

Transportation of Li-ion batteries: The State of Charge Parameter

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Abstract

The achievement of higher energy densities within smaller volumes is a permanent aim of the battery industry. Improvement of the Li-ion technologies has allowed miniaturization as well as increase in autonomy of electronic devices. The increase in power demand and consumption has required the development of systems capable of supplying higher power. Li-ion technology can provide high energy density while remaining a compact and lightweight solution. Such cells are being used in a wide range of consumer electronic, medical, business, aerospace and military applications.

Like other electrical compounds, Li-ion cell failures can occur through various modes, energetic or non-energetic. The safety aspects associated with the use of Li-ion cells remain a challenge to address. Thermal, mechanical or electrical abuse can lead to thermal runaway of Li-ion cells. The amount of energy released depends on various parameters such as the battery chemistry, the state of charge (SOC), the ambient environmental temperature and the design of the Li-ion battery. The severity of the thermal runaway can transition to fire from the Li-ion cell. Storage and transport can be seen as t critical periods of the life cycle of Li-ion cells with regards to fire hazard because their quantity, at these times, is expected to be large potentially favoring a propagation of the fire and increasing its intensity. Transportation regulation is paramount to ensure safe shipments. Although omitted in the past, new air transportation regulations now impose a limitation on the SOC of Li-ion cells being shipped. The present work demonstrates the role of defining a maximum allowed SOC of Li-ion cells during their transportation.

Keywords: Li-ion battery, transportation, fire hazard, heat release rate, calorimetry

Introduction

The search for higher energy densities within smaller volumes is a constant aim of the battery industry. The development of innovative Lithium-ion (Li-ion) cell technologies has allowed the emergence of Plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) as a viable means of transportation. Li-ion batteries are nowadays considered a potential replacement for internal combustion engines. Improvement of the Li-ion technologies has allowed miniaturization as well as increase in autonomy of electronic devices. The increase in power consumption demand has required the development of systems capable of supplying higher power. Li-ion technology can provide high energy density and still remain a compact and lightweight solution. Such cells are being used in a wide range of consumer electronic, medical, business, aerospace and military applications. Market research data suggests that the Li-ion battery market will grow approximately 15.43 % per year over the next four years [1].

Li-ion cell failures can occur through various modes, energetic or non-energetic. Although the likelihood of Li-ion cell failures still remains low, their overall use has increased along with the number of failures reported. Some failures have required large product recalls of notebook computer [2] and cellular phone batteries [3]. These failures have raised public awareness and highlighted the need to conduct more research with regards to Li-ion battery safety. The safety aspects associated with the use of Li-ion cells remains a challenge to address. Thermal, mechanical or electrical abuse can lead to thermal runaway of Li-ion cells. The amount of energy released depends on various parameters such as the cell chemistry, the cell state of charge (SOC), the ambient environmental temperature and the cell design. The severity of the thermal runaway can lead to a transition to fire from the Li-ion cell. Storage and transport can then be seen as critical periods of the life cycle of Li-ion cells with regards to fire hazard because their quantity, at these times, is expected to be large potentially favoring a rapid propagation of fire and larger fire intensity.

A majority of the production of Li-ion cells occurs in Asia. Cells are shipped by air to every part of the world where a demand exists. There have been reports of Li-ion battery fires during air transport. The Federal Aviation Administration (FAA) listed 138 incidents involving Li-ion batteries (smoke, fire, extreme heat or explosion) and associated with aircraft transport that occurred between March 20, 1991 and December 22, 2016 [4]. Common causes of Li-ion battery incidents are short circuits and improper packaging. Over the last few years, the Li-ion cell shipping regulation has become more stringent. There has been a harmonization between the requirements associated with the transport of Li-ion batteries in the United Nations (UN) Recommendations on the Transport of Dangerous Goods, Model Regulations [5], the International

Civil Aviation Organization (ICAO) Technical Instructions [6], the International Maritime Dangerous Goods (IMDG) Code [7] and the US Code of Federal Regulations [8]. Limitation for transport mainly depends on the energy they can supply, the quantity of batteries and the type of packaging. To be eligible for air transport, cells must meet the provisions from performance tests defined in the UN Manual Tests and Criteria [5][9]. Cells are subjected to altitude, thermal, vibrations, shock, external short-circuit, impact/crush, overcharge and forced discharge to evaluate their hazard during transportation. They must be packed in strong outer packaging, completely enclosed in inner packaging, protected from short circuits and their energy must be less than 20 Watt-hour and 100 Watt-hour for Li-ion batteries [5][6].

Actual regulations impose limitations on the power of Li-ion cells that can be offered for air, road or maritime transportation. On April 1, 2016, the ICAO amended their document *Technical Instructions for the Safe Transport of Dangerous Goods by Air* and now requires that Li-ion cells and batteries be shipped at a state of charge of no more than 30 % of their rated capacity unless approved by appropriate authorities [10]. The SOC of Li-ion cells is a critical heat release parameter that can influence the combustion kinetics and therefore the associated fire hazard. Despite the absence of requirements limiting the SOC of Li-ion cells being shipped, a few studies have shown that it is a critical contributor to heat generation when a Li-ion cell undergoes thermal runaway [12]. Prior to the ICAO amendment, the general industry practice was to limit the SOC of Li-ion cells to 50 % when shipped. It was considered a threshold value beyond which thermal runaway of a Li-ion cell could transition to a severe heat release [10]. Limited data is available to verify this assumption.

As stated there are several factors that influence Li-ion cell. The present work utilizes the Cone Calorimeter to qualitatively address the influence of the combustible components and the SOC of the cell on the heat released from a cell fire. In addition, this work will aid in quantifying thermal safety aspects of Li-ion cells. The Cone Calorimeter provides access to the heat release rate (HRR) of a combustion reaction, parameter regarded as the most important variable in fire hazard [15]. The combustible electrolyte of Li-ion cells is often considered one of the major contributors to the cell combustion reaction but the influence of the SOC can be questioned. The objective of this work is to identify the main contributors to the overall combustion reaction by conducting HRR experiments at various SOC as well as experiments with dried cells (i.e. Li-ion cells for which the electrolyte has been removed) to better understand the overall combustion phenomenon involved in Li-ion cells fires.

Experimental Setup

The present study investigated the burning behavior of small, commercially available Li-ion cells. The cells chosen were

60 mm x 60 mm x 4.7 mm in size of pouch type construction with a weight of 37.85 grams \pm 0.23 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 reviewed in previous work by Somandepalli et al. [14]. The electrolyte organic solvent was a mixture of ethylene carbonate, dimethyl carbonate, diethyl carbonate and propylene carbonate.

Experiments were conducted using the Cone Calorimeter [14][15]. Fig. 1 shows a schematic layout of a Cone Calorimeter. The cone calorimeter's conical heater exposes samples to a uniform heat flux. The sample is exposed while smoke and gases are captured using a pump and collection hood and analyzed. The device is instrumented with analyzers that monitor and record oxygen, carbon monoxide and carbon dioxide levels in the exhaust gas stream for calorimetric analyses. Using these measurements the heat release rate (HRR) of the burning material is calculated using the oxygen consumption (OC) calorimetry principle [16][17].

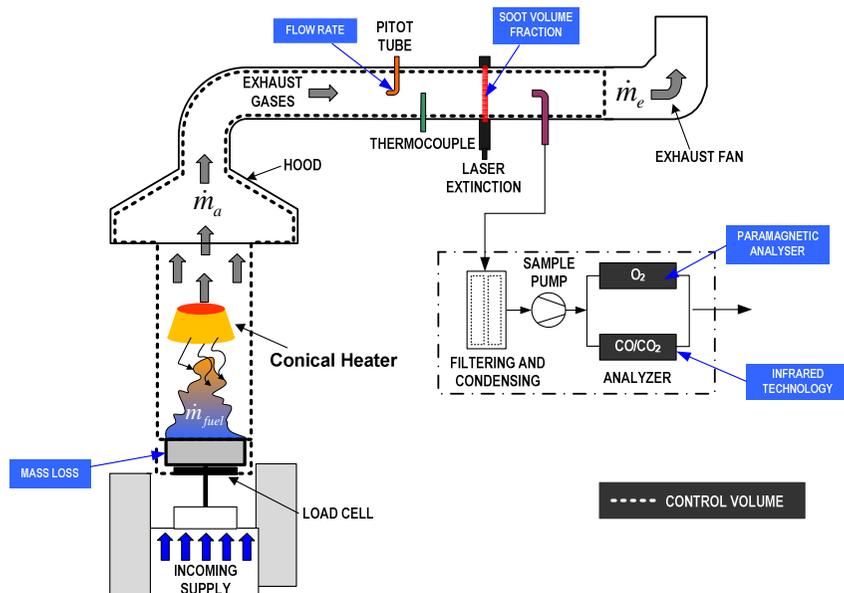


Fig. 1. Schematic layout of the Cone Calorimeter.

Each experiment was carried out under piloted ignition using the Cone Calorimeter's radiant heater set to provide an external heat flux of 35 kW/m². The standard collection hood was extended to ensure collection of all gases as these several of these cells responded in an aggressive manner upon exposure. Tests were performed at 8 different SOC: 0 %, 10 %, 20 %, 30 %, 40 %, 50 % and 100 %. The charge / discharge procedure can be found in [14]. In addition, the electrolyte of a 100 % SOC cell was removed using a vacuum pump and the cell was

subsequently tested using the cone calorimeter. The intent was to assess the contribution of the electrolyte inside of the cell to the overall energy release.

Results and Discussion

Results are presented in Table 1 and Fig. 2. Of particular interest is the ability of the Cone Calorimeter to correctly capture the evolution of the heat release rate and the influence of the Li-ion cell SOC with regards to the intensity of the combustion reaction. The results show that the HRR and burning rate increase as SOC of the Li-ion cells increases. The applicability of OC calorimetry with the general energy assumptions is questionable given the complex chemistry involved in the combustion of Li-ion cells [14]. Consequently, peak HRRs are presented in Table 1 for reference only. It can be seen that an order of magnitude separates the combustion of Li-ion cells at 0 % SOC and 100 % SOC. To allow a clearer qualitative comparison, HRR results were normalized using the HRR measurement at 50% SOC as reference (see Fig. 2).

Table 1. Flammability parameters from the combustion of Li-ion cells at various SOC.

SOC	Peak HRR* (kW)	Normalized Peak HRR	Total Energy Released (kJ)	Maximum Mass Loss Rate (g.s ⁻¹)	Total Mass Loss (g)
0%	1.99	0.14	165.87	0.1	7.9
10%	2.11	0.15	169.90	0.1	8.2
20%	2.54	0.19	161.35	0.2	7.7
30%	7	0.51	160.15	0.4	7.7
40%	8.7	0.84	166.25	0.5	7.6
50%	13.74	1	171.63	0.6	8.0
100%	21.58	1.57	197.46	0.8	8.8
100% dried	11.85	0.86	104.82	0.6	7.9

* Values for reference only, estimated using OC calorimetry and $E_{O_2}=13.1 \text{ kJ.g}^{-1}$.

Between 0 and 20 % SOC, the intensity of the fire is relatively low (normalized peak HRR between 14 % and 19 % of referenced peak HRR). The flaming duration varied from approximately 225 seconds to 170 seconds. Between 30 % and 40 % SOC, the fire intensity is moderate (normalized peak HRR between 51 % and 84 % of reference peak HRR). Flaming duration varies from approximately 127 seconds to 87 seconds. At 50 % SOC, the fire intensity is significant. Flaming duration is about 66 seconds. The first 10 seconds after ignition show a combustion reaction similar to the lower SOC. After the initial 10 seconds of slow growth, the reaction rate increases and flame height rapidly reaches the top of the exhaust hood approximately 0.56 m. At 100% SOC, the fire

intensity is substantial (peak HRR is 157% of reference peak HRR). Flaming lasts only approximately 15 seconds. The reaction rate and flame height were similar to that of the 50 % SOC cells.

The 100% SOC dried cell released energy levels comparable to full Li-ion cells with a SOC between 40 % and 50 %. The peak HRR of the 100 % SOC dried cell corresponds to 86 % of the one obtained at 50 % SOC and about half of the peak energy release of the same Li-ion cell with electrolyte and 100 % SOC. Given this information, at 100 % SOC, the electrolyte contributes to half of the energy release.

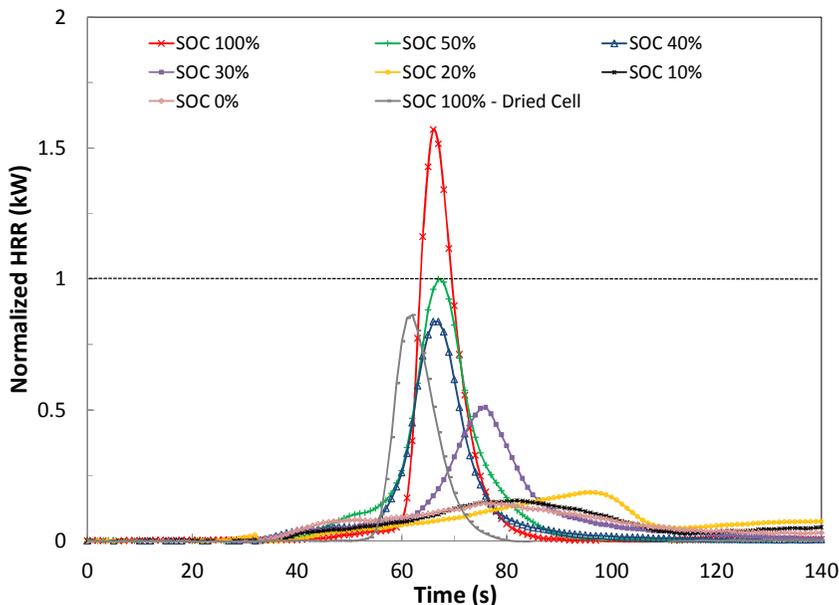


Fig. 2 Normalized HRRs of tested Li-ion cells at various SOC.

The electrolyte is a large contributor to the energy release but the SOC increases the reaction rate. In a Li-ion cell, the SOC is controlled by the balance of lithiation between the anode and cathode which modifies the electrodes composition. At 0 % SOC, Li^+ ions are mostly intercalated into the cathode with a chemical composition LiCoO_2 . When the cell is charged, the cathode becomes progressively de-lithiated. At 100 % SOC, the composition of cathode is approximated by $\text{Li}_{0.5}\text{CoO}_2$ [18]. The thermal decomposition of a delithiated cathode is characterized by a release of O_2 which may account for the fast and large release of heat at high SOC. In addition to the internal O_2 supply, cell combustion will cause shorts within the Li-ion cell releasing enough heat to vaporize the combustible electrolyte and, therefore, increase the combustion kinetics. As cell SOC increases, the amount of stored electrical energy that can be released as heat due to shorting increases.

Conclusion

The electrolyte of a Li-ion cell is a large contributor to the energy released during its combustion. While the research community is currently trying to develop safer cell designs including the development of less flammable electrolytes, it is valuable to characterize what is commercially available now. The Cone Calorimeter, with a slightly modified collection hood, can be used to help aid in the characterization, of the electrolyte contribution to the heat release during combustion of a cell. The Cone Calorimeter is a valuable tool to qualitatively assess the fire performance of Li-ion cells.

The present study shows that at 100 % SOC, the electrolyte contributes to about half of the overall energy release, however, the SOC is another critical safety parameter to take into account. Recent amendments to the ICAO Technical Instructions now require Li-ion cells to be limited to 30 % SOC during air transportation. Prior practice among the manufacturers was to generally limit the SOC of Li-ion cells to 50 %, which as shown during testing, yielded the potential to create a substantial heat release. The experimental results clearly demonstrate that exposure of a 30 % SOC cell reduced the peak heat released to half that of a 50 % SOC cell. Clearly this demonstrates the relevance and value of the new limitations on the SOC to at most 30 % during the transportation of Li-ion cells or batteries. Notably, as the SOC decreased below 30 %, the peak heat released during exposure was even less and nominally equivalent for a cell with no charge at all (0 % SOC).

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