Thermal Runaway and Safety of Large Lithium-Ion Battery Systems

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Abstract

Battery packs and modules have been used extensively in industries such as consumer products, transportation, telecommunications and grid energy storage. In recent years, the trend has been to use higher capacity batteries or packs, allowing the user to store more energy, to extract it at a higher rate, and to extend the application to new fields such as smart grid and off-grid storage. However, understanding the safety aspects of these large battery systems and managing failures in higher energy cells such as lithium-ion batteries is a growing concern for many industries.

One of the most catastrophic failures of a lithium-ion battery system is a cascading thermal runaway event where multiple cells in a battery fail due to a failure starting at one individual cell. Thermal runaway can occur due to exposure to excessive temperatures, external shorts due to faulty wiring, or internal shorts due to cell defects. Thermal runaway events result in the venting of toxic and highly flammable gases and the release of significant energy in the form of heat. If ignited, these gases can cause enclosed areas to overpressurize, and if unmitigated, this overpressure can result in an explosion and severe damage to the battery and surrounding equipment or people. An explosion scenario can be even more severe for a large battery pack, where the heat generated by one failed cells can heat up neighboring cells and lead to a thermal cascade throughout the battery pack. Understanding the reasons for thermal runaway and the consequences of such an event is helpful for purposes of avoiding or planning for cell failures. Thermal failures of batteries make news headlines, whether in the transportation industry or others.

This work provides an overview of the cause and consequences of thermal runaway events and mitigation strategies with respect to gases released during these events. The results of recent research on thermal runaway events are explained. In particular, vent gas composition, energy release, flammability and other hazards are quantified. These results are compared to more common hazardous gases such as methane, hydrogen as well as other combustible materials. This comparison can serve as a basis to adapt common safety practices used in other industries, to protect people, the batteries and the facilities that use these large battery systems.

Single Cell Failure

Thermal runaway occurs when the temperature of a cell increases in an uncontrolled manner, leading to its failure. This temperature increase generates gases, which vent when the pressure inside the cell rises above a design value. For lithium-ion cells, these gases are hot and combustible, which can become a hazard if a pack was not designed to control the causes and consequences of thermal runaway.

The following paragraphs describe the different steps involved in a thermal runaway and summarize the latest quantitative data related to thermal runaway in lithium-ion cells. Results from recent work on small format lithium-ion pouch cells (7.7 Wh nominal, 2.1 Ah, 3.7 V) are summarized below. However, the testing and analytical methods used in these studies can be applied to large format cells. The cells consisted of a negative electrode with graphite active material and a positive electrode with $LiCoO_2$ active material. Note that cell chemistry, cell geometry, as well as the way the thermal runaway process is initiated influence the quantitative behavior of the failure.

Temperature Increase and Pre-Failure Processes

All thermal runaway events are a result of a rise in cell temperature. This temperature rise can have multiple causes, including, but not limited to:

- The use of cells in high temperature environment
- A defect inside the cell can result in an internal short circuit, which causes the cell to heat up at the location of the defect.
- A surge in the charging or discharging current. When cells are charged or discharged, heat is generated. The higher the current, the higher the heat generation.
- An improper electrical connection at the tab of a battery. This causes an increased electrical resistance which generates heat at the electrical contacts.
- Mechanical damage to the cell or battery which can also lead to internal shorts and result in heat generation.

Cells generate heat, even under normal operating conditions. The heat generation from charging and discharging cycles are not expected to induce a thermal runaway event unless this heat is allowed to accumulate and slowly heat up the cells and the battery to a point where irreversible changes to the cell and failures may occur. However, if the cell develops an internal short due to manufacturing defects, mechanical abuse or external heating, the heat generated from the cell may be large enough to initiate a thermal runway event.

In addition, exothermic chemical reactions occur within the cell even if the cells are not in use. Accelerated Rate Calorimetry (ARC) is one test method that can be used to quantify the self-heating rates. The typical ARC test involves placing a lithium-ion cell in an insulated test chamber, often referred to as the *bomb*. As the cell heats, external heaters apply heat such that the chamber temperature mimics, or tracks, the cell temperature. This process allows for the temperature evolution of a cell to be measured under adiabatic conditions.[1] Figure 1 shows the rate of temperature rise of a lithium-ion cell during an ARC experiment. As the temperature increases, the self-heating rate also increases. At approximately 240 °F, the self-heating rate increases dramatically. Figure 1 shows the self-heating rates in a small format lithium-ion pouch cells. The exothermic reactions are negligible at low temperatures, but become significant as the cell temperature increases. At higher temperatures, the cell short-circuits. Gases build up within the cell and eventually vent. The ARC results demonstrate the consequences that occur when batteries are allowed to overheat and undergo a thermal runaway process.

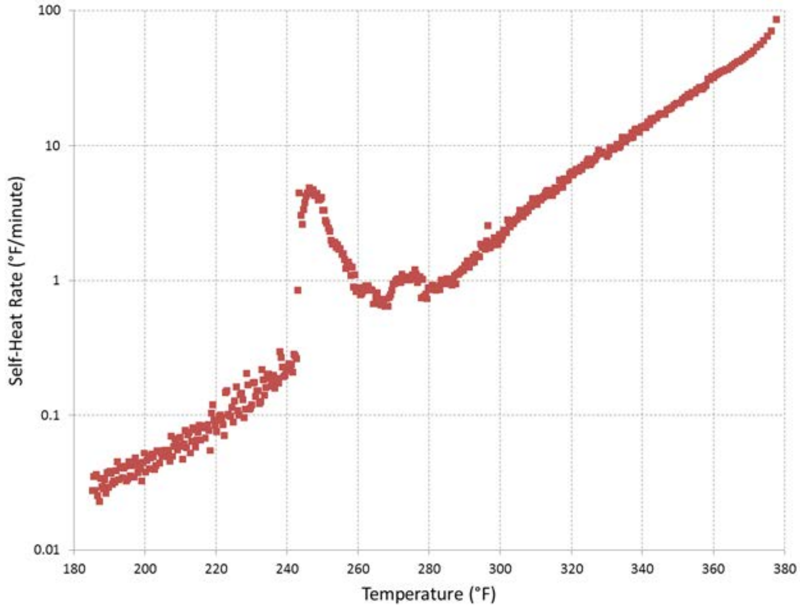

Figure 1. Self-heating rate versus temperature of cell at 100% SOC

Vented Gases

During a thermal runaway event, the cell produces gases that build up within the cell. Some cell designs include a specially designed vent that opens, and releases the gases. In some cases, this vent can become obstructed or may not open correctly, which may result in rupturing of the cell enclosure. Other cell form factors, such as pouch cells, do not include a specific vent and the gases will release at weak points in the external pouch, typically near the tabs of the cell or along the pouch seams in unconstrained cells. The release of vented gases avoids the catastrophic failure of the cell containment structure, but it creates a new hazard associated with the flammability of the vented products if ignition occurs.

Previous work has been conducted to quantify the amount of vented gases, their composition and their flammability characteristics.[2] A summary of their results is presented here. To investigate the hazards presented by the vent gases, a test method was developed where thermal failure of a cell was initiated in an enclosed chamber filled with an inert gas (argon). After the cell vented, the resulting gases were collected in a sample canister and analyzed for composition analysis using gas chromatography-mass spectroscopy (GC-MS). Although the cells tested were vented into an inert environment, partial combustion could still take place due to the decomposition of the positive electrode active material, which releases oxygen during decomposition. For other cell chemistries that do not produce oxygen during thermal runaway, partial combustion is not expected in the inert chamber environment.

Table 1 summarizes the amount of gas vented during a thermal runaway event, for pouch cells at three different states of charge. For comparison, the volume reported is referenced to standard pressure and temperature (80 °F, standard atmospheric pressure). It should be noted that for large battery packs, the amount of gas that is released can be substantial.

Table 1. Venting gas volumes for a 7.7 Wh pouch cell at standard pressure and temperature. As a comparison, the cell has a volume of 0.014 L.

State of Charge	Vented Gas Volume	Volume per Wh
50%	0.8 L / 0.2 Gal	0.10 L/Wh
100%	2.5 L / 0.7 Gal	0.33 L/Wh
150%	6.0 L / 1.6 Gal	0.78 L/Wh

Table 1 shows that the higher the state of charge, the larger the amount of gases released. This relationship is not linear and a cell that is charged at 100% will generate more than twice the amount of gas than a cell at a 50% SOC.

The gas composition analysis shows that the cell vents combustible gases. Table 2 summarizes the gas composition for different SOCs. With the exception of carbon dioxide, all the substances reported in Table 2 are flammable. In addition, carbon monoxide and some of the hydrocarbons are not only flammable, but also can pose significant health hazards.

Table 2. Vented gas composition for a 7.7 Wh pouch cell.[3]

Gas		50% SOC (%vol)	100% SOC (%vol)	150% SOC (%vol)
Carbon Dioxide		32.3	30.0	20.9
Carbon Monoxide		3.61	22.9	24.5
Hydrogen		31.0	27.7	29.7
Hydrocarbons	Methane	5.78	6.39	8.21
	Ethylene	5.57	2.19	10.8
	Ethane	2.75	1.16	1.32
	Propylene	8.16	4.52	0.013
	Propane	0.68	0.26	2.54
	Isobutane	0.41	0.20	0.13
	n-Butane	0.67	0.56	0.39
	Butenes	2.55	1.58	0.60
	Isopentane	0.45	0.07	0.036
	n-Pentane	1.94	0.73	0.30
	Hexanes +	4.94	2.32	8.21
	Benzene	0.14	0.11	0.33
	Toluene	0.061	0.018	0.052
	Ethyl-benzene	0.009	0.002	0.003

Note that Table 2 summarizes the species volume fraction of the vent gases. The absolute volume of each species depends on the total volume of gas vented, which increases as the SOC increases. Therefore, the total volume of hydrogen released from a 150% SOC cell is significantly more than from a 50% SOC cell despite having similar hydrogen volume fractions.

If the flammable gases produced during thermal runaway are ignited in a confined environment, they can present overpressurization and explosion hazard. This is particularly true for large battery packs, where the battery modules are often contained in an enclosure. An explosion can occur when the uncombusted vented gases mix with remaining air in the enclosure or with fresh air that enters the enclosure from vents and openings and the resulting mixture is ignited by either the failing cells or a different ignition source in the enclosure.

To quantify the explosion severity of the vent gases, the gases collected in the test chamber are metered in to a 20-L combustion chamber. The vent gases are mixed with air over a range of equivalence ratios and ignited. The explosibility parameters, the maximum overpressure P_{max} reported in bar and the explosion index, K_g in m-bar/second, are determined from the measured 20-L chamber pressure. The explosion index is proportional to the rate of pressure rise of the gas and is an indication of the speed at which the combustion process takes place. These two values are commonly used to characterize and compare the combustion characteristics of substances such as gases or dust. Generally speaking, the higher the maximum overpressure and the explosion index, the more explosive the mixture.

Figure 2 shows the peak over-pressure measured when the vent gases are mixed with air and ignited. The figure shows that at both 100% and 150% SOCs, the gases will not ignite if their combined concentration is lower than 6% (*i.e.* 94% air), or higher than 40% (*i.e.* 60% air). These two limits are commonly called the LFL (Lower Flammability Limit) and UFL (Upper Flammability Limit). The maximum pressure that can be obtained when vented gases ignite in the presence of additional air would therefore be approximately 7.1 barg and 7.7 barg, in the case of the failure of cells at 100% and 150% SOCs, respectively. This highest pressure increase occurs at a fuel concentration of about 18% (*i.e.* 82% air). A 50% SOC cell failure does not produce enough vent gases to be able to fill the combustion chamber in which this testing was performed, and such failure was not analyzed for combustion characterization.

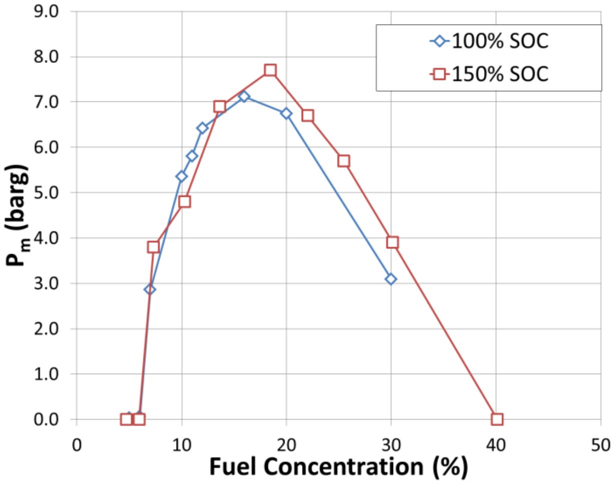

Figure 2. Overpressure resulting from the combustion of vent gases released during a thermal failure of 7.7 Wh cells at 100% and 150% SOCs.

The combustion characteristics of the vented gases is summarized in Table 3 and compared with those of common gases. The combustion properties of the vented gases are similar to typical hydrocarbons despite the large presence of carbon dioxide. In other words, mitigation techniques used in the oil and gas industry or in the chemical industry to mitigate the consequences of leaks of hydrocarbons could be modified and adapted to mitigate the consequences resulting from vent gases in the event of lithium-ion cell failures. Another point to note is that the gases vented from lithium-ion cell failures have a broader combustion range than typical hydrocarbons.

Table 3. Combustion characteristics of vented gases released during a thermal failure of 7.7 Wh cells, and of common gases.[4]

Gas	LFL	UFL	P_{max} (barg)	K_g (m-bar/s)
Li-Ion Vent Gas (100% SOC)	6%	~38%	7.1	65
Li-Ion Vent Gas (150% SOC)	6%	40%	7.7	90
Methane	5%	15%	6.7	46
Propane	2%	10%	7.2	76
Ethane	3%	12%	8.0	171
Hydrogen	4%	75%	6.5	250

Cell Combustion

Cells consist of organic materials such as the separator, the packaging and the electrolyte—all of which are flammable. Often, the combustion event does not only involve the combustion of the gases, and the cell itself also burns and releases energy. This is particularly true if a pack is involved in a fire irrespective of whether the fire is ignited at the pack or propagates to the pack. A detailed review of the combustible materials contained in a 7.7 Wh cell is provided in Somandepalli *et al.*[5] Their results are summarized here.

To quantify the amount of energy that can be released by a cell involved in a fire, Somandepalli and coworkers tested the cells in a cone calorimeter. Cone calorimeters are typically used to estimate the heat released during the combustion of fabrics or other materials. In a cone calorimeter, the combustion products and the energy released during combustion is determined by heating a sample (in this case a cell) until it ignites, then by collecting and analyzing the oxygen, carbon dioxide and carbon monoxide contents of the exhaust gases. The standard method by which the cone calorimeter results are processed had to be modified to account for the actual complex composition of a lithium-ion cell.[5] During the test, both the vented gases and the cell itself will ignite and burn. Figure 3 shows a schematic and photo of the cone calorimeter test apparatus.

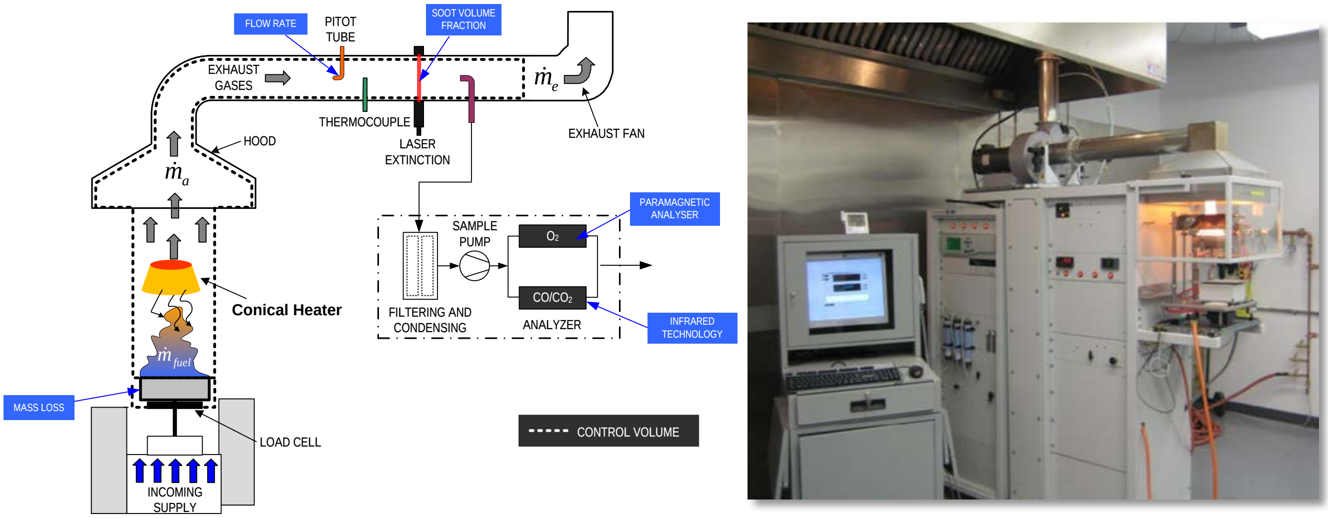

Figure 3. Schematic layout of a cone calorimeter (left) and Exponent's cone calorimeter (right).

Although the cone calorimeter can be used to determine several parameters (*e.g* critical heat flux for ignition, ignition time, etc.), one of the most important parameters measured is the heat release rates (HRR) as a function of time. The HRR is the rate of energy produced by the combustion process (expressed typically in kW). It is the single most important parameter for determining the fire hazards associated with a given material or product and for designing fire protection systems. Figure 4 shows the evolution of the heat release rate as a function of time for a 7.7 Wh lithium-ion cell at 50% SOC. At the peak of the combustion event, the fire releases 18 kW of power. Once again, the heat release rate is very dependent on the state of charge of the cell. A cell that is completely discharged (0% SOC) has a peak heat release rate of only approximately 2 kW. The heat release rate for a fully charged cell was not obtained because the combustion products from the cell could not be completely contained by the calorimeter.

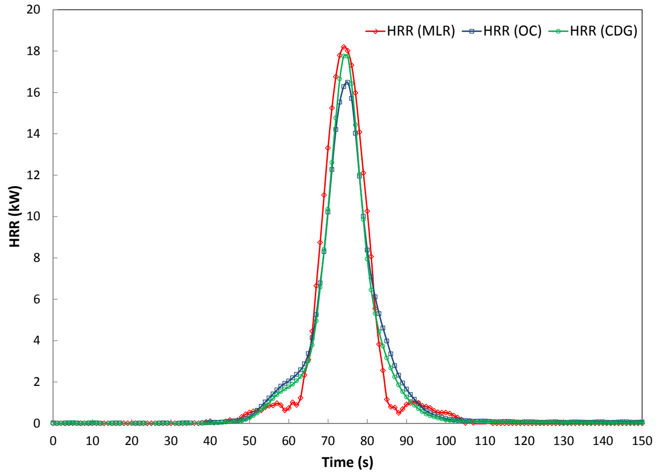

Figure 4. Heat release rate (HRR) during the combustion of a 7.7 Wh lithium-ion cell at 50% SOC. The three different curves correspond to three different HRR estimates based on the same cone calorimeter test.

The net heat of combustion of a cell could be estimated using the total energy released during the combustion of the cell. A comparison with common materials reveals that the heat of combustion for a 50% SOC lithium-ion cell falls between that that of PMMA and Acetone (see Table 4).

Table 4. Heat of combustion of selected organic materials compared to a 50% SOC lithium-ion cell.[6]

Material	Net Heat of Combustion (kJ/g)
Douglas Fir	19.6
PMMA (clear plastic)	25
50% SOC li-ion cell	28.1
Acetone	30.8
Gasoline	44.1

Interestingly, the 50% SOC lithium-ion cell is able to store 0.6 kJ/g of electrical energy well below the amount of energy released during a fire. The amount of electrical energy per unit mass stored in the cell can be calculated by using the cell capacity (*i.e.* 7.7 Wh), the cell mass (*i.e.* 23 g) and the SOC (*i.e.* 50%).

Propagation of Failure, Hazards and Prevention

Thermal runaway events can result from uncontrolled increases in cell temperature. During the failure process, the cell self-heats and combustible gases are vented. In addition, these vented gases, as well as the battery itself can ignite, generating even more energy released. Thermal runaway is therefore a highly exothermic, self-propagating process. As a result, there is a risk that a failing cell could heat neighboring cells causing a cascading event where thermal failure propagates from cell-to-cell, and battery to battery. Lithium-ion cells are still a relatively new technology and thermal runaway events are not completely understood. However, tests such as those presented above, provide a basis that can be relied upon when trying to develop strategies to mitigate the consequences of thermal runaway or possibly prevent thermal runaway from occurring.

To avoid thermal runaway, and to prevent propagation of the failure from cell to cell, one needs to be able to control the temperature of individual cells or of small groups of neighboring cells. Many potential thermal management systems exist and depending on the application, they can involve fins, fans circulating cooling air, phase changing materials that absorb a significant amount of heat without changing temperature, *etc*. They can also be used in combination with control algorithms that either stop drawing currents if the cell is overheating, or discharge neighboring cells if one cell in the pack is expected to fail. The design of such a thermal management can be trivial for simple applications, but becomes more complex when more energy is stored, when space is limited, or in harsh environmental conditions. Three-dimensional numerical simulations using Computational Fluid Dynamics (CFD) can provide comparative information of the efficiency of various designs under various failure scenarios. A typical simulation will provide information about temperatures and air flow rates, and is able to detect areas where heat cannot be easily dissipated. The results of a typical CFD simulation of a thermal management system are shown in Figure 5.

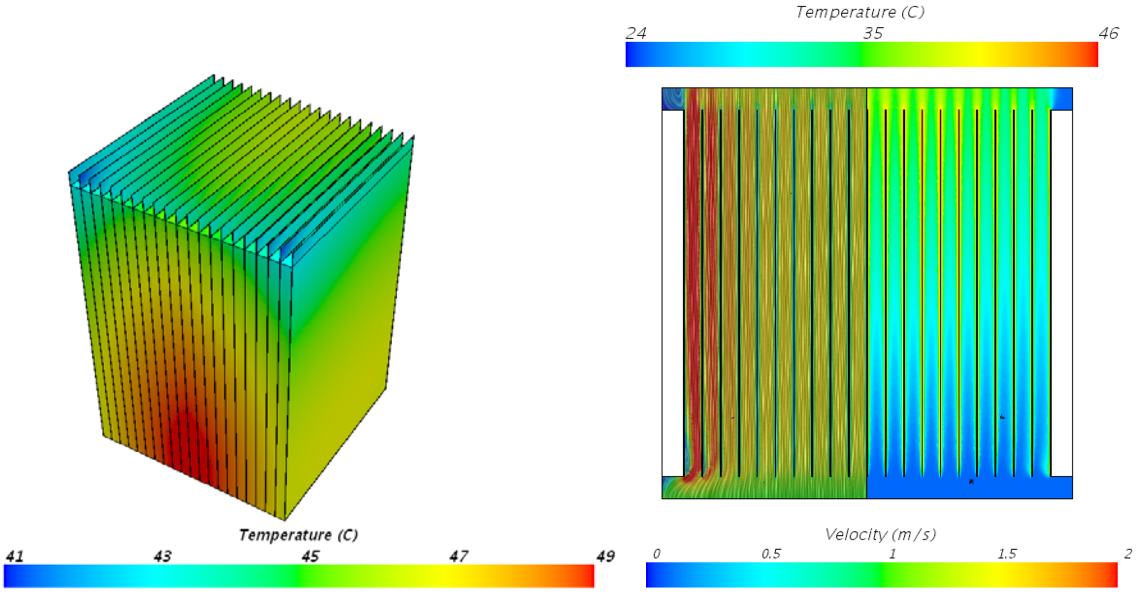

Figure 5. Typical results of a numerical analysis of a thermal management system. Temperature of cells and fins (left) and associated air flow characteristics (right).[7]

Beyond controlling temperatures, mitigation techniques can be used to limit the consequences of a failure. In particular, vented gases are hot and can even melt metal if the cell vents right next to it. Depending on the application, a review of the design for purposes of assessing the risk associated with the fate of the vented gases injuries may involve a simple review of the pack layouts, or could require tests or full numerical analysis of the fate of the gases in complex geometries (see for example Figure 6).

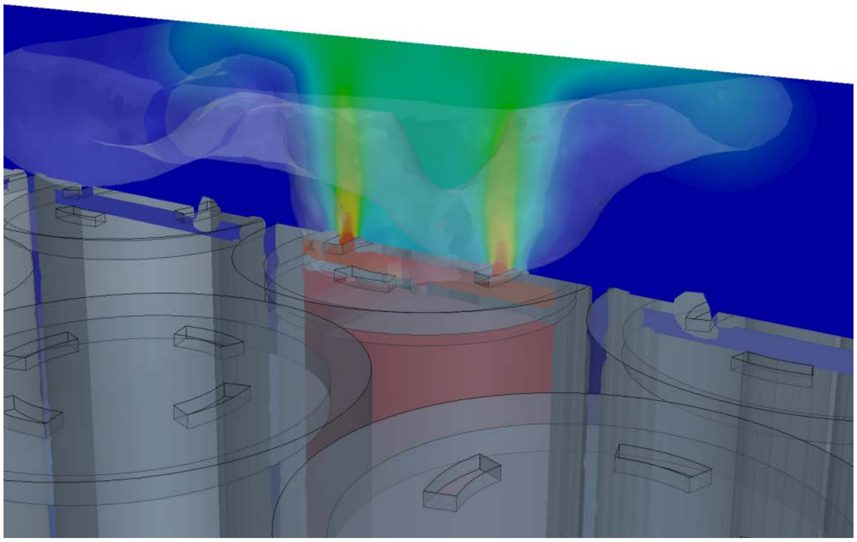

Figure 6. Example of a simulation modeling the fate of vent gases inside a pack of 18650 cells during a thermal runaway event.[3]

Failing cells generate a relatively large quantity of gases at high temperatures. If the cells are enclosed in a casing, the pressure inside the casing can increase either because of overpressurization or explosion due to combustion of the vented gases. Casings can be designed to be able to contain such a pressure rise, or can include vents that open when the pressure rises above a predetermined threshold. Such vents are commonly used in many industries to mitigate the risks of explosions. NFPA 68 provides guidance for the design of vents to prevent high overpressures in enclosures. The ability to quantify both the maximum overpressure and the explosion index allows for direct application of NFPA 68 to battery systems. Similarly, NFPA 497 can be used to prevent flame propagation by using flame arresters.

The above paragraphs are not meant to give an exhaustive list of mitigation techniques, but present a sample of analyses and design considerations that rely on cell test data and that can help reduce the risks associated with thermal runaway.

Conclusions

An overview of the cause and consequences of thermal runaway events and mitigation strategies was provided. In particular, vent gas composition, energy release, flammability and other hazards were quantified. These results were compared to more common hazardous gases such as methane, hydrogen as well as other combustible materials. This comparison can serve as a basis to adapt common safety practices used in other industries, to protect people, the batteries and the facilities that use these large battery systems.

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