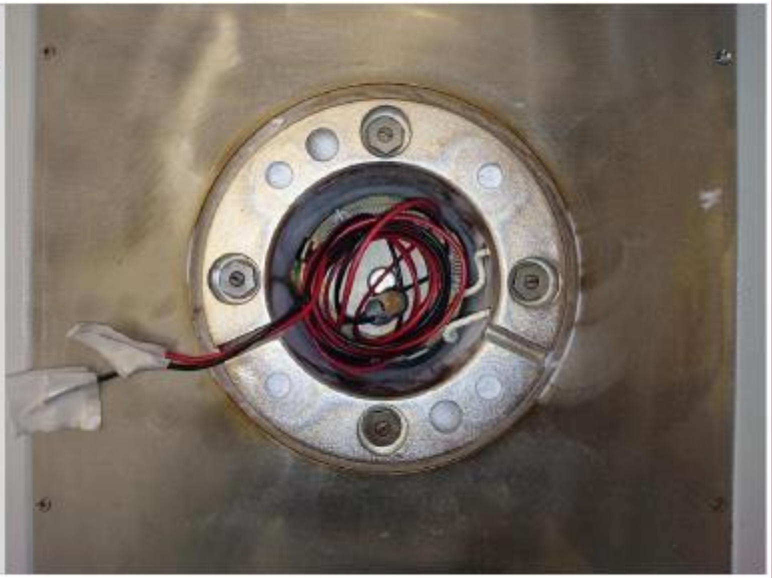
In the standard or EV calorimeter, heat loss can occur down the cables – Therefore, either calibrate with cables attached or place a length of cable inside the chamber.

It is good to measure heat capacity over the temperature range used for cycling. Heat capacity versus temperature can then be plotted and the heat output during cycling can be calculated based on the changing heat capacity.

Ideally, do no use a holder! Suspend the cell or rest it on a throne. Liquid N_2 can be used to start from lower temperatures.







Overcharge Testing

Overcharging the cell is the more violent that other types of safety tests. Because of this, a cell which might show a weaker reaction in standard test might show a different result when overcharged.

100% SoC HWS – case intact, burst disk rupture

Overcharge – case blown open

Keep this in mind when designing the test as the reaction could be faster/more energetic than expected

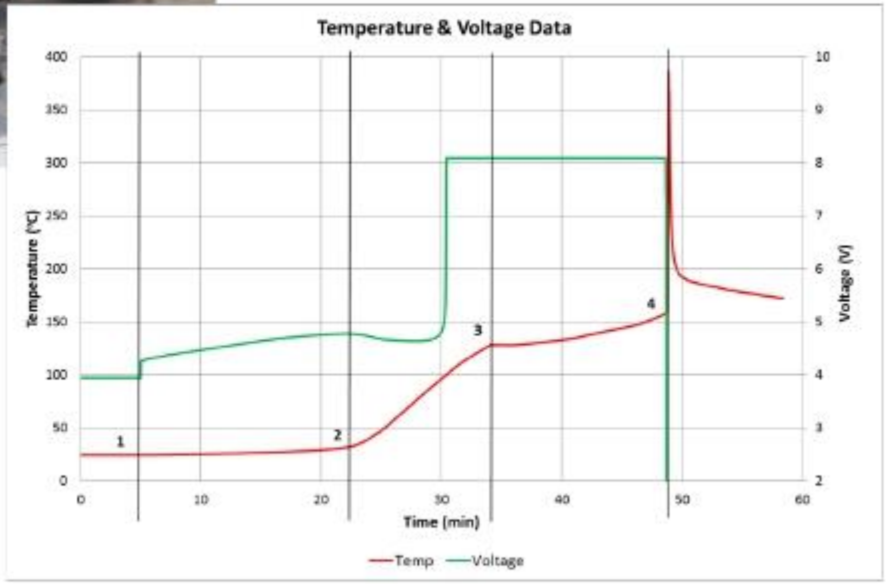
Typical overchargethermal profile:

1. Overcharge starts, slow resistive heating

2. Voltage reversal, cell damage, rapid heating

3. Rapid heating stops after current stops

4. Thermal runaway after chemical self-heating



Short Circuit Testing

Short circuit testing is a common type of abuse test but it has several issues in terms of obtaining repeatable thermal runaway results.

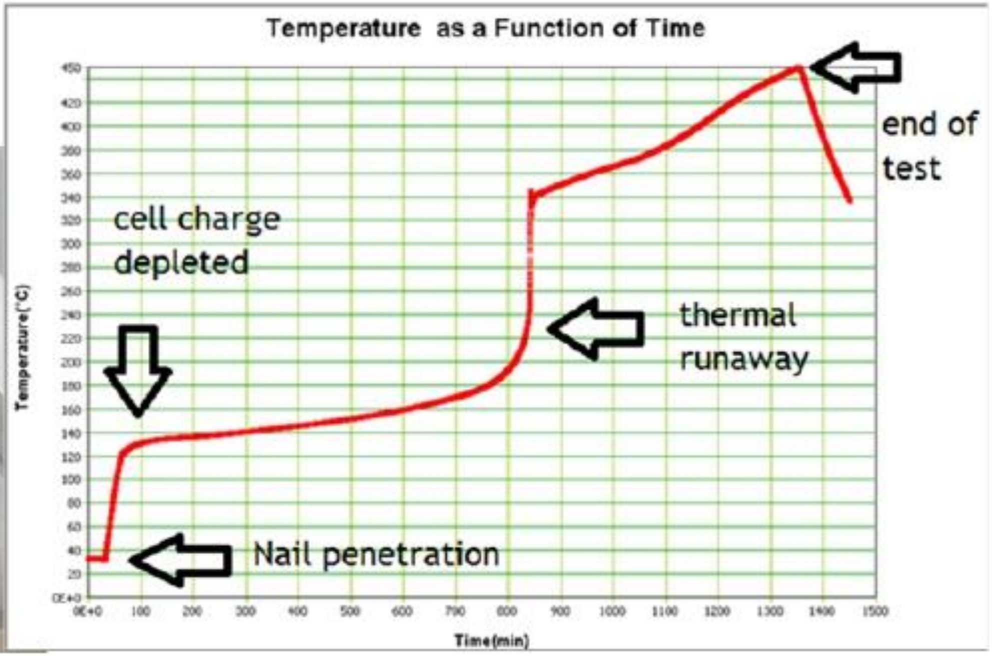
1. Many mass produced cells have an internal fuse triggered by high current or temperature which prevents the short circuit forcing the cell into thermal runaway.
2. The short circuit cables/contactor are key to the test result. The impedance of these components should be low compared to the internal resistance of the cell. To carry out tests at specific resistance values, an inline shunt resistor can be used (ensure it can cope with the expected current).
3. A shunt resistor can be used to provide a fixed resistance, but if it is not suitable for high current, it will heat up and the resistance will change.
4. A current transducer with fast data logger will report the short circuit current which can tell you the severity of the short.

Nail Penetration Testing

Probably the most commonly use abuse test besides the standard ARC test, because it can bypass the cell's protective measures and directly create an internal short. However because of the physical aspect of the test, it can lead to a variety of results even from one cell, however this also depends of the type of cell. From our experience thinner pouch cells tend to be more resistant to nail penetration than prismatic and cylindrical cells.

Some key points:

- The nail should pass through the cell completely
- The nail should be conductive to facilitate the internal short
- Try to standardise the nail and position between tests.
- If a nail penetration does not lead to a thermal runaway immediately, under adiabatic conditions a thermal runaway, may develop later
- The nail penetration test can be combined with a spark source



Pressure Test Design Choices

4.

5.

2.

1.

3.

Picture	Name	Height	Total ⌀	Opening ⌀	Volume	Max Capacity
1.	Small	80mm	80mm	30mm	0.4 L	Up to 1Ah
2.	18650	120mm	120mm	60mm	1.2 L	Up to 5Ah
3.	Medium	170mm	170mm	100mm	4L	Up to 12Ah
4.	Large EV	400mm	200mm	150mm	12 L	Up to 25Ah
5.	Large EV+	360mm	280mm	170-220mm	22 L	Up to 40Ah

A 3000 mAh 18650 cell can generate around 7 bar of peak pressure in a 1.2 L vessel. In a 4 L vessel the peak pressure would be 2.1 bar. In a 0.4 L vessel it would be 21 bar.

As a general rule, the more energy-dense chemistry such as LMO generates 3 bar litres per ampere-hour at peak pressure. This can vary significantly, depending on cell SoC and chemistry. The peak pressure in the vessel during a test should be below the safe operating pressure.
Gas collection cylinders can increase the volume for gas dissipation and thus lower the peak pressure.

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Pressure Test Setup

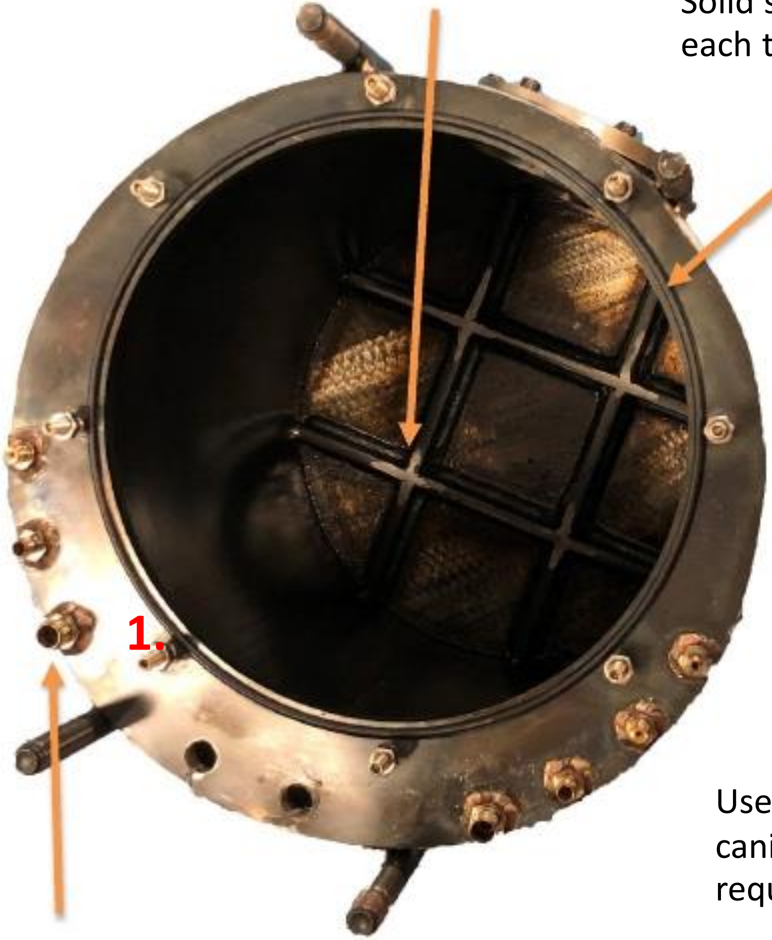
Tighten all nuts on the lid tightly to ensure a good seal,
A socket spanner/wrench is good for this

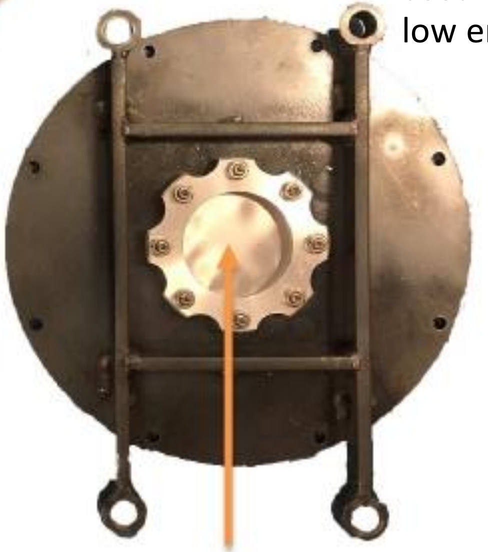
Lay glass fibre insulation on the base of the canister to thermal insulate the cell from it. Alternatively use a tripod or other holder/support to achieve this.

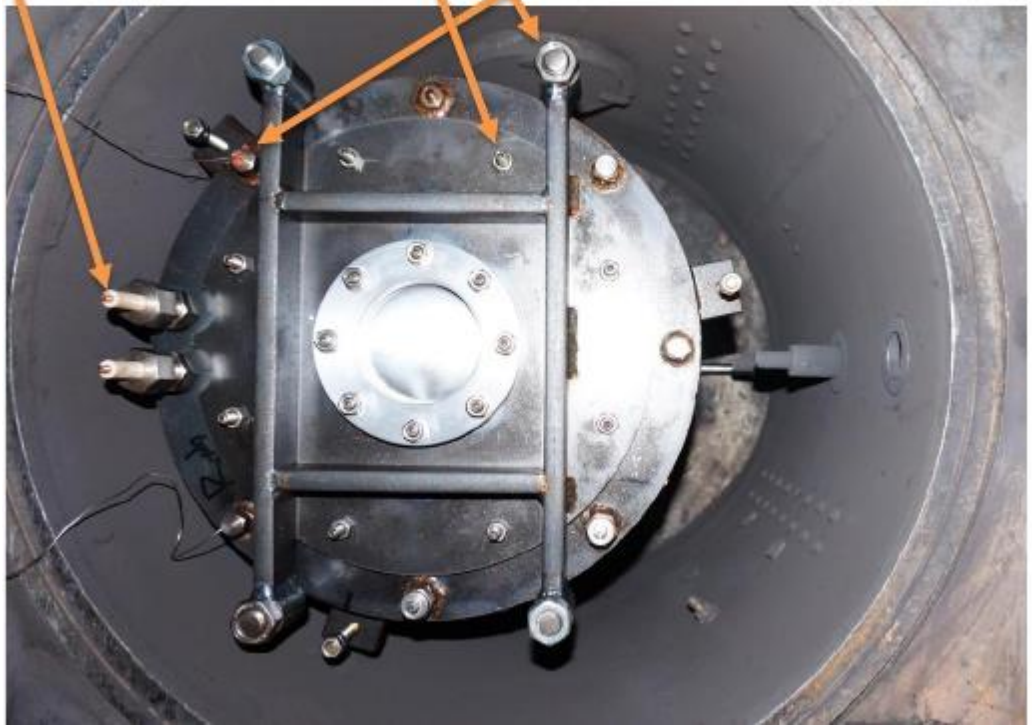
Use viton o-ring to seal lid against canister body. Place some silicon oil over the o-ring to create a better seal. Solid silicon o-rings can also be used. Replace o-ring after each thermal runaway test

Thermocouples pass through 1mm connectors, and sealed using a piece of silicon which is compressed around the thermocouple when the nut is tightened. It’s good idea to use an extra TC to monitor the air temperature inside.

Use copper feel-throughs for monitoring cell voltage. Can also be used for overcharge, but may not be low enough impedance for short circuit.





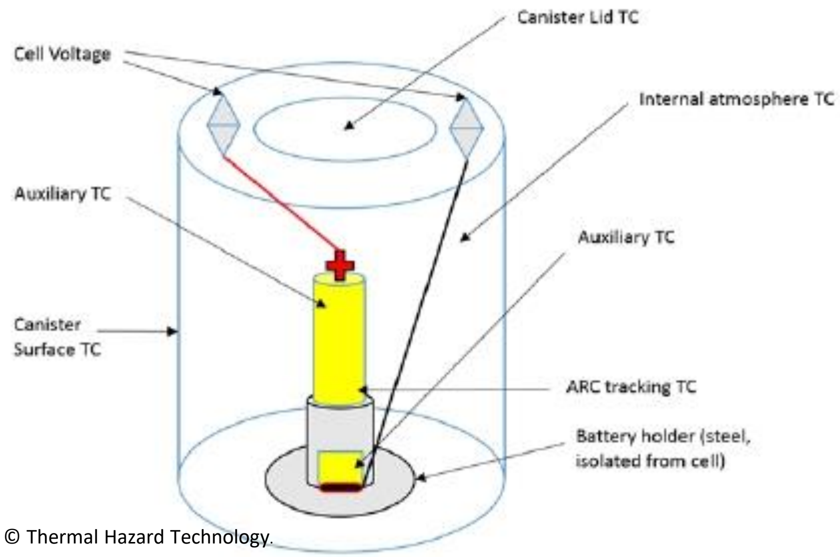


Use burst disk to prevent damage to the canister. These should be steel shim. Also requires a viton o-ring underneath

¼’’ or 1/8’’ Swagelok fittings can be used with flexible tube for gas collection, also for nitrogen flushing or gas release. The 1/16’’ is for the pressure line.

Pressure Test Considerations

- It’s a good idea to fill the 1/16’’ pressure line with silicon oil using a plastic syringe to stop corrosive gases reaching the transducer.
- It’s a very good idea to pressure test for leaks before running the test. This can be combined with the flushing procedure. Pressurise the canister from a gas bottle (around 5 bar is good), then close the supply value. Record the pressure value on the ARC after 5 minutes. Wait an additional 30 minutes and see if the pressure measured on the ARC has dropped by a lot. Note there is always some noise in the pressure signal.
- Change the viton/silicon seals on the canister between each test.
- If the ARC does not have a SSS/other automated gas release function, consider a gas release line with manual valve for this purpose.



Gas collection and analysis

Gas collection may be automated if the SSS or SSU options are available. Otherwise, a manual valve can be used to sample gas from the sealed system into a gas collection bag or cylinder.

Typical gas analysis list:
Carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), oxygen (O_2), methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propylene (C_3H_6), propane (C_3H_8), butane (C_4H_8) and isobutane (C_4H_{10}), n-Butane, isopentane (C_5H_{12}), n-Pentane, pentenes, hexanes, hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen cyanide (HCN), hydrogen sulphide (H_2S), nitrous oxide (N_2O), Acetaldehyde (C_2H_4O), dimethyl carbonate ($C_3H_6O_3$), ethyl methyl carbonate ($C_4H_8O_3$)

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Online gas analysis is the “holy grail” of representative gas analysis but it is much more difficult compared to sampling post-test.

Data Analysis – Pressure

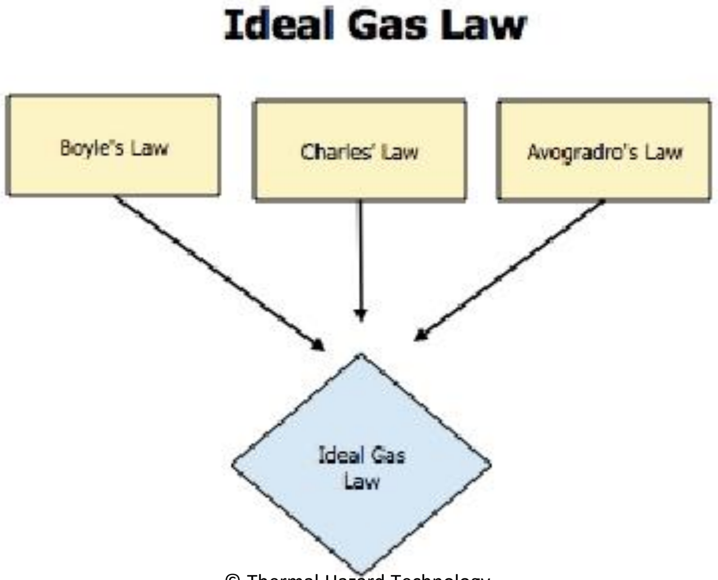
Calculations of gas volume from ARC pressure data use the ideal gas law: **PV = nRT**

Step 1: Subtract the “gas pad” from the pressure data. This is the linear increase in gas pressure with temperature and does not relate to gas generated from a reaction.

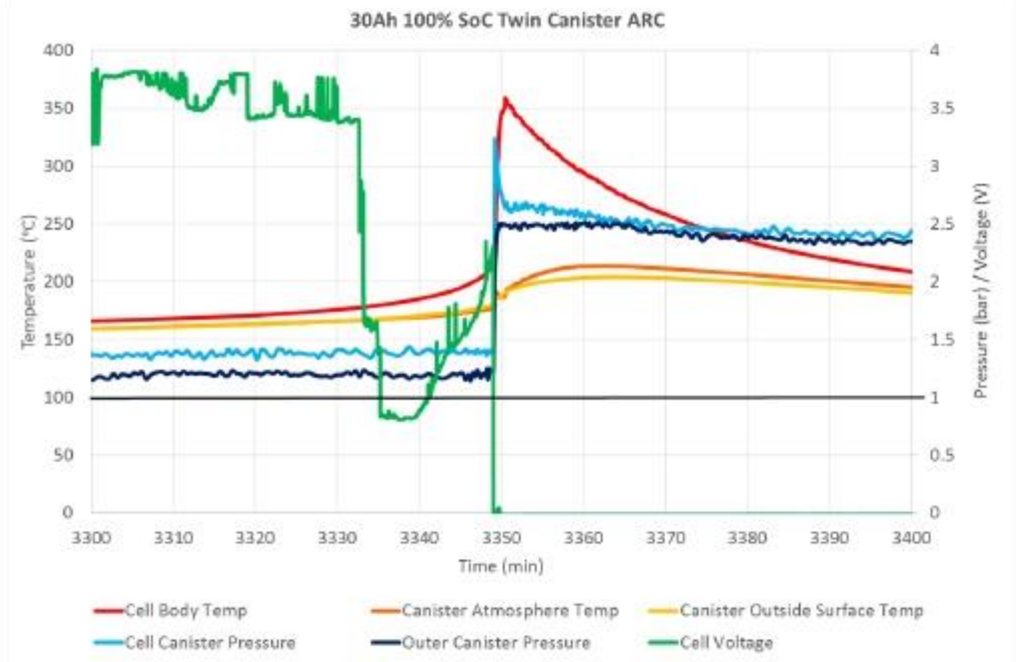
Step 2: Find the maximum recorded stable pressure. Use the ideal gas law to convert this to moles of gas using canister volume and gas temperature (from internal thermocouple reading).

Step 3: Put the number of moles of gas calculated above back into the ideal gas law under standard conditions to find the volume of gas released by the cell.

Step 4: Compare the cooling pressure data to the calculated gas volume to find how much of the gas has condensed at room temperature.



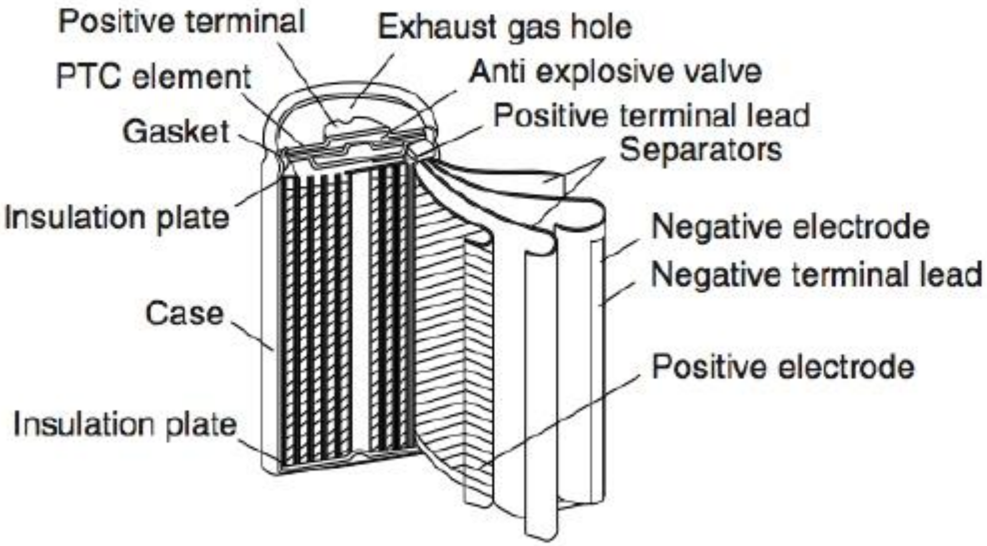
Find $\mathbf{P_{max}}$ → $\mathbf{P_{gas} = P_{max} - P_{air}}$ →
Find moles of gas at $\mathbf{P_{gas}}$ →
Find $\mathbf{V_{gas}}$ at STP using $\mathbf{mol_{gas}}$ →
Compare $\mathbf{V_{gas}}$ to **V** calculated from residual pressure

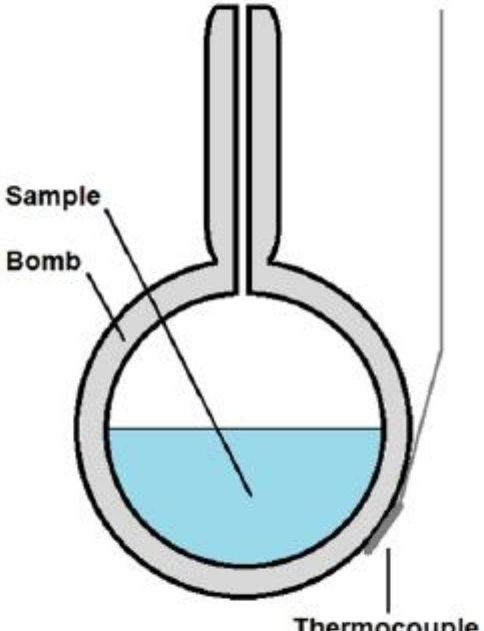


Data Analysis - Phi

Phi factor – When using a sample holder, heat is lost to the sample holder as well as the sample. A correction factor can be used to account for this. With batteries it is better to minimize the holder size and try to avoid using one at all unless it is necessary (for example when a pressure measurement is required).

Note: The cell case can also be considered the "holder" in order to work out energy release of active material in the cell, independent of the cell case. For this the mass of each component in the cell must be know/measured.





$$\phi = 1 + \frac{C_b m_b}{C_s m_s}$$

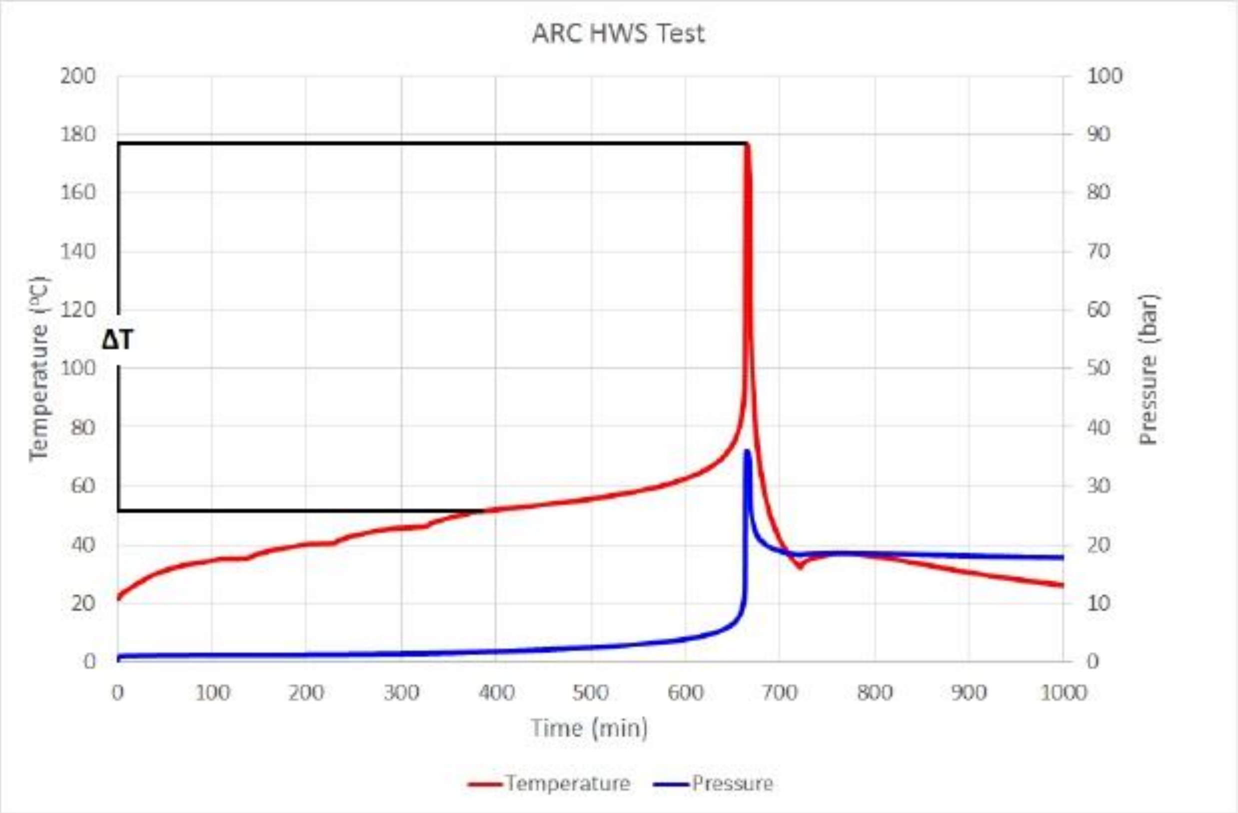
$$\varphi = 1.181 = 1 + \frac{0.5 \times 13}{0.8 \times 45}$$

Example phi calculation for battery holder pictured here. ~18% of heat is lost to holder.

Interpreting the ARC Data

Basic Thertextmal Data

- Onset temperature, T_{onset}
- Max cell temperature, T_{max}



Cooling data allows non-condensable gas estimation based on pressure

Heat of reaction (J),

$$\Delta H = \Delta T * C_s * \phi * m$$

where

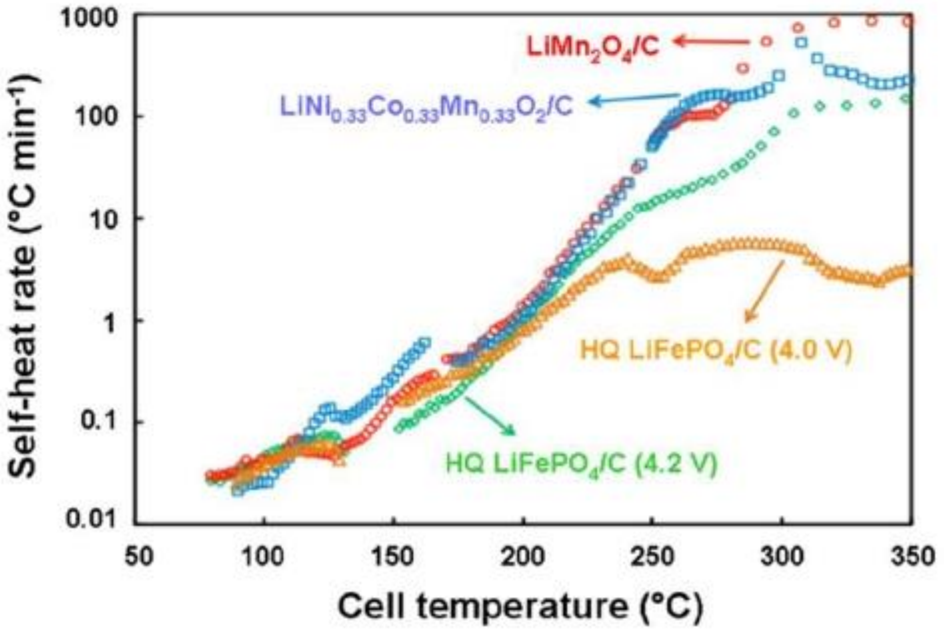
$$\Delta T = T_{max} - T_{onset}$$

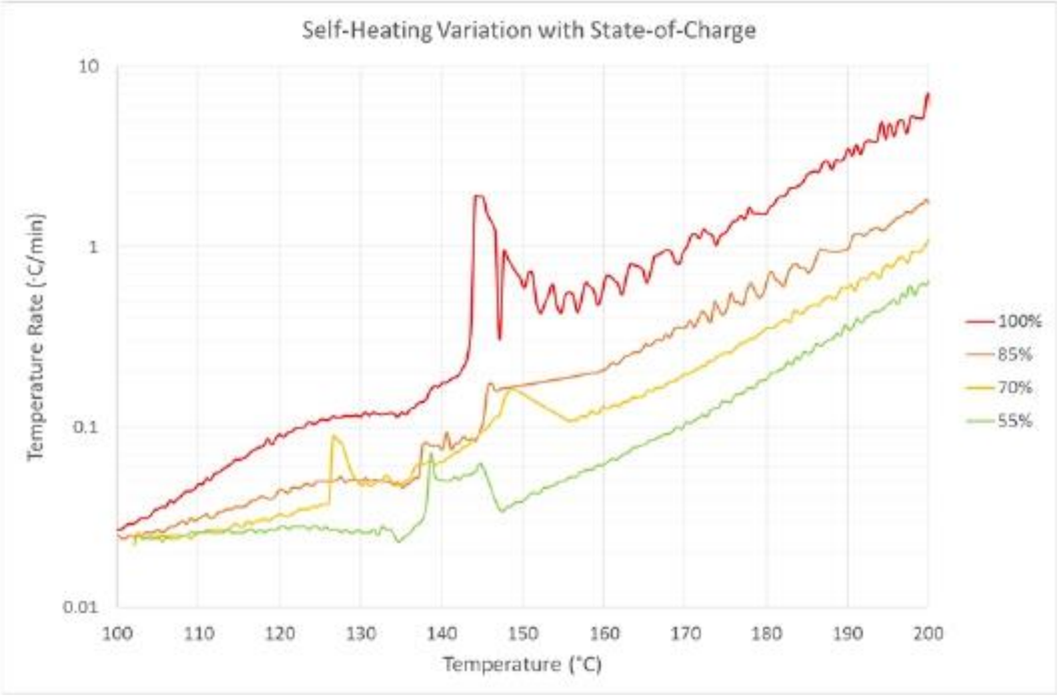
Other basic parameters are taken directly from the data:

- Residual pressure
- P_{max}
- dT/dt > convert to Watts using Cp
- dP/dt

Interpreting the ARC Data

The key graph – dT/dt Vs Temperature



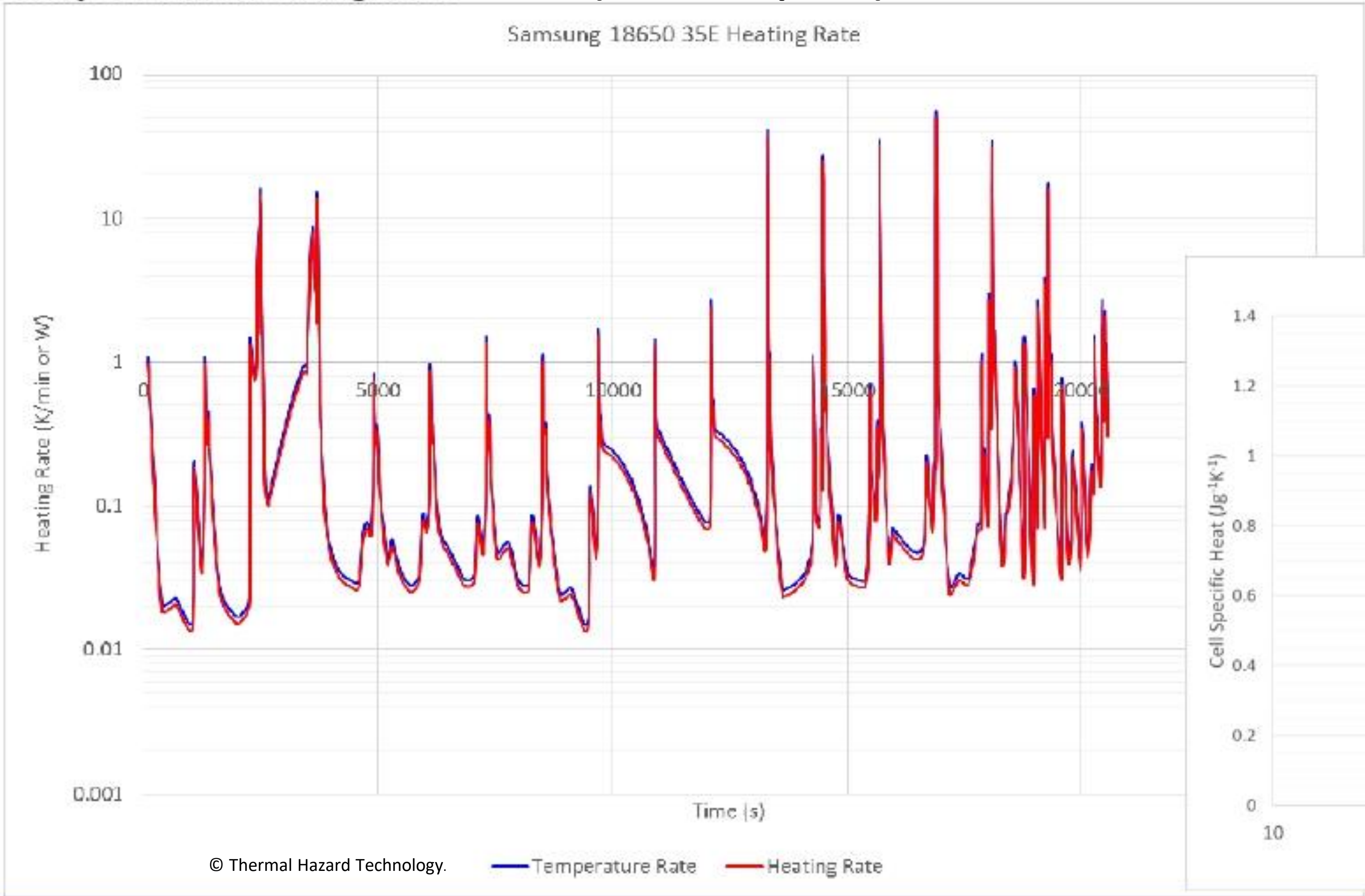


For thermal runaway data, the self-heat rate is plotted logarithmically, this allows better identification of the detail of the slow reaction while still showing the fast final reaction

This type of graph is ideal for quick visual identification of differences in the reaction profile of whichever type of sample is being compared.
Higher position on the Y-axis indicates a faster reaction, while further to the left on the X-axis indicates a lower temperature reaction.

Interpreting the ARC Data

Temperature/Heating Rate $\Delta H = (\Delta T * C_s * \phi * m) / 60$



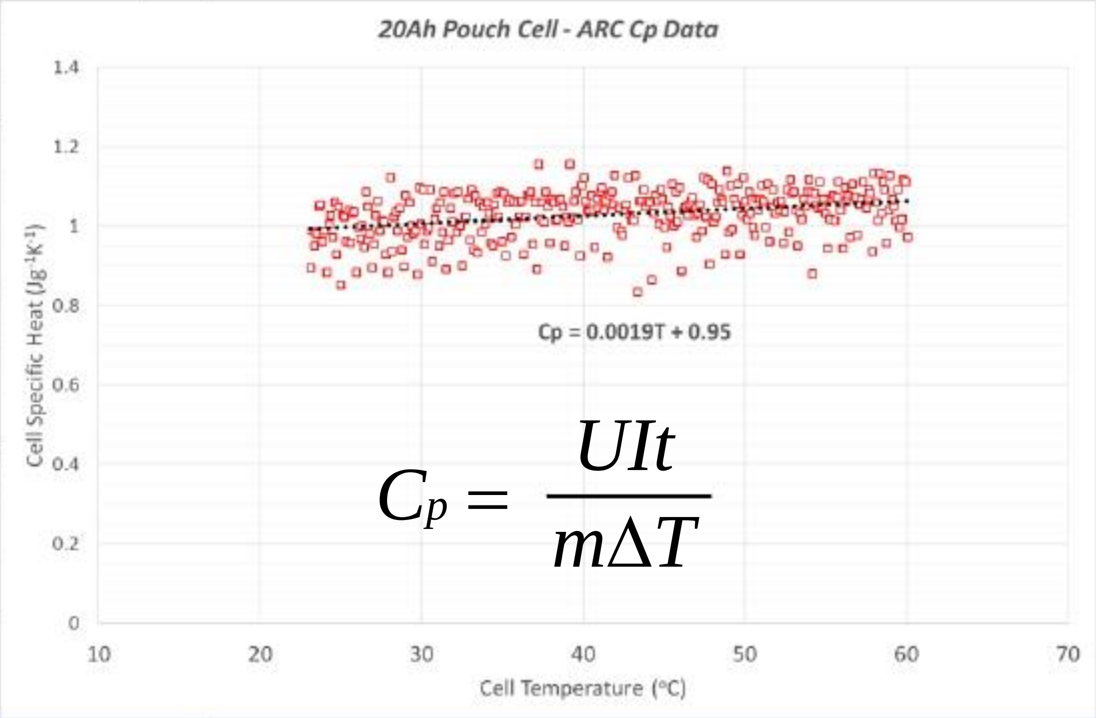
ΔH – Heating rate in Watts

ΔT – Heating rate in K/min, need to change to per second

C_s – Cell heat capacity, measure in ARC test

ϕ - Phi factor, see previous slides

m – cell mass, weigh before test



$$C_p = \frac{UIt}{m\Delta T}$$

The End…

Any questions?