

Quantification of Combustion Hazards of Thermal Runaway Failures in Lithium-Ion Batteries

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ABSTRACT

As lithium-ion cells and systems become larger and more ubiquitous in automotive applications, fire and explosion hazards that are rare or non-existent in smaller systems may exist in these larger systems. One potential hazard can occur when flammable gases emitted from a lithium-ion cell failure accumulate in or around automobiles and are ignited by electrical activity or by the cells themselves and result in a fire or explosion. In some instances, the safety aspects related to fires and explosions protection of electric vehicles and hybrid vehicles using these large energy storage battery packs are a significant challenge to address. This paper describes and characterizes the combustion and explosion hazards that can occur when a lithium ion battery pack fails and goes into thermal runaway in an enclosed space. Metrics such as gas composition, maximum overpressure, rate of pressure rise, and flammability limits are described. This information can be helpful to battery and pack designers, vehicle designers, first responders and emergency personnel in developing strategies to mitigate and prevent explosion hazards from the use of battery packs in automobiles and other fields where large battery packs are used. Measurements of this type can also be used to provide design guidance for containment enclosures and explosion venting or blow off panel design that can mitigate the hazard of combustible gases vented during failures in lithium ion cells and large battery packs.

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INTRODUCTION

Over the past few years, the market share for electric vehicles (EV) and hybrid vehicles has steadily increased. Automotive manufactures have used several types of rechargeable batteries for EV and hybrid vehicle applications including nickel-metal-hydride and lithium-ion (Li-ion). From a technological standpoint, Li-ion technology is an attractive option for automotive applications because of its high energy density. However, from a safety and fire protection standpoint, a high energy density coupled with a flammable organic, rather than aqueous, electrolyte has created a number of new challenges with regard to the design of batteries containing Li-ion cells, and with regard to the storage and handling of these batteries. Historically, there have been reports of incidents of fire and explosion hazards resulting from Li-ion batteries, ranging from consumer electronic devices such as cellular phones, and laptops. Recently, fire incidents have also been reported for electric vehicles and other transportation systems.

Thermal hazards from Li-ion battery failures can be the result of various failure modes. Because the Li-ion cell chemistry has an inherent high energy density, a cell failure can generate significant amounts of heat capable of combusting other cell components. Another hazard can result from a breach in the

cell packaging (before or after a thermal event), which can allow flammable electrolyte vapors to permeate and fill available space, creating a possible flash fire or explosion risk. Additionally, the degradation and reaction products of a thermal event in a lithium-ion cell and a battery pack can create potentially combustible gases [1] which pose similar or more powerful explosion risks to that of the un-combusted flammable electrolyte. For large power packs used in electric vehicles and power-storage units, the volume of vented gases may be significant. Combined with the partial or full confinement within an enclosure such as a vehicle interior, ignition of the vented gases could pose an explosion hazard. Owing to the variability of lithium-ion cell chemical composition due to proprietary manufacture and design, the potential explosion severity of the vented gases is not well documented or characterized.

In the present work, the combustion characteristics of vent gases produced due to thermal failure of lithium-ion cells are studied experimentally. The goal of the work is to characterize the explosion characteristics of the vent gases to assess potential flash fire and explosion hazards associated with venting of lithium-ion cells and packs during thermal runaway events. The gases vented from small format lithium-ion cells during thermal runaway are sampled and analyzed experimentally, and the explosion characteristics including

maximum pressure rise, explosion severity and lower and upper flammability limit of the vent gas composition are also measured. Similar analysis can also be applied to large format lithium-ion cells used in EV and hybrid vehicles.

EXPERIMENTAL SETUP

Testing was conducted at Exponent's laboratories in Natick, MA, using a test chamber specifically designed for sampling and analysing vent products from Li-ion battery failures. Two different experiments were conducted—one where vent products were sampled and analysed for composition, and two, these vent products were vented into a combustion chamber and ignited to determine combustion characteristics. Lithium-ion cells used for these tests were small format, commercially available 2.1 Ah (7.7 Wh nominal) Li-ion cells. The cells consisted of a negative electrode with graphite active material and a positive electrode with LiCoO_2 active material.

Gas Sampling

Vent products resulting from thermal failure of cells were captured in a custom designed 6 in diameter cylindrical stainless steel cell test chamber (Figure 1). The chamber test section is approximately 13 in long and is enclosed on either side with 0.5 in thick stainless steel flanges. On one flange, K-type thermocouples, signal wire pairs, and a high voltage power feed thru ports allow for temperature and voltage measurements and power access inside the chamber to monitor the cell health. A pressure transducer, a 50 psig pressure relief valve and a gas sampling and vent port were installed on the other flange to monitor and capture the gases released when these cells were made to fail in thermal runaway conditions.

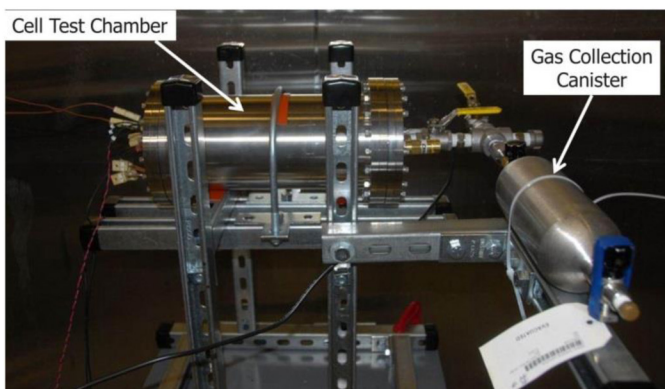


Figure 1. Photograph of cell test chamber with a gas sampling canister.

For the lithium-ion cell venting experiments, the battery surface temperature, the chamber gas temperature, and the chamber pressure were monitored throughout the duration of each test. Prior to each test, a cell was wrapped with a 100 W, 0.165 in thick heat cable and placed on a thermal brick inside the vent chamber. The vent chamber was sealed, evacuated with a vacuum pump to approximately 0.04 bar, and refilled with argon to atmospheric pressure. Catastrophic failure and

subsequent thermal runaway of lithium-ion cells at 50%, 100%, and 150% state-of-charge (SOC) was induced by applying external heat to the cell by powering the heat cable. Power to the heat cable was terminated once the cell failed and gaseous products vented, and the resultant vent products were allowed to collect in the chamber. The gaseous products were allowed to cool to 60°C and sampled through the vent port into an evacuated sample canister. The species composition of the gas sample was analyzed using gas chromatography-mass spectroscopy (GC-MS). Prior to analysis, the samples were heated to 60°C to sample any gases that may have condensed in the container after the sampling was completed.

Combustion Chamber Testing

To determine the maximum over pressure, explosion severity, and lower and upper explosion limit (LEL and UEL) of the vent gases from cell failures, the cell test chamber was attached to a 20 L combustion chamber (Figure 2). A description of the 20 L apparatus is detailed in Ref. [2]. The cell test chamber and combustion chamber were evacuated to approximately 0.15 bar. For these tests, the cell test chamber was not purged with Argon. The valve between the two chambers was closed, and cell failure was induced in the same manner as the gas sampling experiments described above. Once the cell went into thermal runaway and vented, the resultant gases were metered into the evacuated 20 L combustion chamber. After the chamber was filled with a predetermined amount of vent gas, the chamber was filled with air to atmospheric pressure to create a fuel-air mixture of known concentration. The resultant mixture of cell vent products and air were ignited using a 250 J chemical igniter. The maximum pressure rise and the explosion severity index were determined from measuring the induced pressure from the resultant deflagration within the combustion chamber. The upper and lower explosion limits of the vent gases were determined by varying the vent gas-to-air ratio in the combustion chamber.

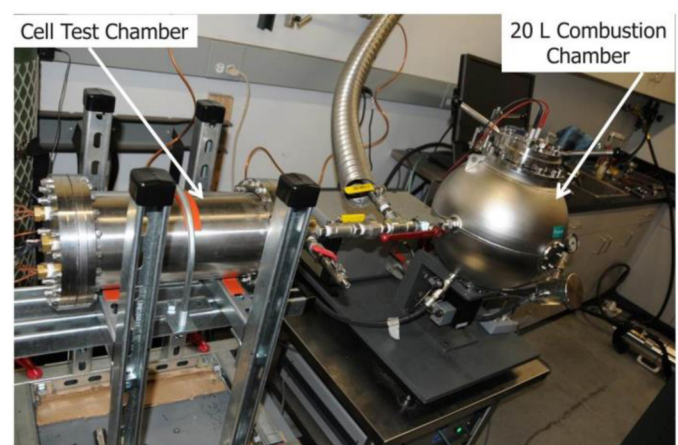


Figure 2. Photograph of cell test chamber attached to the 20-L combustion chamber.

EXPERIMENTAL RESULTS

Thermal failure of 7.7 Wh lithium-ion cells at various states-of-charge (50%, 100%, 150%) were induced in the vent chamber. The chamber gas temperature, chamber pressure, battery surface temperature, and cell voltage were monitored throughout each test.

Vent Gas Volume

During the testing, when the battery surface temperature reached approximately 250°C, the cell voltage dropped to zero indicating that the cell had shorted. Immediately following the decrease in voltage, the pressure and temperature of the chamber increased dramatically indicating that the cell had failed (likely die to internal shorting and subsequent thermal runaway) and gases had vented from the cell into the cell test chamber. Figure 3 shows an example time trace of chamber pressure, chamber temperature, cell temperature and cell voltage during the 100% SOC test. The total amount of gas produced is estimated from the peak values of the chamber temperature and chamber pressure.

At standard pressure and temperature (300K, 1 atm), the volume of gases released from the failure of cells at 50%, 100% SOC and 150% SOC were 0.8 L, 2.5 L and 6.0 L of gases, respectively. Figure 4 shows the volume of gases released normalized by the nominal energy of the cell. The volume of gases released does not increase linearly with SOC. The volume of gases released increases by a factor of approximately 3 as SOC increases from 50% to 100%, but only 2.3 as SOC increases from 100% to 150%. Further work is necessary to study if a relationship exists between the SOC and volume of gases that could be released from li-ion cells during a thermal event.

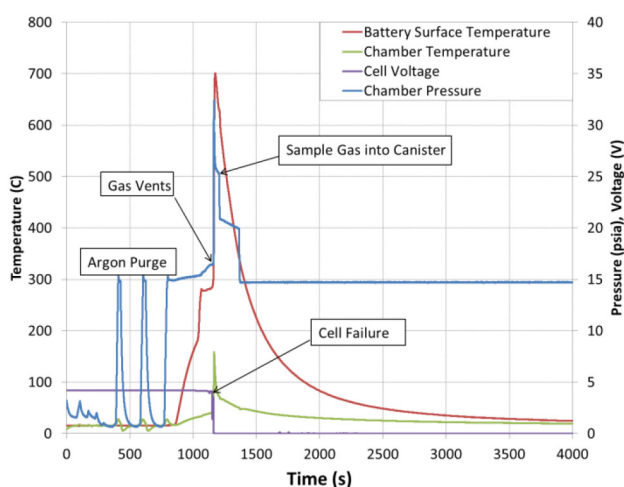


Figure 3. Time trace of cell voltage, chamber pressure, chamber temperature, and battery surface temperature during testing of lithium-ion cells at 100% SOC.

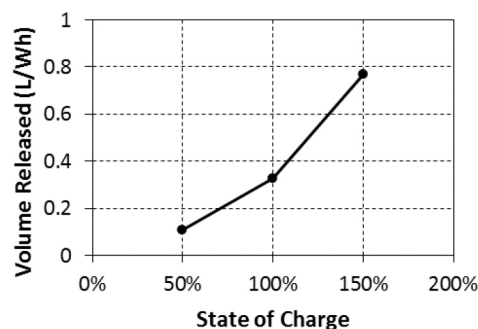


Figure 4. Total volume of gas released from 7.7 Wh li-ion cells at 50%, 100%, and 150% SOC.

Gas Composition Analysis

An evacuated sample canister was attached to the sampling port to sample the vent gases from the cell test chamber. The chamber temperature was allowed to cool to 60°C prior to opening sampling port valve. The sample gas was then analyzed for composition using GC-MS. The results of the GC-MS analysis are summarized in Table 1 and

Table 2. The volume fraction of each species has been normalized to account for the initial argon and trace oxygen and nitrogen in the chamber. Although the batteries were vented into an inert environment, combustion can still take place due to the decomposition of the positive electrode active material, which gives off oxygen during decomposition. The amount of oxygen produced by the battery is small and is not likely to be sufficient for the fuel to be consumed completely. In all cases tested, significant amounts of hydrogen, hydrocarbons and carbon monoxide were released from the cell. As SOC increased, carbon dioxide decreased and methane increased, and hydrogen remained relatively unchanged. The total volume fraction of hydrocarbons at the SOC tested range between 20-30%. For 50% SOC, the carbon monoxide produced is 6-7 times less than both the 100% and 150% SOC cases. It is important to note that Table 1 and

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

Table 1. Volume fraction of major gas species released from 7.7 Wh li-ion cells at 50%, 100%, and 150% SOC.

Gas	50% SOC (%vol)	100% SOC (%vol)	150% SOC (%vol)	Roth et al.[4] (%vol) Test 1/Test 2
Carbon Dioxide	32	30	20.9	61.4/75.8
Carbon Monoxide	3.61	22.9	24.5	15.1/6.4
Hydrogen	30	27.7	29.7	5.1/5.9
Total Hydrocarbons	34	19.3	24	---
Methane	5.78	6.36	8.21	7.4/1.9