

## Experimental understanding of gas volumes and forces generated due to swelling during lithium-ion pouch cell failure

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Lithium-ion pouch cells are commonly used as an energy storage source across a wide range of applications. Several cells are typically used together to form a battery module. Common uses include but are not limited to consumer electronics, electric vehicles, portable equipment, and energy storage. In safety terms, overcharging, short circuiting, penetration, or external heating, can lead to failure of the pouch cell. During cell failure, gases are produced as a result of thermal decomposition of the electrolyte components. This gas generation results in an increase in pressure within the cell which leads to expansion of the physical dimensions of the cell through swelling and can ultimately result in cell rupture with the venting of gases and possibly flame. To better understand the nature of the failure mechanism, pouch cells with a capacity of 5 Ah, at 100 % and 50 % State of Charge (SoC) were initiated to failure through external heating. In the first instance, pouch cells were tested by allowing the cell to fail under different conditions and their expansion monitored. In a second series of tests the pouch cells were failed within a pressure vessel while unconstrained. The gas volumes generated were calculated and the gas compositions analysed using mass spectrometry. In addition, cell temperatures were recorded to provide indicative data on the relationship between observed cell temperature and failure mechanism. The results of these experimental tests, particularly those where the cell was constrained, provides a real-world understanding of the failure behaviour of pouch cells. The constrained test scenario is representative of the common situation where individual pouch cells are tightly packaged into a device or where many cells are in place as part of a battery module with little room for cell expansion thus leading to possible escalation of an incident.

**Keywords:** Lithium-ion cell, pouch cell, pressure, gas analysis, net zero

### Introduction

Lithium-ion batteries are becoming an increasingly popular choice when choosing renewable energy storage sources due to increasing pressures on companies to produce environmentally friendly products. One source of this pressure comes from the UK government's Net Zero initiative to cut all greenhouse gas emissions to net zero by 2050 (Shepherd, et al., 2020). Key to enabling this target to be achieved is the introduction and increased use of renewable energy technologies including solar, wind, and battery power. New products continually being developed using batteries as their only or primary energy source include consumer electronics, portable equipment and for both residential and commercial applications. Pouch cells in particular are an attractive choice of cell design as they are able to store large amounts of energy in compact and lightweight design which can be made in many shapes and sizes. Several pouch cells can be joined together to form a battery module and modules joined to make packs increasing energy storage further. This design choice is becoming popular for use in electric vehicles and is currently the choice for containerised battery energy storage systems (BESS). The increase in electric vehicles has led to an increase in battery fires in cars (P. Sun, 2020), therefore it is important to understand the hazards associated with the use of lithium-ion batteries especially pouch cells, where less data is available.

Despite their increasing popularity many questions remain about the failure mechanisms and safety of pouch cells when exposed to conditions outside of their normal usage, for example when exposed to high temperatures for a prolonged period of time, overcharged, over discharged or short circuited. Studies have shown that when outside of normal operating conditions, lithium-ion batteries can enter thermal runaway. Onset of thermal runaway behaviour begins at the stage of battery failure when the amount of internal heat produced by the cell exceeds the amount of heat able to be lost to the cell's external environment (Yuan, et al., 2020). It has been demonstrated through tests where pouch cells are subjected to heat from an external source, they are susceptible to swelling due to the production of gases formed as a result of thermal decomposition occurring within the electrolyte contents of the cell. Eventually the increase in pressure causes the external casing of the cell to rupture, releasing the built-up gases. This failure behaviour is different to that observed in cylindrical and prismatic cells, which are encased within a rigid metal container and therefore unable to swell and expand to the same degree. In addition, venting from cylindrical and prismatic cells often takes place through a vent cap, typically incorporated into the cell design (Jinyong, et al., 2021). Once the cell has begun to vent the thermal runaway processes continue until the cell reaches final failure resulting in greater volumes of gas being released and/or flames depending on the initial state of charge (SoC) of the cell. This process occurs in all cell types.

The generation of these gases can cause considerable pressure within the cell, which becomes of increasing concern when either single cells are constrained within products or are tightly packaged within battery modules. In these situations, cells often have little room for cell expansion or gas venting causing considerable pressure to build up (Kennedy, et al., 2021). There is limited data available about the pressure generated by these cells and that is therefore applied to neighbouring cells and whether this pressure can be reduced by including space for expansion when designing new products using pouch cells.

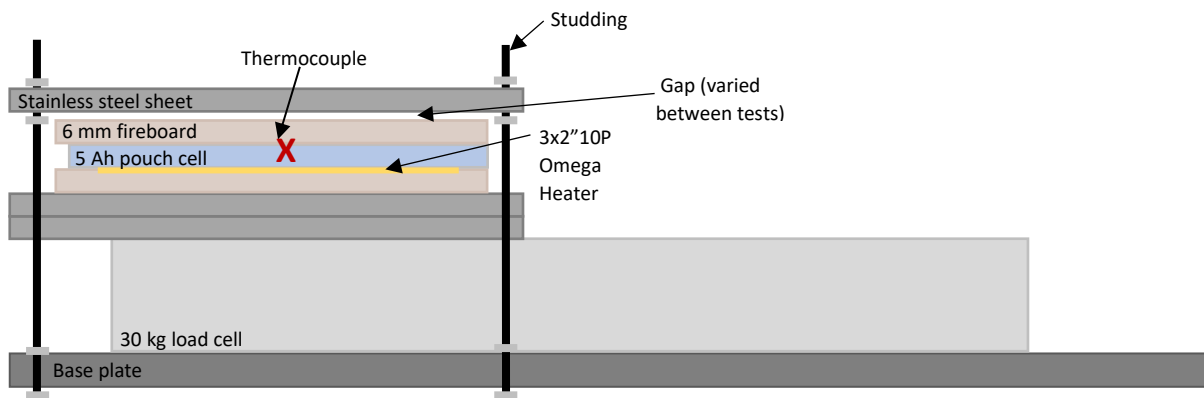
This paper aims to determine the range of pressure reached upon pouch cell expansion and failure, as well as determining the types and quantity of gas produced as a result of thermal decomposition within pouch cells. This information can be used to establish the types of safety implications associated with the types of events witnessed by the failure of a relatively small (5 Ah) pouch cell.

**Methodology**

All test types were conducted using 60 x 90 x 5 mm, 5 Ah pouch cells, which have a nickel manganese cobalt (NMC) based chemistry and were externally heated to failure using a 3 x 2"-10P adhesive heater (Omega) attached to the outer surface. The heater was supplied with a power of 60 W for each test. A piece of 6 mm calcium silicate fireboard, to provide heat insulation, and a stainless steel sheet, for mechanical strength, were placed either side of the pouch cell (the precise way in which they were held together varied between test types). The temperature of the pouch cell under test was measured throughout all tests using a thermocouple attached to the surface opposite the heater. All tests were carried out within our bespoke battery abuse testing facility, equipped with data logging, video recording and systems to allow the initiation of cells from within a remote control room.

**Measurement of Pressure Generated by Pouch Cells**

The pouch cell, fireboard and stainless steel sheets were placed on a metal plate bolted to a load cell with a 30 kg range. Studding was placed through holes cut in the base plate for the load cell and all four corners of the top and bottom stainless steel sheeting allowing it to be held together. The initial height at which the top stainless steel sheet was held above the pouch cell was varied for each test at 0, 1 and 2 mm. The test rig is depicted in Figure 1 and Figure 2. Tests for all 3 height variations were carried out on pouch cells with a 100 % state of charge. Additional tests with a no gap were conducted on pouch cells with a 50 % state of charge.



**Figure 1 - Side view diagram of the load cell test setup where a 1 mm gap was left between the top aluminium sheet and fireboard**



**Figure 2 - Side (left) and front (right) view of the test set up**

As the cell expanded, the pressure exerted by the pouch cell on the load cell was recorded using a datalogger recording at a frequency of 100 Hz. The output of which was converted to a mass using a known calibration curve generated before tests were conducted. From the converted mass value, force (N) could be calculated using the following equation, where the acceleration was taken as gravity (9.80665 m/s<sup>2</sup>):

$$Force (N) = Mass (kg) \times Acceleration (m/s^2)$$

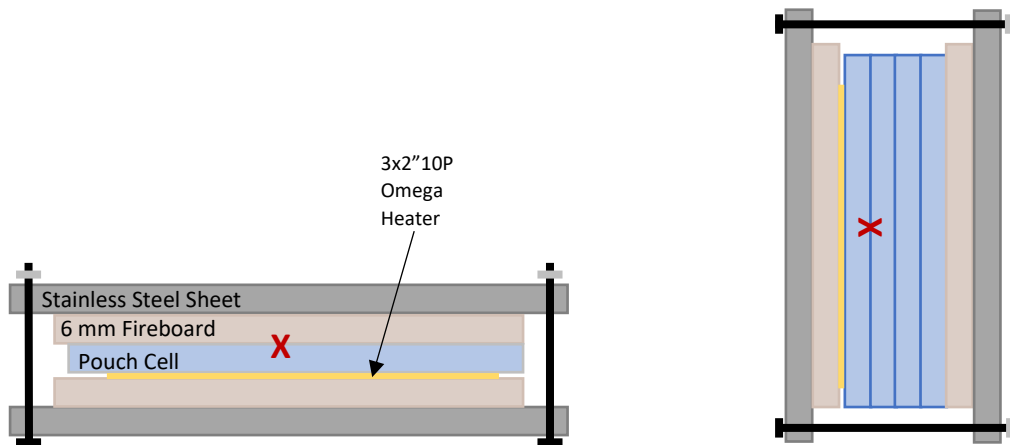
The force was then converted to a pressure measured in kPa, taking into account the area of the pouch cell (0.0054 m<sup>2</sup>).

$$Pressure (Pa) = Force (N) / Area (m^2)$$

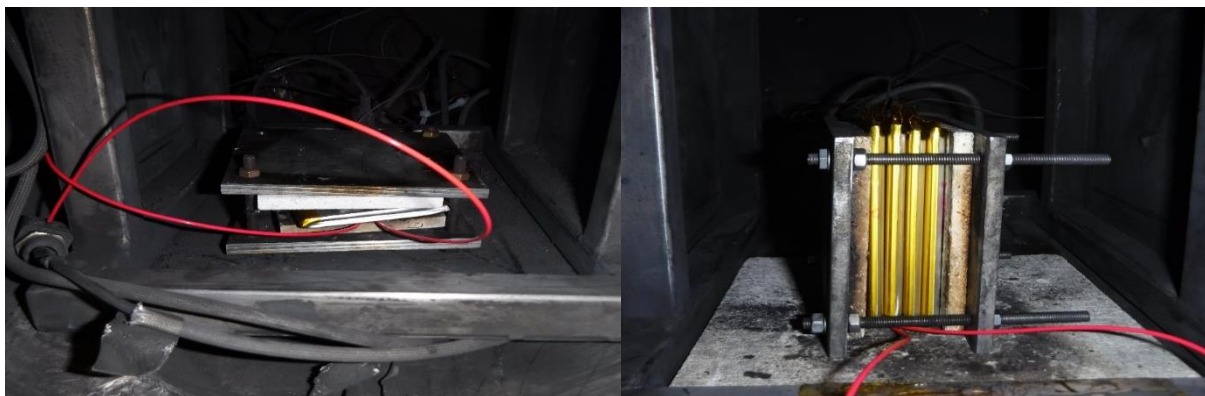
**Gas Volume and Composition Analysis**

The cell was constrained between fireboard and stainless steel sheets all of which were bolted together (Figure 3 and 4). This configuration was placed in a partially enclosed ‘baffle box’ within a 46 L pressure vessel rated to 10 bar. Single cell tests were conducted in an air or nitrogen atmosphere and the cell block test under nitrogen atmosphere. Introduction of nitrogen atmosphere was achieved through purging the pressure vessel with nitrogen before the test took place. This gave an atmosphere with a nitrogen concentration of approximately 99.5 %. The purpose of the baffle box was to limit any flame impingement on the vessel wall. Additional temperature readings were taken using thermocouples located both above the cell (‘above’ temperature) and at the back of the pressure vessel (ambient temperature).

A single further test on a cell block consisting of four pouch cells placed next to each other in a vertical orientation and once again held together through use of fireboard and stainless steel sheeting which was then bolted together (Figure 3 and Figure 4). The heater was placed on the outer surface of the outside (initiating) cell, with a thermocouple placed on the opposite side of the initiating cell to record the temperature. Pressure measurements were recorded by a pressure transducer sampling at 100 Hz. Note: For safety reasons, all pressure vessel tests were performed within a blast cell and were operated remotely.



**Figure 3 – Diagram of the pressure vessel test setup for a single cell (left) and a cell block (right). The red cross shows the location of the thermocouple throughout the test**



**Figure 4 - Single cell (left) and cell block (right) test setup**

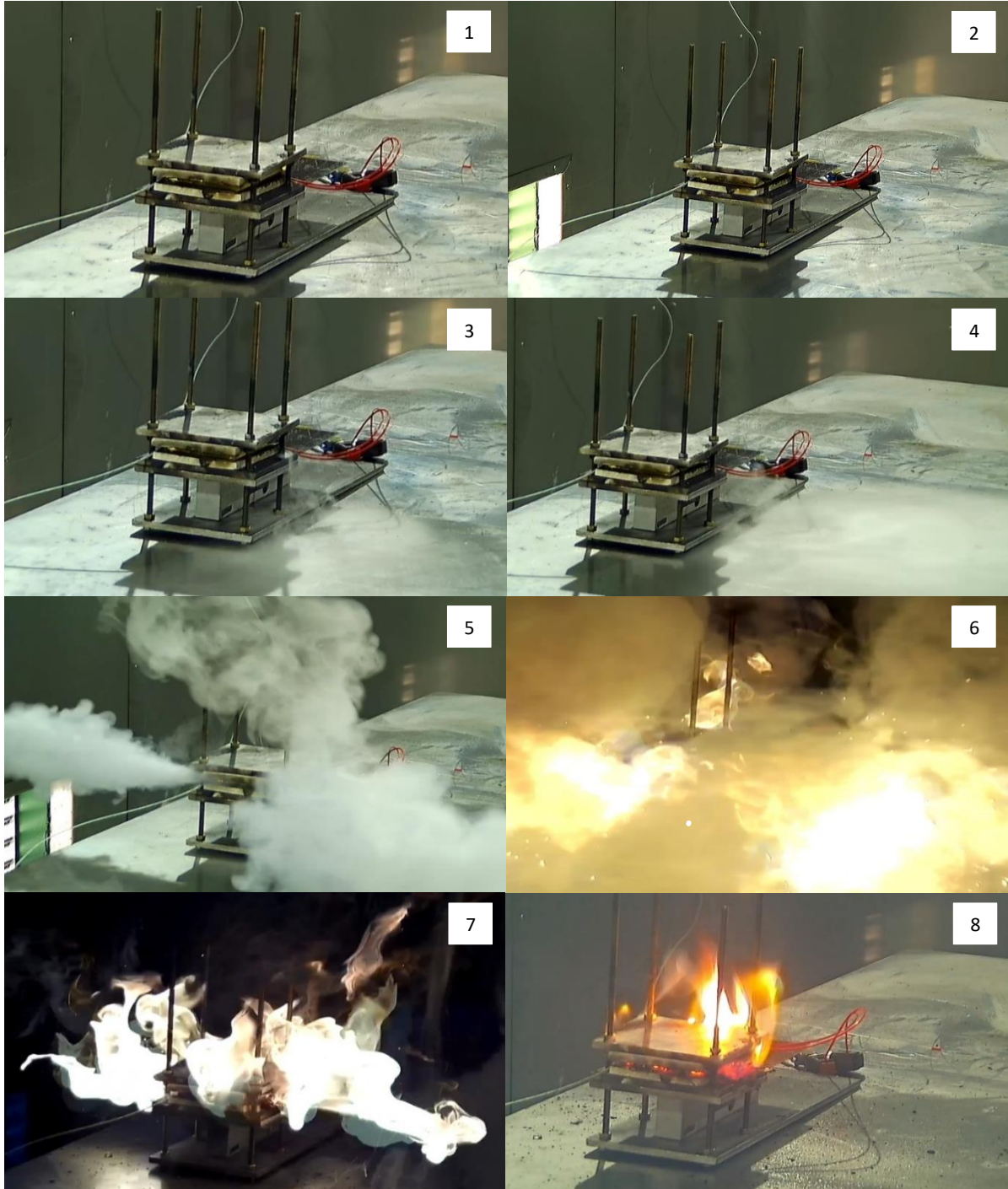
The volumes of gas generated by the pouch cells upon failure was calculated (assuming ideal gas behaviour) using the recorded temperature and pressure values. The initial number of moles of gas present at the start of the test was calculated using the ambient temperature and observed initial vessel pressure which was monitored throughout the test. After cell failure, the number of moles of gas present was then normalised to calculate the amount of additional gas generated by cell failure. To allow for comparison of all gas volumes generated by each test, the volume in litres, was re-calculated at standard atmospheric temperature and pressure (298 K, 101325 Pa).

Gas samples were collected in 5 L gas bags through a sample line connected to the inside of pressure vessel after the cell had failed and the temperature inside the pressure vessel had returned to ambient. The collected gas samples were analysed using mass spectrometry for the following gases: hydrogen, carbon dioxide, carbon monoxide, ethane, ethylene, propane, and methane (Sturk, et al., 2019). Other gases may be present however it assumed that they would be in negligible, trace concentrations.

## Results and Discussion

### Cell Failure Mechanism

All pouch cells with a 100 % state of charge that were externally heated to final failure showed the same characteristics. Initially the cell began to swell, before venting, with gas being released. This gas appeared to pool around the bottom of the cell, before ignition produced large flames (Figure 5). Pouch cells with a 50 % state of charge showed the same overall characteristics as those at 100 % with the exception that upon final failure only large amounts of smoke were produced and no flames were observed.



**Figure 5 - Failure mechanism of a single pouch cell with a 100 % state of charge. Initial venting to failure took on average 5 minutes**

Figure 6 shows a typical cell (100 % state of charge) after failure.

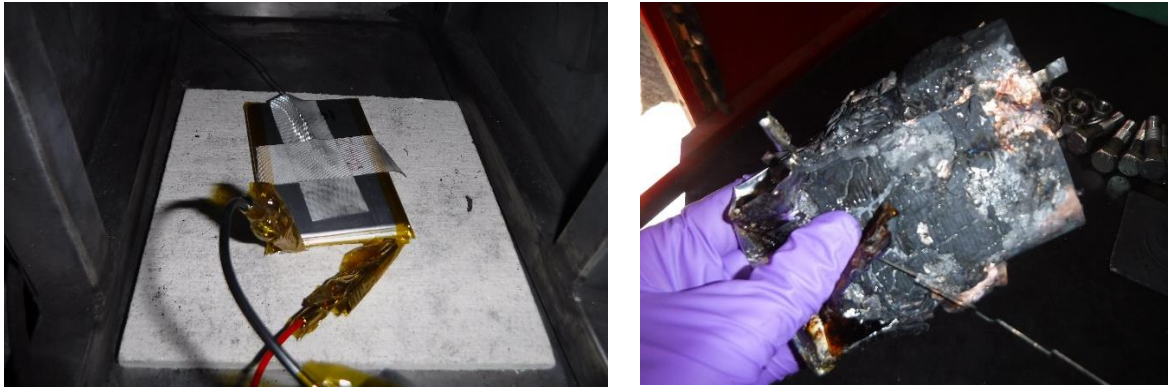


Figure 6 - A single pouch cell before failure (left) and after failure (right)

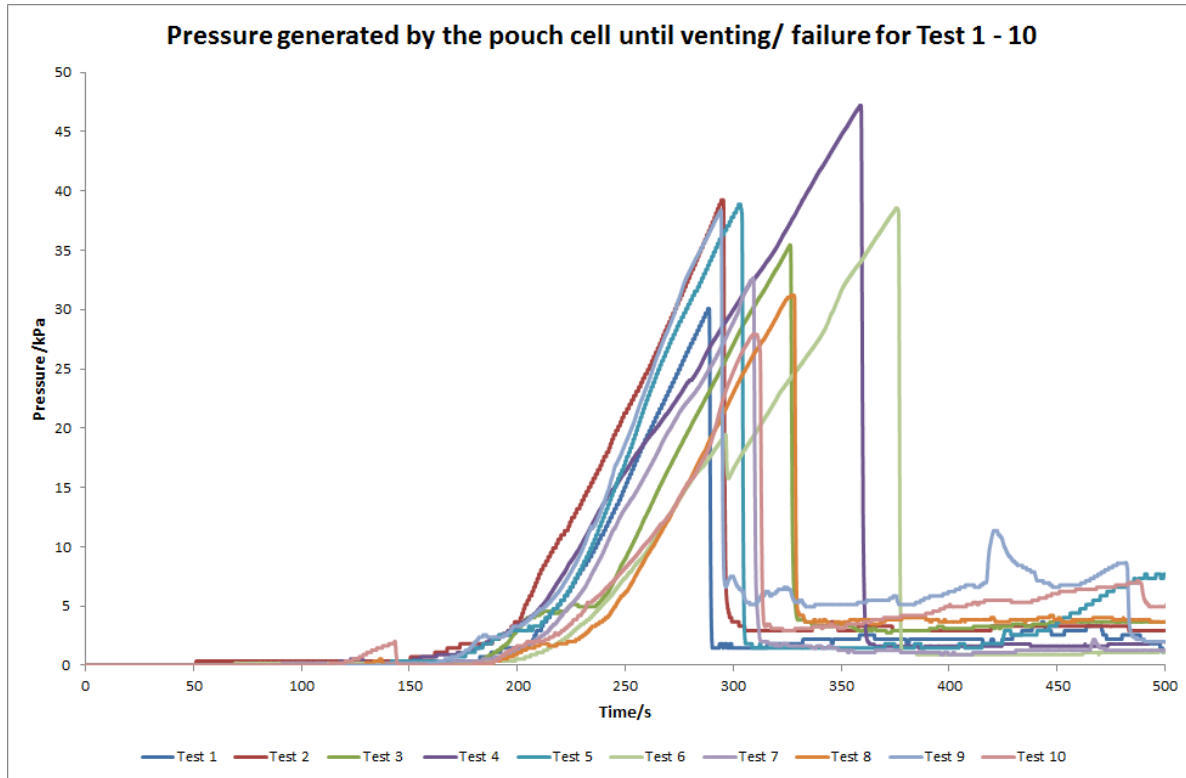
**Pressure Measurements**

The maximum pressure exerted by the cell up until the point venting and/or failure is summarised below (Table 1).

**Table 1 - Results summary for each load cell test type including maximum expansion pressure on the load cell before cell final failure**

Test	Space between fireboard and top stainless steel sheet (mm)	Cell state of charge (%)	Maximum pressure on load cell before cell failure (kPa)
1	0	100	30.1
2	0	100	39.2
3	0	100	35.4
4	1	100	47.2
5	1	100	38.9
6	2	100	38.6
7	2	100	32.7
8	0	50	30.3
9	0	50	38.4
10	0	50	27.9

The pressure changes exerted by the pouch cell before venting and/or failure as recorded by the load cell are shown in Figure 7:



**Figure 7 - Pressure generated by each pouch cell with different expansion gaps and states of charge up until the point of venting and/or failure**

Before cell failure, each pouch cell began to vent due to rupture of the external casing of the cell. The timing of this rupture varied between tests. The maximum pressure generated remains broadly similar value, even between tests with variations in the expansion gap distance above the cell and the cell state of charge. This lack of change in maximum pressure generated across all tests performed may be as a direct result of the failure mechanism observed for pouch cells. As gas produced by thermal decomposition builds up, the outer casing of the cell is only able to withstand a certain amount of pressure before the cell casing splits leading to the venting of gas. It appears that it is possible to reach the internal pressure at which the cell vents, regardless of the cell being constrained completely or with space for expansion.

**Gas Volumes and Analysis**

The total volume of gas released from cell failure was investigated by tests within a 47 L pressure vessel. Table 2 gives a summary of the gas volumes and composition for single cell pouch cell tests.

**Table 2 - Pressure vessel test description summary**

Test Number	Cell State of Charge (%)	Abuse Condition	Pressure Vessel Atmosphere	Test Setup
11	100	External heat	Air	Constrained single cell
12	100	External heat	Air	Constrained single cell
13	100	External heat	Air	Constrained single cell
14	100	External heat	Nitrogen	Constrained single cell
15	100	External heat	Nitrogen	Constrained single cell
16	100	External heat	Nitrogen	Constrained single cell
17	100	External heat	Nitrogen	Constrained four cell block

Figure 8 below gives an example of the temperatures and pressures recorded within the pressure vessel (after the cell had vented gas).

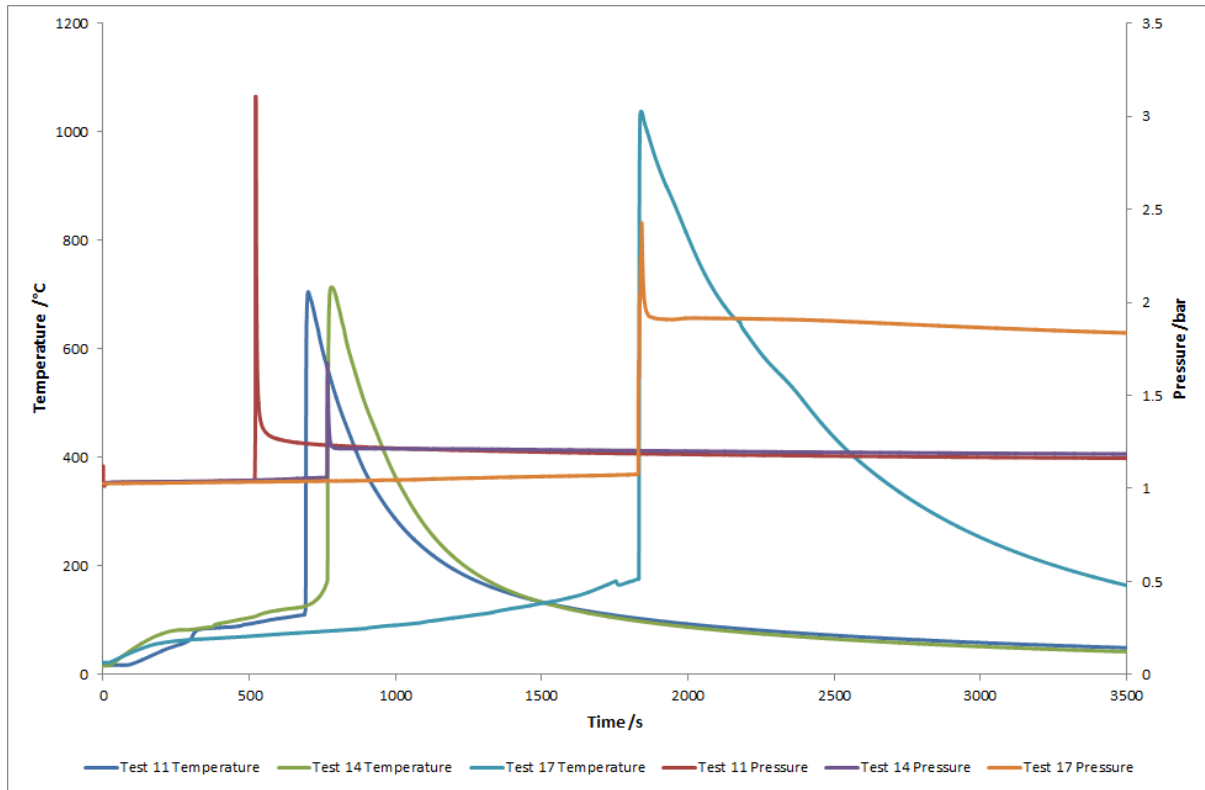


Figure 8 – Cell surface temperature and pressure vessel internal pressure graph for tests 11, 14 and 17

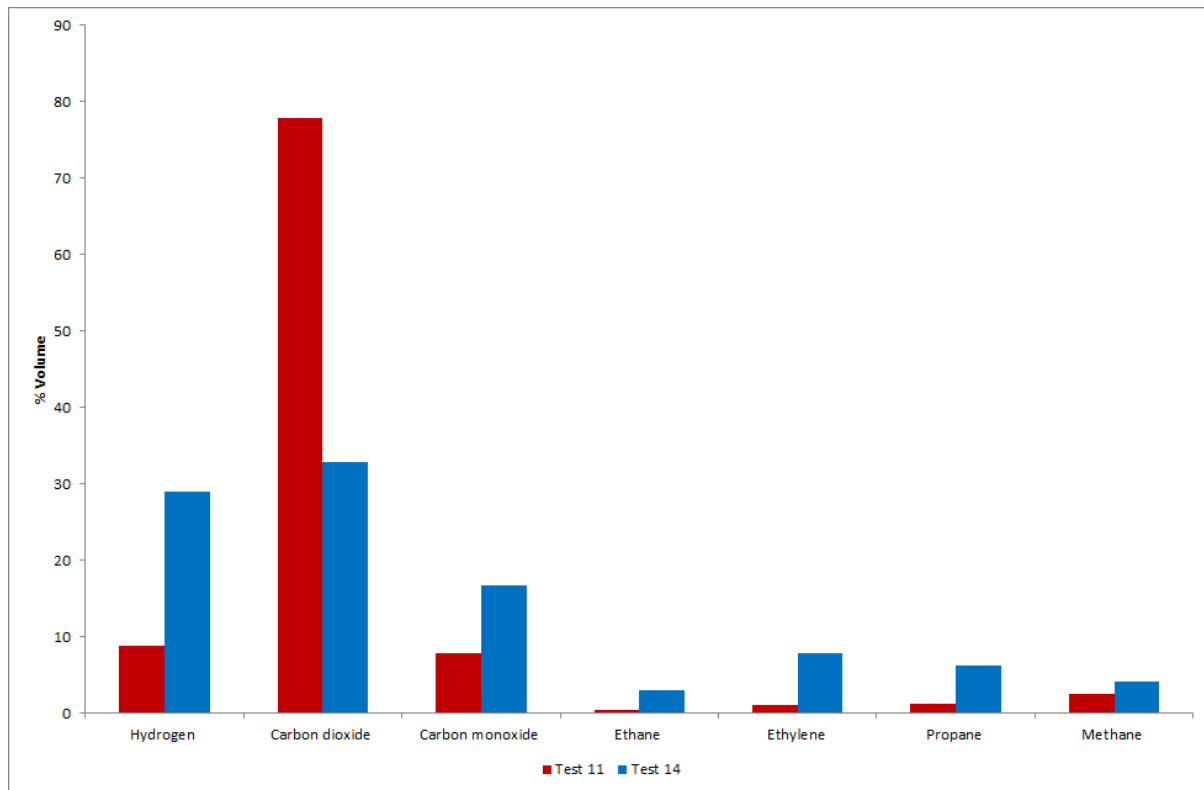
**Single Cell Tests**

Table 3 shows the final volume and % volume composition of the gases vented during cell failure of single pouch cells. Tests carried out in an air atmosphere give the percentages of gases after combustion has taken place. (Note: Test 13 and 16 only give a final gas volume generated as gas samples were not taken therefore gas analysis was not carried out).

**Table 3 - Gas volume and gas composition given as a percentage for each single cell pressure vessel test**

Test	Net Gas Volume Produced (L)	v/v% gas composition						
		Hydrogen	Carbon dioxide	Carbon monoxide	Ethane	Ethylene	Propane	Methane
11	4.7	8.8	77.9	7.9	0.5	1.1	1.2	2.5
12	4.9	13.8	69.2	9.5	0.7	2.2	1.3	3.3
13	3.2	-	-	-	-	-	-	-
14	6.0	29.0	32.9	16.7	3.1	7.9	6.3	4.1
15	6.4	25.9	33.9	19.3	2.7	9.4	5.3	3.6
16	7.1	-	-	-	-	-	-	-

Figure 9 shows the gas percentage volumes for the gases identified during gas composition analysis.



**Figure 9 - Gas percentage volumes for hydrogen, carbon dioxide, carbon monoxide, ethane, ethylene, propane, and methane for tests 11 (air atmosphere) and 14 (nitrogen atmosphere).**

The single pouch cell tests which took place in either a nitrogen or air atmospheres gave rise to similar maximum temperatures of approximately 700 °C. However, the pressure recorded differed between the two test atmospheres, with maximum pressures upon failure for tests in air being approximately double those in nitrogen. This is due to the vent gases igniting and producing flame and additional combustion gases in air, whereas those in nitrogen were unable to ignite as the oxygen concentration was not high enough.

These differences also affected the volume of gas produced and the observed gas composition between tests. In general, the hotter the gas temperature the higher the pressure. By conducting tests in both an air and nitrogen atmosphere it allows the gas composition to be determined when combustion of gas has and has not taken place (Baird, et al., 2020). The average volume of gas for the tests conducted in air atmosphere was 4.3 L compared to 6.5 L of gas produced in a nitrogen atmosphere. The higher gas volume observed for tests in a nitrogen atmosphere can be explained due to differences in gas production and failure mechanism. Upon the failure of a cell in an air atmosphere the concentration of oxygen is high enough to allow for complete combustion to take place producing carbon dioxide and water, the latter of which condenses, and is therefore not taken into account when determining final gas volume. In addition, oxygen present in the pressure vessel is also consumed by combustion. In a nitrogen atmosphere there is insufficient oxygen for complete combustion to take place preventing the reaction of flammable gases and therefore water vapour, increasing the gas volume. This is supported by the different gas compositions produced in each test type. For example, in the gas composition for the tests in the air atmosphere, hydrogen made up an average of 11.3 % compared to an average of 27.5 % in a nitrogen atmosphere. Despite insufficient oxygen for combustion in a nitrogen atmosphere, carbon dioxide and carbon monoxide are produced as a result of breakdown of the organic electrolyte present within the cell. The percentage volumes of small hydrocarbons; ethane, ethylene, propane, and methane is also higher in a nitrogen atmosphere compared with air as there is insufficient oxygen for their combustion. The difference in gas volumes and composition varies between atmospheres is therefore greatly affected by the concentration of oxygen present.

The residual oxygen percentage for tests conducted in air provides an indication of the amount of oxygen consumed during combustion of the cell. The oxygen to argon ratio for both test atmospheres also provides an indication of whether or not any combustion took place. For tests conducted in nitrogen, the ratio of oxygen to argon was calculated by analysing a sample of nitrogen taken from the pressure vessel after purging but prior to testing. The ratio oxygen to argon ratio was found to be 5:1, this is particularly relevant for tests in a nitrogen atmosphere as no combustion should occur due to low oxygen concentrations. This data is summarised below:



**Table 4 - Summary of oxygen:argon and oxygen consumption for tests where gas analysis was performed**

Test Number	O <sub>2</sub> : Ar After Test	Oxygen Before Test (%)	Oxygen After Test (%)	Oxygen Consumed (%)	Volume of Oxygen Consumed (L)
11	-	19.6	1.8	17.8	8.2
12	-	19.6	2.9	16.7	7.6
14	6.5 : 1	0.5	1.15	-	-
15	4.4 : 1	0.5	0.90	-	-

The oxygen to argon ratio for both tests performed in a nitrogen atmosphere was similar to the ratio of 5:1 before the test. The relative lack of change in ratio indicates that no combustion of the cell took place. (Any variation may be attributable to the fact that only one representative sample of the nitrogen atmosphere was taken as a reference (and not before each individual test).

**Cell Block Test**

Table 5 shows a summary of the gas volume and composition generated by a pouch cell block upon the failure of all four cells at a 100 % state of charge:

**Table 5 - Gas volume and gas composition given as a percentage for a cell block test with four pouch cells**

Test	Gas Volume (L)	v/v% gas composition						
		Hydrogen	Carbon dioxide	Carbon monoxide	Ethane	Ethylene	Propane	Methane
17	31.4	30.7	43.6	6.8	2.0	9.7	4.1	3.2

The cell block took longer to reach the failure temperature for the initiating cell as some of the heat was transferred to the other cells. Once the initiating cell had reached failure, the heat generated provided enough heat for all remaining cells to enter thermal runaway, via thermal propagation (Archibald, et al., 2020). This led to full failure of all four cells in the cell block. Another consideration when using multiple pouch cells within a block is that pressure generated by the swelling of the first cell is exerted upon the other cells in the block. This effect should be considered when designing containers to house pouch cells.

The volume of gas generated from the cell block test that was undertaken in a nitrogen atmosphere was approximately 4 times larger than the single cell tests conducted in nitrogen. This is to be expected as the volume of gas generated by each individual cell should be similar of similar volumes to those generated in single cell tests. The gas composition was also similar as the way in which gas was generated will also not differ between single and cell block tests.

**Conclusion**

The considerable pressures exerted by the cell and gas volumes generated when a 5 Ah pouch cell fails demonstrate the dangers of pouch cells when exposed to conditions outside of their normal operating conditions. The pouch cells used in this set of experiments were relatively small compared to other commercially available pouch cells, especially those used readily in vehicles and BESS. When using larger pouch cells or battery modules the results are likely to produce more catastrophic failures, which should be considered when designing new products or systems which operate using pouch cells, especially when fire mitigation relies on confinement to minimise the amount of oxygen available for combustion in the event of cell failure.

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