

Cone Calorimetry as a Tool for Thermal Hazard Assessment of Li-Ion Cells

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ABSTRACT

The emergence of Plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) as a viable means of transportation has been coincident with the development of lithium-ion (Li-ion) battery technology and electronics. These developments have enabled the storage and use of large amounts of energy that were previously only possible with internal combustion engines. However, the safety aspects of using these large energy storage battery packs are a significant challenge to address. In addition, the rapid advances in electrode and electrolyte materials for Li-Ion batteries have made comparisons and ranking of safety parameters difficult because of the substantial variations in cell designs. In this work, we outline a method for quantifying the thermal safety aspects of Li-ion battery technologies using a Cone Calorimeter.

The Cone Calorimeter is a suitable tool to measure and quantify critical information such as the heat release rate and total energy released from the combustion of organic material. Such techniques cannot be directly applied to study the energy release characteristics, during combustion, of non-organic and energetic material like Li-ion cells. Combining data from the Cone Calorimeter with compositional analysis of the Li-ion cell components, we have adapted a calorimetric procedure to better quantify the heat release rate and the total energy released from cells when they undergo a combustion event. Using these tests, thermal hazard parameters of cells with different chemistries, sizes and form-factors can be compared directly in a quantifiable and repeatable manner. Data generated from these tests can be used in the design and implementation of fire risk mitigation strategies for battery modules and packs that are used in EVs and PHEVs. This information can also be used in developing and improving computational and analytical models for analyzing thermal runaway and cascading thermal failures in modules and packs.

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INTRODUCTION

The emergence of Plug-in Hybrid Electric Vehicles (PHEVs) and electric vehicles (EVs) as a viable means of transportation has been coincident with the development of rechargeable li-ion battery technology and electronics that have enabled the storage and use of large amounts of energy that were previously only possible with internal combustion engines. However, the safety aspects of using these large energy storage battery packs are a significant challenge to address. One of the main risks associated with their use is thermal runaway. Thermal runaway occurs when the heat generated by shorting or electrochemical reactions within the cell exceeds the heat dissipation from the cell body [1].

A large number of studies have been focused on the identification of reactions between the different components of the batteries that contribute towards heat generation and the quantification of the energy released in these reactions [2,3,4,5,6,7,8]. In spite of this basic understanding of electrochemistry and thermodynamics, the advances in electrode and electrolyte materials for Li-Ion batteries have made comparisons and ranking of safety parameters difficult because of the substantial variations in cell designs. Developing thermal management systems for upset conditions in battery packs requires a clear understanding of the heat generation mechanisms and kinetics associated with the failures of Li-ion batteries.

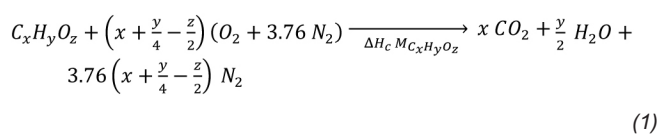
Many tools and techniques have been developed to estimate the amount of heat released by burning materials and quantify the thermal hazard posed by these materials. Direct application of these tools and techniques to Li-ion cells is questionable given the complexity of their thermal decomposition and combustion chemistry. In this paper we propose a framework to quantify the thermal safety aspects of Li-ion cells through a framework combining combustion data obtained from a Cone Calorimeter (ISO 5660-1, ASTM E1354) with cell electrochemistry and composition information [9,10]. In this framework, knowledge of the Li-ion cell chemistry and its composition is combined with measurements of the gases evolved during its combustion to quantify fire safety and combustion parameters such as the heat release rate (HRR), the total energy released and the production and consumption rates of various combustion gases. This information allows for direct comparisons to be made between different cell types and chemistries with respect to their performance when involved in a thermal runaway event or in a fire. Similarly, the combustion characteristics of these cells can also be compared to the combustion characteristics of well characterized organic materials like polymers, used in the construction of everyday material, to understand the fire hazard posed by Li-ion cells. The results generated from these tests will also allow further development and improvement of computational and analytical models for analyzing thermal runaway and cascading thermal failures in modules and packs.

EXPERIMENTAL

Cone Calorimeter

The Cone Calorimeter is a widely used tool that was developed in the 1980s [11] by the fire safety and research community to assess the flammability and the fire hazard of materials in order to rank the fire risk associated with their use [12]. It has become the most commonly used fire calorimeter [13] and is used to quantify the heat release rate (HRR) of a material. The HRR is considered the most important variable in quantifying the severity of a fire [14]. The Cone Calorimeter relies on a technique called Oxygen Consumption calorimetry (OC) to estimate the HRR of a material. This technique was first introduced by Thornton [15] in 1917, who observed that HRR is proportional to the quantity of oxygen consumed during the combustion of most organic liquid and gaseous fuels.

The complete combustion reaction of a chemical $C_xH_yO_z$ can be represented as:



where ΔH_c is the heat of combustion of the chemical $C_xH_yO_z$ expressed in kJ.g^{-1} and $M_{C_xH_yO_z}$ is the molecular mass of the $C_xH_yO_z$ expressed in g.mol^{-1} .

The HRR due to the combustion reaction in (1) can be formulated as,

$$\dot{q} = \chi \Delta H_c \dot{m}_{fuel} \quad (\text{kW}) \quad (2)$$

where $\dot{m}_{fuel}$ is the mass loss rate (in kg.s^{-1}) of the burning material $C_xH_yO_z$ and χ represents the combustion efficiency. For complete combustion, χ^{-1} is a valid assumption [16].

Thornton observed that for a majority of combustion reactions involving organic compounds,

$$\dot{q} \propto \Delta \dot{m}_{O_2} \quad (\text{kW}) \quad (3)$$

where $\Delta \dot{m}_{O_2}$ is the mass flow rate (in kg.s^{-1}) of oxygen consumed by the reaction. In 1980, Huggett [17] further developed Thornton's statement by relating ΔH_c , which represents the heat released by a complete combustion reaction per unit mass of fuel consumed, to an equivalent parameter, the heat released by a complete combustion reaction per unit mass of O_2 consumed, E_{O_2} , as:

$$E_{O_2} = \frac{\chi \Delta H_c M_{C_xH_yO_z}}{32 \left(x + \frac{y}{4} - \frac{z}{2}\right)} \quad (\text{kJ.g}^{-1} \text{ of } O_2) \quad (4)$$

Using this relation, equation (2) can be rewritten as,

$$\dot{q} = E_{O_2} \Delta \dot{m}_{O_2} \quad (\text{kW}) \quad (5)$$

where E_{O_2} is the O_2 energy coefficient expressed in kJ.g^{-1} of O_2 consumed. Huggett calculated E_{O_2} for a large number of organic fuels. He observed that the heat released per unit mass of O_2 consumed remains relatively constant for these fuels and E_{O_2} can be approximated by [17],

$$E_{O_2} = 13.1 \pm 0.7 \text{ kJ.g}^{-1} \text{ of } O_2 \quad (6)$$

Equation (5) shows that the other variable needed to estimate the HRR of a material undergoing complete combustion is the O_2 consumption flow rate which can be obtained by measuring the volumetric flow of air, the combustion products and the O_2 concentrations through the system where this combustion reaction occurs. Further work by Parker [18] improved the accuracy of equation (5) to account for the production of carbon monoxide CO in the case of incomplete combustion.

Uncertainty analyses on the OC method have determined that the error associated with this method varies from 10% to greater than 30% [19, 20, 21]. The accuracy of the OC calorimetry method depends on the precision of the measurements of air flow and gas concentrations and on the validity of the assumption of E_{o_2} being constant. Standard test methods such as ISO 5660-1 and ASTM E1354 that are used to estimate the HRR of burning materials assume that the energy constant hypothesis is correct for any material [9, 10]. Studies have shown that the E_{o_2} value of materials with complex chemistries such as polymers containing fire retardants, nano-composites, or materials containing oxidizers deviates from the constant calculated by Huggett beyond its error range. The validity of Huggett's value has also not been verified for burning Li-ion cells. [22].

Figure 1(a) shows a schematic layout of a Cone Calorimeter and Figure 1(b) a Cone Calorimeter at Exponent's Bowie, MD facility. The Cone Calorimeter is instrumented with analyzers that monitor and record oxygen, carbon monoxide and carbon dioxide levels in the exhaust gas stream for calorimetric analyses.

A Cone Calorimeter consists of three complementary systems [23]:

- A truncated radiant cone heater and ignition system;
- A load cell system for mass loss measurements and
- A gas collection and analysis system

These systems are designed to initiate combustion of a test material and, simultaneously, measure the consumption of O_2 as well as the production of CO_2 and CO from the combustion of the test material while also tracking its mass loss. For regular fire safety testing, the apparatus construction and operation are governed by two standards: ISO-5660-1 [9] and ASTM E 1354 [10].

The radiant cone heater is capable of irradiance levels up to 110 kW/m^2 to heat a sample of material being tested. Piloted ignition, when needed, is initiated using a spark ignitor located 13 mm below the conical heater. A sample of the test material is placed 25 mm under the conical heater in a sample holder specific to the Cone Calorimeter. A layer of refractory fiber material is placed under the sample to prevent heat losses from its unexposed face. A load cell measures and records the evolution of the sample mass during combustion. Dilution air and combustion products from the sample are extracted through the hood and the exhaust duct using a fan. The exhaust flow rate is measured using an orifice plate flow-meter instrumented with a pressure transducer and a thermocouple. After a homogeneous mixture is established in the exhaust duct, the exhaust gases are sampled and analyzed. A paramagnetic O_2 analyzer and an infrared CO_2/CO analyzer measure the evolution of gas concentrations during the combustion reaction. Using these measurements, the Cone Calorimeter can quantify the HRR, the effective heat of

combustion, and the mass loss rate of a material during combustion. Other combustion properties such as ignitability, soot formation, smoke evolution and toxic gas releases can also be studied using this instrument.

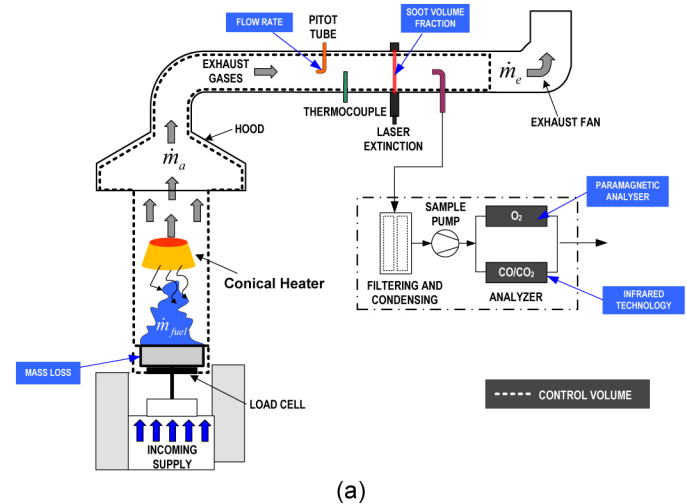


Figure 1. (a) Schematic layout of a Cone Calorimeter and (b) The Cone Calorimeter at Exponent's Bowie, MD facility.

Li-Ion cell

For this study, small, commercially available Li-ion cells were used. The cells chosen were $60 \text{ mm} \times 60 \text{ mm} \times 4.7 \text{ mm}$ in size of pouch type construction with a weight of $37.85 \text{ grams} \pm 0.23 \text{ grams}$. The cells were labeled from the manufacturer as nominal 3.7 VDC with 2100 mAh (7.8 Wh) capacity. The composition of the cells and the electrolyte was determined through various physicochemical analyses and the summarized results of these analyses are presented in are presented in Table 1 and Table 2.

Table 1. Chemical composition of an exemplar of the Li-ion cells tested.

Component	Chemical Compound	Molecular Formula	ΔH_c (kJ.g ⁻¹)	Mass %
Tape	Polyester Terephthalate	(C ₁₀ H ₈ O ₄) _n	22.00 [25]	0.2%
Label	Polypropylene	(C ₃ H ₆) _n	42.66 [24]	0.5 %
Separator	Polypropylene ¹	(C ₃ H ₆) _n	42.66 [24]	6.4%
Electrolyte w/o Salt	See Table 2.		19.31 ^(*)	9.5%
Outer Packaging (Top)	Nylon 6	(C ₆ H ₁₁ NO) _n	28.74 [25]	2.2%
Outer Packaging (Bottom)	Polypropylene	(C ₃ H ₆) _n	42.66 [24]	2.1%
Positive Tab	Polyester Terephthalate	(C ₁₀ H ₈ O ₄) _n	22.00 [25]	0.9%
Negative Tab	Polyester Terephthalate	(C ₁₀ H ₈ O ₄) _n	22.00 [25]	0.9%
LiCoO ₂ coated, positive electrode (aluminum)	Lithium Cobalt Oxide	LiCoO ₂	Inorganic Material	42.4%
Graphite-coated negative electrode (copper)	Lithium-intercalated Graphite (charged)	LiC ₆	Inorganic Material	34.9%

^(*)The heat of combustion of the electrolyte was calculated based on its composition and the heat of combustion of each component.

Table 2. Electrolyte composition (without salt) of the Li-ion cells tested.

Chemical Compound	Molecular Formula	ΔH_c (kJ.g ⁻¹)	% Volume in Electrolyte	% Mass in Electrolyte
Ethylene Carbonate	C ₃ H ₄ O ₃	12.30 [26]	15.1	12
Dimethyl Carbonate	C ₃ H ₆ O ₃	13.40 [27]	3.1	3
Diethyl Carbonate	C ₅ H ₁₀ O ₃	21.15 [26]	70.8	76
Propylene Carbonate	C ₄ H ₆ O ₃	16.53 [26]	9.8	9

Testing

For the results and analyses presented in this paper, the Li-ion cells described above were tested in the Cone Calorimeter to study the combustion characteristics of these cells. Of particular interest was the evolution of the heat release rate with time, the composition of the gases released during combustion and the total energy released during the combustion of these cells. For these tests, the cells were heated using the Cone Calorimeter's radiant heater set for a heat flux of 35 kW/m² and ignited using the instrument's spark

ignitor pilot. Recent studies, such as Ribière et al. [28] have shown that the intensity of the combustion reaction increases with the State-of-Charge (SOC) of Li-ion cells. To quantify this combustion behavior of Li-ion cells, tests were performed at three different SOC: 0%, 50% and 100%. All cells were charged/discharged at least one full cycle in preparation. For this testing, 100% SOC is defined as being charged to 4.2 V using constant current/constant voltage (CC/CV) charge, with the rate limited to 1.05 A (C/2) and a charge termination at 105 mA (C/20) during the CV portion (4.2 V). Cells prepared to 0% SOC were discharged from 100% SOC to 3.0 V at a 1.05 A rate. Cells prepared to 50% SOC were charged to 100% SOC then discharged half of the discharge capacity (obtained from previous full cycle).

A specimen of the Li-ion cell used for these tests is shown in Figure 2(a). Figure 2(b) shows the specimen fitted onto the sample holder with the refractive layer on the back side to prevent heat losses. The Li-ion cell is then positioned 25 mm under the cone heater. As the test starts, the specimen is exposed to the set external heat flux. 40 to 70 seconds later, gases venting from the cell are ignited and the combustion reaction is initiated (See Figure 2(c)). 50 to 150 seconds later, flaming combustion of the cell material ends and residue is left behind on the sample holder, Figure 2(d).



(a)

Figure 2. (a) A sample of the Li-ion cell used in the present tests,

1. Polypropylene was identified as the main compound of the separator through FTIR analysis. The technique was unable to identify the other compounds.