Fire Behaviour of NMC Li-ion Battery Cells

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ABSTRACT

The main features of Lithium-ion (Li-ion) batteries are high energy and power density, which make this storage technology suitable for portable electronics, power tools, and hybrid/full electric vehicles. Moreover, during conditions that lead to failure, Li-ion battery cells could undergo into a process called thermal runaway, which has resulted in numerous fire accidents. Thermal runaway implies a rapid increase in battery cells temperature, accompanied by the release of flammable gases. These flammable gases could be easily ignited by the battery's high temperature, resulting in a fire. In addition, the combustion of these gases when venting from the battery poses another safety concern: the accumulation and potential explosion of the gases themselves. Thermal runaway may also be responsible for mechanical effects such as the projection of fragments as well as the release of toxic gases and vapours. This study reports and discusses the results of fire tests performed on single Li-ion cells. Lithium Nickel Manganese Cobalt oxides cells from Panasonic were used in the tests. The tests were carried out in a cone calorimeter changing the state of charge of the cells and the radiant power of the conical heater. In order to assess the ignition and combustion characteristics, ignition time, mass loss, heat release rate and surface cell temperature were measured and recorded. The volatile organic compounds released during the tests were also measured by a photoionization detector. Since the appropriate fire prevention and protection measures have not yet been developed, this paper investigates the effects of thermal abuse conditions on Li-ion cells of battery systems for hybrid/full electric vehicles, in order to develop safe instructions and procedures for a rescue team that is called to respond to accidents involving these vehicles.

KEYWORDS: Li-ion battery, thermal runaway, fire, explosion, cone calorimeter, heat release rate.

INTRODUCTION

Li-ion batteries are characterised by high energy and high power density, which make this technology the most suitable choice for feeding portable electronics, power tools, and hybrid/full electric vehicles [1]. The electrical work performed by Li-ion cells consists of exchanging lithium ions through electrolytes between positive and negative electrodes separated by ion-permeable polymer membranes. Lithium salts dissolved in high purity linear and cyclic organic carbonates are the typical electrolytes used in Li-ion cells and these materials are combustible [2]. In normal use conditions, electrolyte in a process that is quasi-reversible, with no significant changes in the chemical structure of the cell components. In case of a Li-ion cell failure due to an internal short circuit, the generated power rapidly surpasses the cell external heat losses, thus the polymer separator and the electrodes melt due to the temperature increase. Subsequently, electrolytes mix, then react and thermally decompose. The thermal decomposition produces both flammable gases

and oxidants that are generated within the cell, making the ignition and the combustion of batteries quite different compared to the mechanisms of ordinary hydrocarbon fuels, since the fuel is not exposed and no external oxygen is required. The Li-ion battery failure mechanism that could lead to a fire or an explosion (or both) is called thermal runaway [3].

Besides the related thermal hazard (fires, explosions), thermal runaway may also be responsible for mechanical effects such as projection of fragments as well as toxic gases and vapours [3]. The Liion cell gases formed during the thermal runaway can establish a variety of exhaust gas concentrations and components. However, the majority of the Li-ion venting gases components is made of carbon, hydrogen, and oxygen. As the temperature increases within a lithium battery cell, the organic compound begins to react with other components of the cell. The reactions lead to the increase in cell temperature and the production of flammable hydrocarbon and hydrogen gases. Thermal cracking, an additional possible mechanism for the conversion of organic compounds into smaller hydrocarbon molecules, occurs when sufficient heat is applied [5].

A special regulation has been issued by the International Air Transport Association Dangerous Goods Regulations for Li-ion battery transport [6]. Moreover, following some major air accident during the transportation of Li-ion batteries, a series of real scale tests was conducted by US Federal Aviation Administration to determine the flammability characteristics of primary lithium batteries, as well as and the dangers associated with shipping them in bulk on cargo aircrafts [7].

Li-ion batteries can be non-rechargeable – also called primary type batteries – or rechargeable. Primary batteries are practical for applications that draw occasional power, but they can get expensive when in continuous use. They are generally more hazardous than secondary ones. Among the rechargeable families, the most spread Li-ion batteries are based on Lithium Cobalt Oxide (LCO), Lithium-Iron Phosphate (LFP), Lithium Manganese Oxide (LMO) and Lithium Nickel Manganese Cobalt Oxide (NMC).

LCO was the first material used for the cathodes in secondary cells. Its major limitations are the high cost, low thermal stability, and fast capacity wane when at high current rates or during deep cycling. Low thermal stability refers to the release of significant amounts of energy, when the cathode break down occurs. The onset of chemical breakdown is at a relatively low temperature (about 200°C). LCO has the lowest thermal stability of any commercial cathode material [8]. Among them, LFP cathodes do not break down with the release of oxygen until much higher temperatures (400-500°C) releasing much less energy [9]. Alternatively, Lithium-polymer batteries have evolved from Li-ion batteries. Lithium-polymer differs from other battery systems in the type of electrolyte used. Instead of using a liquid lithium-salt electrolyte (such as LiPF₆) held in an organic solvent, the battery uses a solid polymer electrolyte such as polyethylene oxide, polyacrylonitrile, polymethyl methacrylate or polyvinylidene fluoride.

Recent studies on the safety issues of Li-ion batteries have focused on chemical, electrical and environmental features related to the components materials and battery parts: separators, electrolytes, additives, electrodes [10-13].

Large scale fire tests were also conducted to determine fire protection guidance for warehouse storage of cartoned Li-ion batteries [14]. The fire tests conducted utilizing an external fire as the ignition source showed a rapid fire growth of the carton packaging, causing heating of the stored Li-ion batteries. It could result in the potential involvement of many Li-ion batteries before a sprinkler system operates.

In this study, fire tests were performed on single Li-ion cells. Lithium NMC cells from Panasonic (NCR 18650 BM) were used in the tests. They were carried out in a cone calorimeter by varying the state of charge (SoC) of the cells and the radiant power of the conical heater. The volatile organic compounds (VOC) released during the tests were measured by a photo ionization detector (PID).

The heat flux used in the cone calorimeter simulates the conditions that can occur when a cell is involved in a fire, i.e. when a EV or PHEV catches on fire. The aim of this paper is to investigate the effects of thermal abuse conditions on Li-ion cells of battery systems for hybrid/full electric vehicles, in order to develop safe instructions and procedures for a rescue team in case of accidents.

EXPERIMENTAL SET-UP AND PROCEDURES

The Heat Release Rate (HRR) is a critical parameter for the evaluation of compartment fire growth [15]. The measurement of the HRR is used to quantify the test specimen's ability to ignite and contribute to the fire [16]. It is based on the observation that, generally, the net heat of combustion of a material is directly related to the quantity of oxygen required for its combustion.

During the test, specimens are exposed to ambient air conditions, while being subjected to a certain value of radiant heat (generally 10 to 100 kW/m^2) in the presence of a spark ignition source. The oxygen concentration changes and exhaust gas flow rate are monitored and, from these data, the HRR is calculated. The ignition time and mass-loss rate are also measured.

In the case of batteries the electrochemical energy is released inside the battery for different reasons: a manufacturing defect, mechanical abuse, heating in a fire. The heat flux used in the cone calorimeter simulates the conditions that can occur when a cell is involved in a fire, i.e. when a EV or PHEV catches on fire. Such technique has been directly applied to study the energy release characteristics, during combustion, of energetic material like Li-ion cells. Using these tests, thermal hazard parameters of cells with different chemistries, sizes and state of charge have been compared directly [17-19].

In this study the HRR was calculated following the calculation method proposed by ISO 5660-1:2015 [16]. The methodology to establish the HRR is based on Oxygen Consumption Calorimetry (OC). It was originally based on the observation that HRR is proportional to oxygen consumption during the combustion of most organic liquid and gaseous fuels [20]. The energy released per mass unit of O_2 consumed for a given fuel is assumed constant (13.1 kJ/g O_2). Recently, it was used for combustion analysis conducted for major single organic solvents and their mixtures used in lithium ion battery technology [12]. This methodology allows estimating the HRR directly from measurements; the knowledge of the material chemical composition or the combustion chemistry is not necessary and the HRR can be estimated also for composite and non-homogeneous materials, like Li-ion cell batteries.

Recently, some authors claimed the OC calorimetry is inappropriate for determining HRRs from lithium ion cell venting and combustion, because significant percentages of CO_2 are formed through pyrolysis process rather than combustion [13]. In order to figure out the validity of HRR data obtained by the cone calorimeter for Li-ion cells, the HRR was calculated by employing thermochemistry (TC) technique also, and comparisons of the two HRR results were made [17]. Heat release rate results of the three carbonate solvent mixtures obtained by these two separate methods are found to be in good agreement. Moreover, Ribiere et al. [19] determined total combustion heats and its kinetic of production as a function of the cell state of charge using the method of O_2 consumption. The resulting combustion heat is revealed to be consistent with cumulated contribution values pertaining to each organic part of the cell (polymers and electrolytes) as calculated from thermodynamic data. Thus, oxygen consumption calorimetry is considered to be an appropriate technique to determine the heat release in fires of lithium ion cells.

THE 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 a material. The main components of the cone calorimeter are depicted in Fig. 1.



Fig. 1. Main components of the cone calorimeter.

Fig. 2. A picture of a single cell Panasonic NCR 18650 BM.

A horizontal specimen, is exposed to a conical radiator pre-set to $15-50 \text{ kW/m}^2$ in these tests mounted beneath an instrumented hood and duct. A spark ignition is used and the specimen is mounted on a load cell in order to get the mass loss during combustion. The O₂ concentration is determined. The fire model of the cone calorimeter always appears to be well ventilated. The cone calorimeter and test procedure are describe in details in the international standard ISO 5660-1:2015 [16].

LI-ION CELL SPECIMENS DESCRIPTION

The cells used for the tests are the Panasonic Li-ion NMC named NCR 18650 BM. According to the producer datasheet, these NCR 18650 BM Li-ion cells have high energy and voltage. They also show long stable power with flat discharge voltage, therefore they are ideal for application such us portable communication, portable computing, robotics, and electric vehicle, e.g. Tesla. The specification of the NCR 18650 BM batteries is reported in Table 1.

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Rated Capacity ^a	Min. 2700 mAh
Capacity ^b	Min 2570 type. 2900 mAh
Nominal voltage	3.6 V
Charging	CC-CV ^d , Std. 1925 mA 4.20 V, 3.0 hrs
Temperature	Charge 0 to 45°C. Discharge -20 to +60 °C. Storage -20 to + 50 °C
Energy density	Volumetric 577 Wh/l. Gravimetric 214 Wh/kg
Length	65 mm
Width	18 mm

Table 1.	Panasonic NCR	18650 BM s	specifications
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^aAt 20°C; ^bAt 25°C; ^cBased on bare cell dimensions.

^aCC= constant current; CV=costant voltage

The test specimens have a positive electrode made of lithium nickel manganese cobalt oxide and a negative carbon electrode. The electrolyte is organic and mainly composed of alkyl carbonate: a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), or diethyl carbonate (DEC). The cell enclosure is made of plastic. Figure 2 shows a picture of a single cell.

TEST PROCEDURE

The cells were charged at a constant current of 12 A with a maximum limit voltage of 4.2 V to obtain 100% of SoC or a maximum limit voltage of 3.7 V to obtain 50% of SoC. The tests were carried out in a cone calorimeter by varying the SoC of the cells and the radiant power of the conical heater. HRR and surface temperature were recorded during the test as well as VOC released, which were measured by a photo ionization detector (PID). The VOC are expressed as ethyl methyl carbonate concentration (ppm). Each specimen was weighed before and after each test to determine the total mass loss. 10 cells at a given SoC were tested by varying the radiant power from 15 to 50 kW. The tests were also recorded by a videocamera. Table 2 contains the experimental test conditions and the measured parameters.

Test Id	SoC (%)	Radiant power (kW/m ²)	HRR max (kW/cell)	T max (°C)	Gas venting time (s)	Explosion time (s)	Mass loss (g)	Total Energy (kJ/cell)
1	100	15	0.9	367	580	810	28.08	184
2	100	25	1.3	703	300	385	24.27	132
3	100	35	1.1	328	274	315	34.14	65
4	100	50	0.8	497	171	226	20.89	28
5	100	35	1.1	735	236	294	43.53	72
6	100	50	11 (0.9)	440	240	272	20.24	304
7	50	25	0.1	726	470	580	10.73	15
8	50	35	1.2	367	246	324	17.33	62
9	50	50	1.0	643	204	230	43.97	40
10	0	50	1.3	487	138	196	8.31	33

 Table 2. Experimental test conditions and measured parameters

The gas venting time was defined by a clearly audible sound, immediately followed by an appearance of aerosol jets emanating from the safety vent ports. The explosion time is the time when the failure of cell was observed. The error of HRR values was calculated to be about 20%.

Figure 3 (a) shows the specimens under constant current charge while Fig. 3 (b) depicts a cell before and after cone calorimeter test.

RESULTS AND DISCUSSION

The tests showed that fire behaviour of cells can be characterized in three major phases: i) the onset of thermal runaway; ii) the venting and accelerating heating with flame and/or smoke; iii) the cell failure with flame. These phases are shown in Fig. 4, as an example, for 50% SoC cell during test at 35 kW/m^2 . The results of the tests reported in Table 2 show that the venting time and the explosion time decrease as the radiant power increases up to 35 kW/m^2 than remain almost constant. On the contrary, the HRR increases as the radiant power increases.



Fig. 3. Experimental setup: (a) specimens under charge; (b) specimen before and after cone calolimeter test.



(a) 246 s; venting





(c) 322s; smoke



(d) 324s; cell failure

Fig. 4. Stages of cell thermal runaway of NMC cell at SoC 50% during test at 35 kW/m².

The HRR data for single NMC cells as a function of SoC are shown in Fig. 5 for tests at 50 kW/m^2 . The dependence on SoC for the onset of heat release is evident. The cell tested at 100% SoC shows a first very rapid HRR onset at 80 s, and a secondary peak when the failure of cell occurs (280 s). This first peak (11 kW) was observed in correspondence of the venting of gases from the cell and their subsequent ignition, the second when the cell failure occurs (0.9 kW). On the contrary the 50 and 0% SoC samples have a similar behaviour with a slower HRR onset and a prolonged period of heat evolution when the cell fails.

In correspondence of the HRR peak due to the cell failure, a peak of VOC concentration is observed, which decreases as the SoC of cell increases. The VOC release is an indication of the incomplete combustion of the cell materials, which is higher as the energetic content of the cell decreases. It can be also argued that for 100% SoC cell the first HRR peak is due to the combustion of the vented electrolyte vapours or flammable gases obtained by the decomposition of the electrolyte and its reaction with other components of the cells.

The results relevant to the tests at 35 kW/m² are reported in Fig. 6. In this case one peak of HRR is observed for 50% SoC cell and two peaks for that at 100% SoC. Moreover, the first peak of 100% SoC cell occurs earlier than that at 50% SoC, and is accompanied by a smaller quantity of VOC released.



Fig. 5. HRR, surface temperature and VOC concentration (ppm) during tests at 50 kW/m².

Finally, comparing the results of tests relevant to cells at the same SoC (50%), but heated up by different power (35 and 50 kW/m²), the higher radiant power determines a faster increase of temperature cell and an higher HRR, with higher release of VOC (Fig. 7).

The HRR profile integration allows the estimation of the overall dissipated combustion heat. The calculated values were reported in Table 2, corresponding to a maximum total energy released of 6.4 kJ/g of cell. The SOC has the most influence on the total energy released by a cell decreasing

from 300 kJ/cell to 60 kJ/cell as SOC decreased from 100% to 50%. The effective heat of combustion of the cell contents is then calculated dividing the total energy release by the weight loss. The values ranged from 1-15 kJ/g.



Fig. 6. HRR, surface temperature and VOC concentration (ppm) during tests at 35 kW/m².

CONCLUSIONS

This study reports results of a series of fire tests of Li-ion cells performed in a Cone Calorimeter test rig. The tests were conducted varying the SoC of the cell specimens and the radiant power. The tests showed that fire behaviour of cell can be characterized in three major phases: i) the onset of thermal runaway; ii) the venting and accelerating heating with flame and/or smoke; iii) the cell failure with flame. At 100% SoC these phases occur at shorter times and the peak of the HRR and the total energy released are higher compared to the cells with a 50% SoC. The observed behaviour as a function of SoC implies that the onset of the thermal event is related to the electric Li-ion cell energy content which provides the activation energy needed to initiate the thermal runaway or the combustion of electrolyte.

The maximum overall dissipated combustion heat was calculated equal to 6.4 kJ/g of cell, while the effective heat of combustion of the cell contents is in the range 1–15 kJ/g. These values are in agreement with those reported in literature for secondary cells of different chemistries and

geometries. It was found that the combustion energy ranged in approximately 1–4 kJ/g of original battery and the effective heat of the combustion ranged in approximately 2–25 kJ/g [18].

The heat flux used in the cone calorimeter simulates the conditions that can occur when a cell is involved in a fire. Therefore, 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 safe practices and priorities when responding to accidents involving E-vehicles.



Fig. 7. HRR, surface temperature and VOC concentration (ppm) during tests at 50% SoC.

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