Thermal Safety Management of Lithium-Ion Battery Energy Storage Systems for Use in Ocean-going and Subsea Applications

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Increasing power demands for ocean and sub-sea sensors, unmanned and autonomous vehicles as well as requirements of power storage from ocean based generation sources, have led to newer energy storage technologies such as lithium-ion batteries being widely adopted for these purposes. One of the key challenges that operators and users face is the safe integration of these energy storage technologies into the current vehicles or equipment to mitigate or contain the consequences of unintended releases of the stored energy.

A catastrophic failure of a battery pack can occur if one or more cells in the battery pack undergo a thermal runaway event rapidly releasing the stored energy in the battery. Thermal runaway can lead to a release of flammable gases, heat or explosions and can potentially result in a mission kill, loss of vehicle or sensor, or hazards to property and life. The objective of this paper is to discuss current research and techniques to measure and quantify the hazards posed by unintended release of stored energy from newer energy storage technologies, as well as mitigation of such hazards. In the present work, the combustion characteristics of vent gases produced due to thermal failure of lithium-ion cells are studied experimentally to assess potential flash fire and explosion hazards associated with venting of lithium-ion cells and packs during thermal runaway events. 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 larger format lithium-ion cells that may be used in subsea applications. Information obtained from such testing can be combined with thermal modeling and CFD to design, analyze and optimize systems with mitigation measures to prevent or minimize these unintended consequences.

Keywords – batteries; energy storage; AUV; subsea power; safety; thermal management.

I. INTRODUCTION

Over the past few years, newer rechargeable battery technologies including nickel-metal-hydride and lithium-ion (Li-ion) have become common because of the improvements in technology, lower costs and increased availability of such batteries. From a technological standpoint, Li-ion technology is an attractive option for underwater, subsea and energy storage applications because of its high energy density and small size. 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, thermal failures of battery systems have also been reported for medium and large battery system similar to those used in AUVs, shipping and transportation, and energy storage systems used with off-grid and renewable energy sources.

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 chassis or sensor compartment, 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

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lithium-ion cells used in AUVs, subsea power packs and energy storage systems.

II. 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.

A. 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 (

). 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.

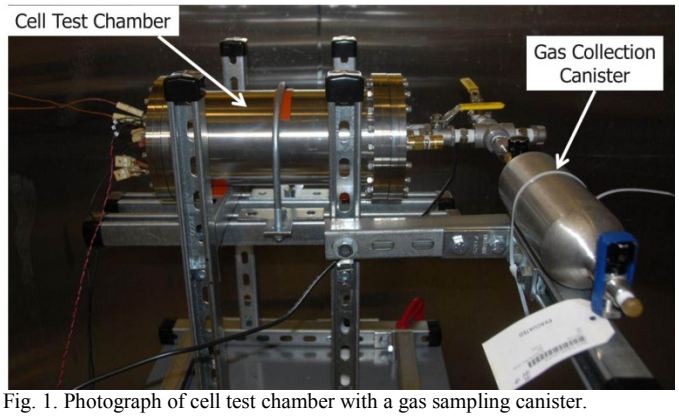

Fig. 1. Photograph of cell test chamber with a gas sampling canister.

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.

B. 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 (Fig. 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.

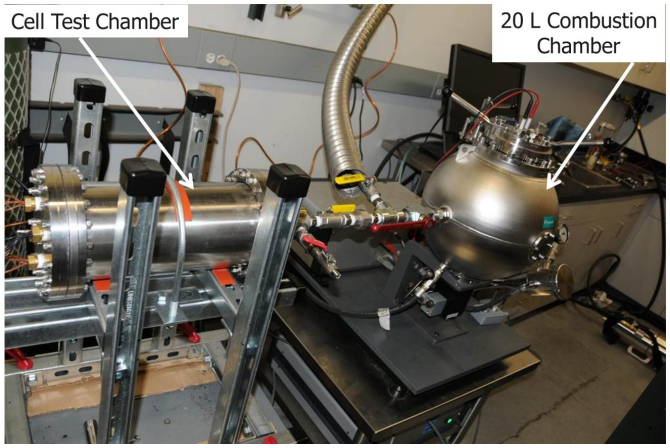

Fig. 2. Photograph of cell test chamber attached to the 20-L combustion chamber.

III. 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.

A. *Vent Gas Volume*

During the testing, when the battery surface temperature reached approximately 250ºC, 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.

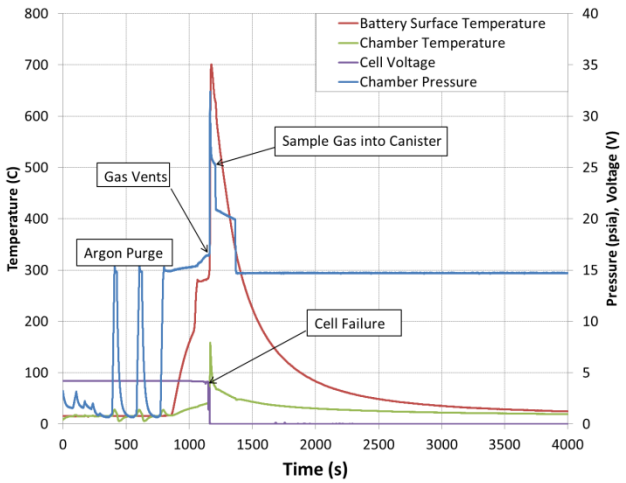

Fig. 3. Time trace of cell voltage, chamber pressure, chamber temperature, and battery surface temperature during testing of lithium-ion cells at 100% SOC.

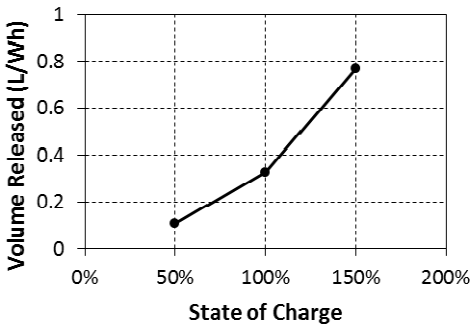

Figure 4. Total volume of gas released from 7.7 Wh li-ion cells at 50%, 100%, and 150% SOC.

B. *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 60ºC 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

Previous studies have reported that the majority of the gas released from a thermally failed cell consist of carbon dioxide [[3],[4]]. A comparison of the volume fractions of the major gas species (CO, CO_2, H_2, CH_4) measured in the present study with the measurements by Roth *et al.* [[4]] is also shown in Table 1. Roth and co-workers vented Li-ion cells into an inert argon/helium environment and found that, in comparison to the present study, the vent gas composition consists of significantly less hydrogen and carbon monoxide, and significantly more carbon dioxide. The ratio of CO_2 to CO measured in the current study is significantly less than the ratio reported by Roth *et al*. The differences in results are likely related to differences in cell composition, cell geometry and heating rates. Roth *et al.* used 18650 cells with an EC:EMC (ethylene carbonate: ethyl methyl carbonate) electrolyte, whereas the current study tested pouch cells with an EC:DEC (ethylene carbonate: diethyl carbonate) electrolyte. Roth *et al.* suggests that a decomposing solvent generates more CO at higher pressure. An 18650 cell is designed with a pressure vent and is expected to reach higher internal pressures before venting compared to a pouch cell. Therefore a higher CO_2 to CO ratio would be expected for a pouch cell compared to an 18650 cell; however the measured results show the opposite—the CO_2 to CO ratio was larger for the 18650 cell.

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

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Table 2 summarize 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	6.39	8.21	7.4/1.9

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Table 2. Volume fraction of hydrocarbon 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)
Methane	5.78	6.39	8.21
Ethylene	5.57	2.19	10.77
Ethane	2.75	1.16	1.32
Propylene	8.16	4.52	0.01
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	0.04
n-Pentane	1.94	0.73	0.30
Benzene	0.14	0.11	0.33
Toluene	0.06	0.02	0.05
Ethylbenzene	0.01	0.00	0.00
m+p Xylenes	0.01	0.00	0.00

Although this data appears to suggest that the gas species generation is more sensitive to other factors, namely electrolyte composition and heating rate; additional parametric testing would be required to confirm any such effect on gas species generation. The experimental methodology used to induce thermal runaway in this study is quite different than that of Roth *et al*. The specific failure mode is expected to have a strong effect on the gas species and volume of gases generated from Li-ion cell failures. Roth *et al.* heated their cells using an Accelerating Rate Calorimeter (ARC) up to 160°C, which most closely simulates thermal exposure at moderately high temperatures over long periods of time. Because the chemical reaction time scale is potentially long in such an exposure, the chemical reaction is likely to be more complete, which would result in a large volume fraction of carbon dioxide and minimal carbon monoxide and other hydrocarbon species. The heating method in the present study is designed to initiate an instantaneous violent thermal

runaway event by applying a fast temperature ramp rate (~100°C/min). The large volume fraction of carbon monoxide measured in the current study is evidence that the violent release of vent gases is likely to have resulted in an incomplete combustion reaction. Therefore, the composition of vent gases due to thermal failure of a Li-ion cell may be highly sensitive to the thermal failure mode. The failure mode considered in the current study is more similar to the *Explosive Decomposition* thermal failure regime described by Roth *et al.* where a "very rapid increase in heat and gas generation rate is observed, with explosive decomposition around 200°C." Although the internal cell temperature is not measured in the current study, the cell surface temperature is approximately 250-300°C when the cell vents, which suggests that the internal cell temperature is high. The failure mode considered in the current study is more representative of field failures in individual cells and packs where the transition to thermal runway resulting from mechanical or thermal damage is fast.

C. Explosion Characteristics of Vent Gases

For all the tests, the methane and hydrogen volume fractions exceeded the lower explosion limit for their respective species. However, the explosion limits are sensitive to the relative amounts of reactive and inert vent products. The ratio of flammable gases, in particular hydrogen, to carbon dioxide directly affects the explosion limits—a larger ratio will widen the explosible range, while a smaller ratio will decrease the explosible range. Depending on cell composition, SOC and other cell characteristics, the vent gas composition, and thus the vent gas explosible limits, may vary significantly. The species volume fractions summarized in Table 1 and

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Table 2 are for the vent gas that has not yet mixed with air. For any venting event, the region of explosible gas will be dependent on the mixing associated with the release. The fluid mechanics of the venting event is likely dependent on several parameters such as the SOC, cell composition, battery packaging type, battery pack design and enclosure geometry. From an explosions hazard analysis point-of-view, proper mitigation is often designed for the worst case scenario, *i.e.* maximum overpressure and rate of pressure rise.

Explosion characteristics of the vent gas were determined from the pressure curves obtained from the combustion chamber testing. For explosible concentrations, the pressure rises quickly, reaches a maximum pressure, and the decays. The rate of pressure rise, *dP/dt*, is determined by the maximum slope of the pressure curve. When using chemical igniters, a concentration is considered to be explosible if the pressure ratio is greater than two. The pressure ratio, *PR*, is defined as follows [[5]]:

$$PR = \frac{P_{ex} - P_{ignitor}}{P_{ignition}} \quad (1)$$

where P_{ex} is the peak pressure measured in the combustion chamber for a gas mixture, $P_{ignitor}$ is the pressure induced by the ignition source, and $P_{ignition}$ is the intial chamber pressure prior to ignition, which in this study is atmospheric pressure.

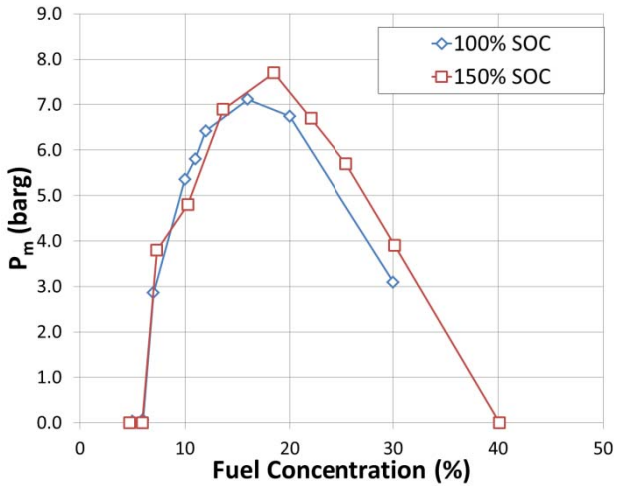

Figure 5. Overpressure measured in a 20-L chamber for vent gases released during a thermal failure of 7.7 Wh lithium-ion cells at 100% and 150% SOC.

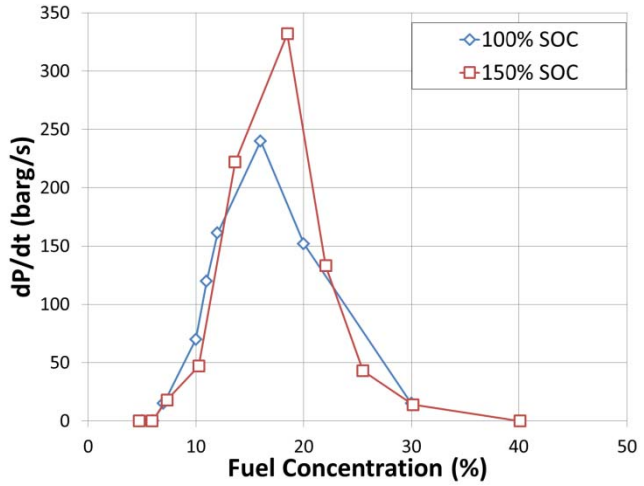

Figure 6. K_g measured in a 20-L chamber for vent gases released during a thermal failure of 7.7 Wh lithium-ion cells at 100% and 150% SOC.

For confined deflagrations, the measured pressure is effected by the ignition source and cooling from the walls. If the confined volume is sufficiently large, these effects are negligible. For smaller volume chambers, such as the 20 L combustion chamber used in this study, the measured pressure can be adequately corrected. Details of this correction are summarized in Ref [[2]]. Figure 5 and Figure 6 show the corrected overpressure, P_m, and the rate of pressure rise, dP/dt, resulting from ignition of vent gases from lithium-ion cells at 100% and 150% SOC over a range of air-to-fuel concentrations. Explosion tests were not performed for 50% SOC as the volume of gases released from cells at this SOC is very small compared to the higher SOC and procuring enough to be able to perform combustion testing would have been cost prohibitive. The maximum measured overpressures for 100% and 150% SOC are similar and within 10% of each other. The maximum measured rate of pressure rise for 150% SOC is nearly 40% larger than for 100% SOC.

The explosion severity for a particular gas species composition is often quantified by the maximum overpressure over all air-to-fuel concentrations, P_{max}, and the explosion index, K_g. The explosion index is defined as

$$K_g = V^{1/3}\left(\frac{dP}{dt}\right)_{max} \quad (2)$$

where, the maximum rate of pressure rise, $\left(\frac{dP}{dt}\right)_{max}$, is determined over all concentrations and is normalized by the cubic root of the chamber volume, V. The explosion severity parameters measured for the 100% and 150% SOC lithium-ion cells in this study are compared to explosion severity parameters for several common gases in Table 3. The measured values of P_{max} and K_g vary from study to study. The data from Senecal and Beaulieu [[6]] was chosen as a comparison because their 22-L test chamber was similar in volume to the 20-L chamber used in this study.

Table 3. Explosion severity parameters, P_{max} and K_g, for vent gases released during a thermal failure of 7.7 Wh lithium-ion cells at 100% and 150% SOC compared to common gases.

Gas	P_{max} (barg)	K_g (m-bar/s)
Li-Ion Vent Gas (100% SOC)	7.1	65
Li-Ion Vent Gas (150% SOC)	7.7	90
Methane	6.7	46
Propane	7.2	76
Ethane	8.0	171
Hydrogen	6.5	250

The P_{max} and K_g determined from the 20 L combustion chamber are dependent on the size of the test chamber and are not intrinsic properties of the gas; however they do provide a quantitative metric used to compare the severity of an explosion relative to other gases [[7]]. The vent gas from li-ion cells has a P_{max} similar in magnitude to common hydrocarbons and hydrogen. The K_g at 100% and 150% SOC are larger than that of methane but significantly smaller than that of hydrogen. The increased explosion severity is likely due to the significant volume fraction of hydrogen. Despite the large volume fraction of hydrogen, the presence of inert carbon dioxide effectively reduces K_g. At an overcharged state of 150% SOC, the K_g is nearly twice as large as K_g for methane and almost 20% larger than K_g for propane. Other parameters, in particular cell composition and battery capacity, are also likely to effect the vent gas composition, which may have a significant effect on K_g. Further parametric tests are needed to fully characterize the variability in explosion characteristics of Li-ion battery vent gases.

The lower and upper explosible limits (LEL, UEL) can be determined using the criterion that a gas mixture is explosible, i.e, if PR >2, which is equivalent to P_{ex} >1. For both 100% and 150% SOC, the LEL of the vent gas is found to be approximately 6.3% by volume, which is larger than both hydrogen and methane. The UEL for 150% SOC was found to be approximately 35%. Although the UEL for 100% SOC cannot be determined explicitly from the measured data, a UEL of 30%-40% can be expected. The larger LEL is due to the presence of carbon dioxide, which partially inerts the vent gas mixture. The LEL of the vent gas may vary across different battery manufactures owing to differences in cell composition, construction and failure mechanism. The effect of cell composition on vent gas composition is unknown. However, for any particular cell, the percentage of hydrogen may be sufficiently large such that the LEL of the vent gas could be lower than that of methane and the UEL of the mixture significantly higher than that of any pure hydrocarbon fuel by itself.

IV. Conclusions

A methodology to capture and characterize the chemical composition of gases vented from Li-ion batteries during thermal failure was developed as part of this work. Using this methodology, gas vented from Li-ion batteries during thermal failure have been studied experimentally and characterized.

The volume of gas generated was found to not have a linear relationship with the state-of-charge of the cell. Contrary to previous studies, the vent gas composition was found to contain significant amounts of hydrogen, carbon monoxide and hydrocarbons. The differing results are likely due to both differences in chemical composition of the cell and the methodology of inducing thermal runaway. The fast temperature ramp rate used in the current study is more similar to the expected conditions of field failures.

The explosible range and explosion severity (P_{max} and K_g) were determined experimentally using the 20 L combustion chamber. Compared to methane, the Li-ion cell vent gases have an extended explosibility range, which is due to generation of hydrogen. The measured P_{max} for the 100% and 150% SOC battery were similar to common hydrocarbons. However, at 150% SOC, K_g was higher than both methane and propane. The vent gas species composition, and hence combustion characteristics, is dependent on the state-of-charge of the cell and may be highly sensitive to the specific chemistry of the Li-ion cell. In addition to state-of-charge and cell composition, cell form factor and capacity may also have a large effect on the vent gas characteristics. To fully characterize the vent gas characteristics, a more complete parametric study is required.

Characterizing the explosion severity of Li-ion vent gases is increasingly important in hazard assessment for large capacity battery packs for use in marine and subsea power applications. Although there is currently no comprehensive industry standard that provides guidance for the safety hazards associated with gas vented from Li-ion batteries, there are related standards that provide guidance for combustible dust and flammable gas hazards. *NFPA 68: Standard on Explosion Protection by Deflagration Venting* [[8]] and *NFPA 69: Standard on Explosion Prevention Systems* [[9]] provide guidelines for designing mitigation systems for combustible dust and flammable gas hazards. The framework of the mitigation techniques presented in these standards is based on the combustion characteristics, namely P_{max} and K_g, of the particular fuel of interest. The methodology presented in the current study provides a basis for quantifying P_{max} and K_g, and can be used as a standard tool for future studies including parametric studies as well as scale-up studies for larger capacity batteries used in marine, subsea power and energy storage applications.

REFERENCES

[1] Harris SJ, Timmons A, Pitz WJ, "A Combustion Chemistry Analysis of Carbonate Solvents Used in Li-ion Batteries," Journal of Power Sources, Vol. 193, 2009, pp. 855-858.

[2] Cesana, C, Siwek, R, "20-L Apparatus Manual," http:// www.kuhner.com/tl_files/kuhner/product/safety/PDF/B000_071.pdf

[3] Crafts C, Borek T, Mowry C, "Safety Testing of 18650-Style Lithium-ion Cells," Sandia National Laboratories, SAND2000-1454C, May 2000.

[4] Roth EP, Crafts CC, Doughty DH, McBreen J, "Advanced Technology Development Program for Lithium-Ion Batteries: Thermal Abuse Performance of 18650 Li-Ion Cells," Sandia Report: SAND2004-0584, March 2004.

[5] ASTM E1226-10: Standard Test Method for Explosibility of Dust Clouds, ASTM International, 2010.

[6] Senecal JA, Beaulieu PA, "Kg: New Data and Analysis," Process Safety Progress, Vol. 17, 1998, pp. 10-15.

[7] Britton LG, Chippett S. "Practical aspects of dust deflagration testing," J. Loss Prev. Process Ind., Vol. 2, 1989, pp. 161-170.

[8] "NFPA 68: Standard on Explosion Protection by Deflagration Venting," 2007 ed., National Fire Protection Association, Quincy, MA.

[9] "NFPA 69: Standard on Explosion Prevention Systems," 2008 ed., National Fire Protection Association, Quincy, MA.