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Battery Aspects on Fires in Electrified Vehicles

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ABSTRACT

Safety issues concerning the use of large lithium-ion batteries in electrified vehicles are discussed based on abuse test results of lithium-ion cells together with safety devices for cells. The presented abuse tests are; propane fire test, external heating test (oven), overcharge and short circuit. It was found that in a fire, cells with higher state of charge (SOC) gave a higher heat release rate (HRR) while the total heat release (THR) had a lower correlation with SOC. One fire test resulted in a hazardous projectile from a cylindrical cell. Toxic gas emissions of hydrogen fluoride (HF) were measured in the fire tests and it was found that the total amount of HF released increased with lower SOC.

KEYWORDS: lithium-ion battery, electrified vehicle, safety, thermal runaway, fire, toxic gases

INTRODUCTION

The lithium-ion (Li-ion) battery technology can enable a broad introduction of electrified vehicles mainly due to its high energy capacity. Li-ion batteries also have other important properties, e.g. long life time and the possibility of fast charging. However, lithium-ion batteries have a drawback compared to most other battery technologies in that the electrolyte is flammable and the battery may go into a thermal runaway, that is, the battery may self-heat, resulting in a rapid pressure and temperature increase in the cell, which will release flammable and toxic gases but can also cause projectiles and fire [1-2]. This may happen moving out of the stable operating window of the Li-ion cell and can be caused by e.g. short circuiting, overheating, overcharging or mechanical damage.

Lithium-ion batteries are used in very large numbers for consumer products like cell phones, laptop computers etc. Incidents have happened with these batteries but the consequences are in most cases not that serious due to the limited size of the batteries. With the increased number of electric vehicles on the roads the safety issues of the lithium-ion technology have become more important taking into consideration the large size of the batteries in automotive applications. Incidents involving electric vehicles have indeed happened some of them resulting in fires. But luckily these fires have not resulted in any more serious consequences yet.

One example is three car fires involving the battery electric vehicle (BEV) Tesla Model S that occurred in 2013. In two of them the driver hit road debris at highway speed while one was caused by a crash into a concrete barrier and a tree resulting in significant deformations. The first fire was a result of penetration from beneath of the battery pack. Mass media attention was high regarding these incidents and the fires made the stock price of Tesla to decrease. Anyhow, compared to the annual average number of automobile fires in the USA, of the order of 1/1000 automobiles [3], the number of car fires in Tesla Model S (estimated as 1/10000 cars) is significantly lower. This comparison does not take into account the age of the cars involved, older cars may be more prone to fires, but it still shows that the risks involving electric vehicles should not be overstated. National Highway Traffic Safety Administration (NHTSA) investigated the fires and did not find any defect trends [4] but Tesla did voluntarily chose to reinforce the underbody of their cars by arming plates [5] in order to lower the frequency and the effect of hitting road debris.

Other incidents include the Fisker Karma plug-in hybrid electric vehicle (PHEV). In October 2012 hurricane Sandy caused flooding of a harbor in Newark, New Jersey. The flooding lasted several hours and thereafter 16 brand new Fisker Karma were destroyed by fire. The cars were completely covered with salt water during the flooding, an extreme situation where electrical short circuits are likely to occur. Again mass media attention was high even though other vehicles including other PHEV/HEV also burnt. Prior to hurricane Sandy some other fires incidents occurred involving Fisker Karma, one of them outside a supermarket shortly after the driver left the car. Fisker Karma is now no longer produced, possible partly due to the fire problems but also due to other causes. These incidents are examples where electric vehicle fires have been in the focus of the mass media. Other fires have happened, during charging or as spontaneous fires, but have not gained as much media interest. The fires and their consequences clearly demonstrate the necessity of putting safe vehicles on the market, not only for the safety of humans in or near the vehicles but also for economical and environmental reasons.

The electrified vehicle (xEV) has a potential to be safer than conventional combustion engine cars, simply because the main fire source, gasoline/diesel is removed [6]. Anyhow, the safety of a battery system depends on several things, e.g. cell chemistry, cell design and system design, including thermal management system and control strategies. Common cathode chemistries contain cobalt, e.g. lithium cobalt oxide (LCO), $LiCoO_2$, lithium nickel manganese cobalt (NMC), $LiNi_xMn_yCo_zO_2$, and lithium nickel cobalt aluminum (NCA), $LiNi_xCo_yAl_zO_2$. Lithium phosphates [7] are also used, e.g. lithium iron phosphate (LFP), $LiFePO_4$. For the anode, various forms of carbons are dominant while lithium titanate oxide (LTO), $Li_4Ti_5O_{12}$, is used in lower volumes. This paper focuses mainly on carbon-LFP cells which are seen currently as state of the art on the market when it comes to safety, although many battery systems for automotive applications use less stable chemistries in order to obtain e.g. higher energy density. Abuse test results from cell level are presented and their impact is discussed on battery system and vehicle level.

CELLS STUDIED

Cylindrical cells as well as pouch and soft-can prismatic cells have been tested. In the pouch cell, the layers are stacked on top of each other and sealed by an aluminum-polymer bag. The pouch cell is often called a coffee bag cell or a polymer cell. Figure 1 shows an X-ray photo of the EiG pouch cell. The layered structure is clearly visible, where the white/grey colored layers are the separator material.

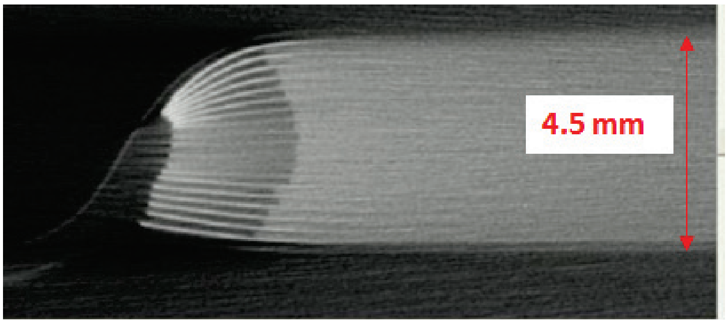

Figure 1 X-ray photo of EiG pouch cell seen at one of the edges.

Table 1 shows the cells and their specifications for the abuse tests presented in this paper. Most of the cells have a LFP-cathode and a carbon based anode as seen from Table 1. The initial state of charge (SOC) level of the cells was achieved by charge/discharge procedures using a Digatron battery test equipment or an ordinary laboratory power aggregate. The cells had not been used prior to the measurements but had different calendar ageing. The EiG and Lifetech cells had approximately 2-3 years of calendar aging while the European Battery cells were less than 6 months old and the Samsung, EVE and GBS cells were about 1 year old. Cylindrical cells of type 18650, i.e. 18 mm in diameter and 65 mm long, are produced in very large volumes and are traditionally used in laptops. Besides the use of 18650 cells in laptops, Tesla Motors has chosen the 18650 cell format as a basis for its serial-production of electric vehicles, while other vehicle manufacturers have chosen the prismatic or pouch cell type. Panasonic is the cell supplier for the Model S battery which uses cells with NCA as cathode material [8].

Table 1 Cell and test specifications.

Cell	**Nominal cell capacity (Ah)**	**Nominal cell voltage (V)**	**Cathode/ anode**	**Cell packaging**	**Test type presented in paper**	**Initial SOC (%)**
EiG ePLB-F007A	7	3.2	LFP/carbon	Pouch	propane fire, overcharge	0-100 100
Lifetech X-1P	8	3.3	LFP/carbon	Cylindrical	propane fire	100
European Battery	45	3.2	LFP/carbon	Pouch	short circuit, overcharge	100 100
Samsung ICR18650-24F	2.4	3.6	Cobalt based/carbon	Cylindrical	External heating (oven)	100
EVE F7568270	10	3.2	LFP/carbon	pouch	overcharge	100
GBS LFMP40Ah	40	3.2	LFMP/carbon	prismatic	overcharge	100

Figure 2 Photo of tested cells, not same physical scale.

THERMAL RUNAWAY

The thermal runaway was studied by external heating abuse test for a commercial 18650 laptop cell. The cell is produced in large quantities by Samsung. The cell was fastened to a brick and placed inside a thermostatically controlled oven, Binder FED 115, and heated up in about 1 hour to the thermal runaway temperature. The cell voltage and the cell surface temperature (measured by four type K thermocouples) as well as the oven air temperature (measured with one type K thermocouple) were measured with 1 Hz. Figure 3 shows the cell voltage and the differential temperature, ΔT, as a function of the oven temperature. The differential temperature is the difference between the average cell surface temperature and the oven temperature. Before the thermal runaway the cell voltage breakdown occurs due to melting of the separator, an endothermic process which is observable as a small local decrease of ΔT. ΔT has negative values up to 220 °C due to higher oven temperature than cell temperature, while the thermal runaway occurs at 220 °C. The cell surface temperature increases to close to 800 °C (ΔT above 500 °C), with a maximum rate of around 5000 °C/min. Observations from the video recording showed that the thermal runaway is accompanied with a pressure wave and instant ignition. The duration of the fire is approximate 1 minute.

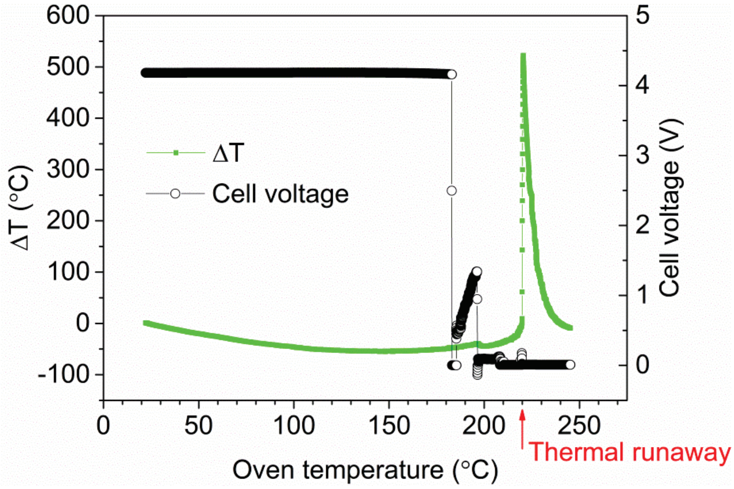

Figure 3 External heating test of a Samsung 18650 laptop cell.

FIRE CHARATERISTICS ON CELL LEVEL

The fire tests were conducted using the measurement and gas collection system of a Single Burning Item (SBI) apparatus that is normally used for classification of building materials according to the European Classification scheme EN13823 [9]. The experimental setup is shown in Figure 4. The battery cells were placed on a wire grating. A 15 kW propane burner was placed underneath the cells and was ignited two minutes after the start of the test.

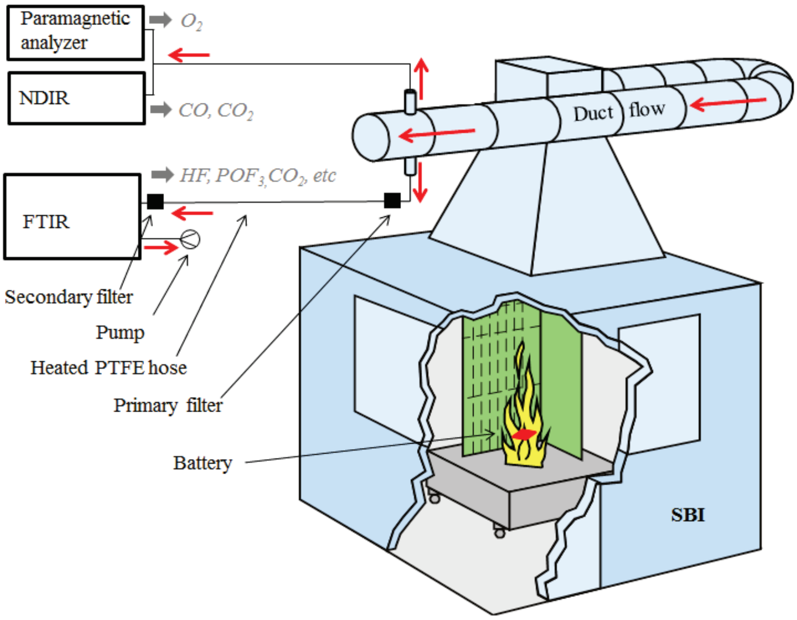

Figure 4 Schematic illustration of the experimental setup.

Tests were performed on EiG and Lifetech cells. Five cells were tested at the same time. The EiG cells were fastened together with steel wire while the Lifetech cells were placed inside a protection box made of walls of non-combustible silica board and steel net at the bottom and top. Additionally, a secondary layer of steel net was used at the top nailed to the wire grating to protect from hazardous projectiles, see Figure 5. A blank test was conducted at the beginning of each test day in order to be able to subtract the burner influence on the heat release rate (HRR) values and to make a blank for the gas analysis. HRR values were calculated by the oxygen consumption method and corrected for CO_2 [9]. The fire emissions from the test object were collected in a duct flow. In the tests of EiG cells with

100% SOC a duct flow of 0.6 m^3/s was used but in order to increase emission concentrations in the ventilation duct the flow was decreased to 0.4 m^3/s for the other tests of EiG cells and for the Lifetech cells. All tests were video recorded. A heated (180 °C) sub-flow was taken out to an FTIR, Thermo Scientific Antaris IGS analyzer (Nicolet), with a gas cell (heated to 180 °C), that measured gases, e.g. hydrogen fluoride (HF). Each test used a fresh primary filter (heated to 180 °C) which was analysed for fluoride content after the test. All fluoride found was assumed to be in the form of HF. For a detailed description of the experiment, see Andersson et al. [10].

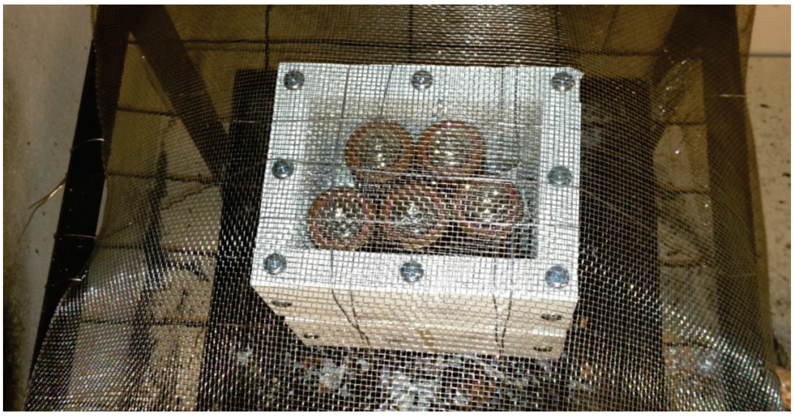

Figure 5 Lifetech single cells before the fire test at 100% SOC with external propane burner.

The heat release rate for various SOC levels for a five-cell-pack of EiG cells is shown in Figure 6. A strong dependence between SOC and HRR can be observed and lower SOC values result in lower heat release rate peaks. For 100% SOC there are rapid heat releases, outbursts, one per cell, while no outburst or HRR peak can be seen for cells with lower SOC. For an example of an outburst see Figure 7. The total heat release (THR) has a relatively low dependence on SOC and was roughly 8 MJ for the five-cell-pack, corresponding to 6.5 MJ/kg battery. Ribière et al. [11] found, based on a 11 Wh pouch cell with $LiMn_2O_4$ (LMO) cathode, a heat of combustion of 4 MJ/kg, which is in the same order as that measured in our study.

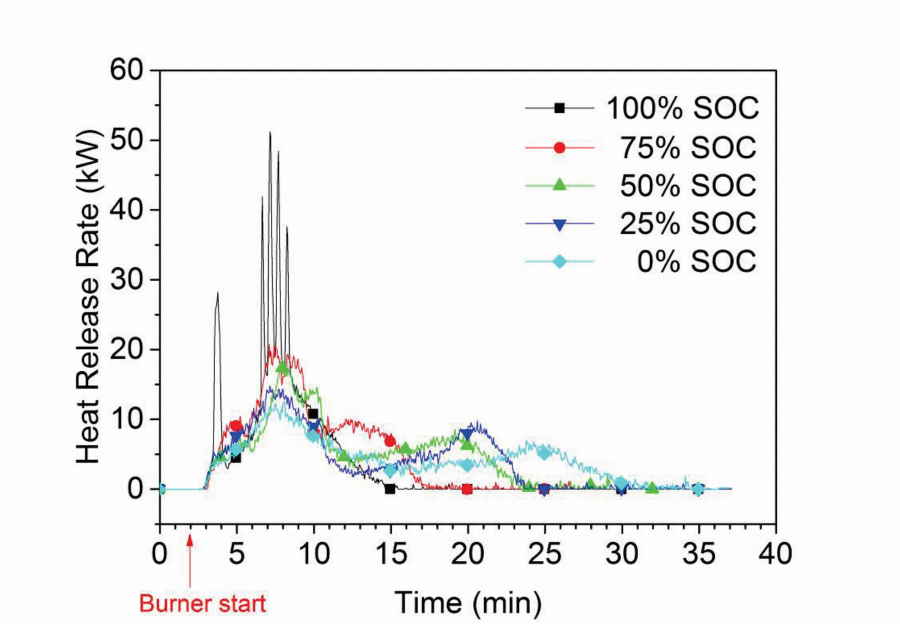

Figure 6 Heat release rate for the five-cell-pack of EiG 7 Ah cell, using an external propane burner (burner HRR has been subtracted from the graph). Cell SOC varied from 0% to 100%.

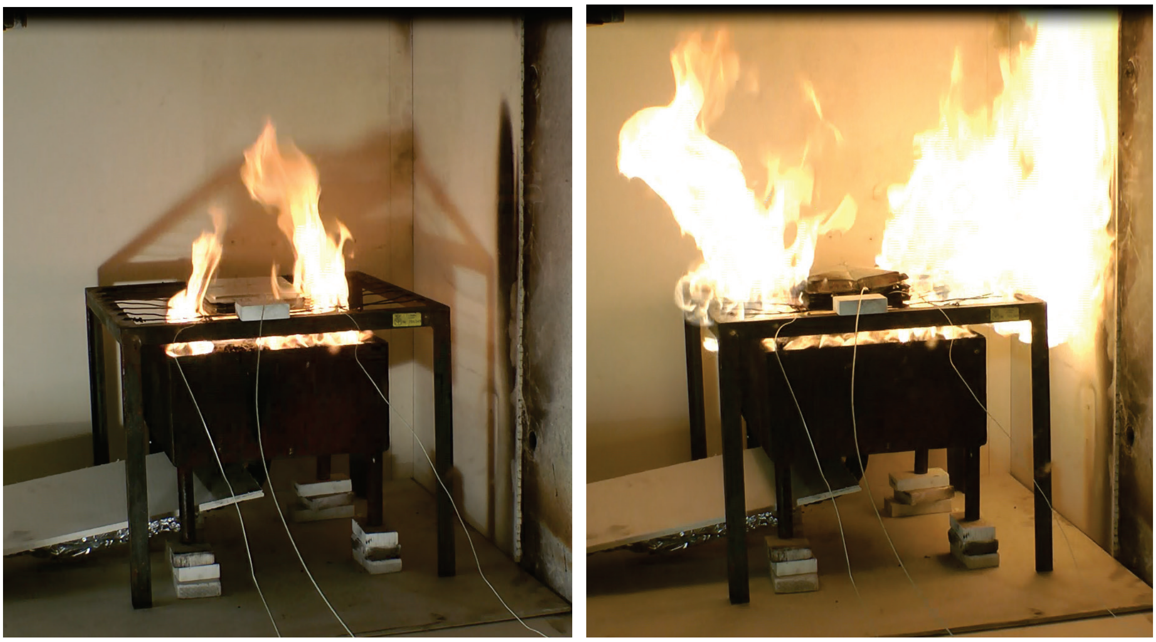

Figure 7 Photo in the beginning (left) of the fire test of a 100% SOC EiG five-cell-pack and photo of an outburst (right) during the fire test.

The nominal energy content of the five-cell-pack is 112 Wh. Electrified vehicles typically have 10-30 kWh of batteries and an extrapolation of our values to the energy released for this size of battery pack gives a THR of 700 - 2100 MJ, which corresponds to a fire of about 20-50 liter of gasoline.

PROJECTILE HAZARDS

Batteries can also cause projectile risks which was demonstrated in one of the fire tests. Even though the cells were equipped with a safety valve this did not prevent the explosion of one of the five Lifetech cylindrical cells as shown in Figure 8. Material from the cell interior was expelled while the cell moved backwards with a clear bang and a pressure wave forming a crater in the bed of small stones in the propane burner. No visual flaws of any kind could be observed for any of the five Lifetech cells before the test. A simple tear-down was conducted but no indications were found to understand why that cell exploded. Figure 9 shows photos during tear-down. No separator could be observed in the cell, which was expected due to the high fire temperatures. The positive current collector of aluminum foil seemed to have melted completely. The copper foil was still present. The weight loss of the cell was 27%.

Figure 8 Photos of the exploded Lifetech cell, after the fire test at 100% SOC with external propane burner.

Figure 9 Photos of the exploded Lifetech cell during tear-down.

CELL VENTILATION AND TOXIC GASES

The gases released from a Li-ion battery cell can be toxic, e.g. CO, but the fluoride emissions are of most concern. Hydrogen fluoride (HF) is one of them, but there are also others, e.g. phosphorous oxyfluoride (POF_3). They are formed from the fluorine content used in the Li-ion cell, the binder (e.g. PVdF) and the commonly used Li-salt, hexafluorophosphate ($LiPF_6$). The reaction formulas for the salt decomposition can be seen in the following equations [12].

$$LiPF_6 \rightarrow LiF + PF_5 \qquad (1)$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \qquad (2)$$

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF \qquad (3)$$

HF has a relatively well-known toxicity [13] while the toxicity of POF_3 is unknown. However, POF_3 might be even more toxic than HF as in the case of the chlorine analogue $POCl_3$/HCl [14]. POF_3 could not be observed in the fire tests on Li-ion cells reported here. A fire study on electrolytes in a Cone calorimeter by Andersson et al. [10] indicated that the POF_3 production might be approximately 1:20 of the HF production, which indicates that POF_3 may have been released also in the present tests but the concentration was below the detection limit (6 ppm). Figure 10 shows the real-time HF production rate for EiG cells with different SOC during the fire tests. The highest rate is for 50% SOC while 100% SOC has the lowest rate. The total amount of HF from both FTIR and the sampling filter is shown in Table 2 and values are between 4.9-13.9 g HF for a five-cell-pack. Ribière et al. [11] measured HF in their studies of another type of pouch cell and if we normalize their values against the cell electrical energy we obtain 37-69 mg/Wh, with the higher HF amounts for lower SOC. These amounts are in the same order as our results, 50-120 mg/Wh, however, in contrast to our study, Ribière et al. [11] found the highest HF production rate for the fully charged (100% SOC) cells.

Table 2 Emissions of hydrogen fluoride for 0%, 50% and 100 % SOC.

SOC (%)	Max rate of HF production (mg/s)	Total amounts of HF (g)	Total amount of HF (mg/Wh)	
			Our measurements	Calculated from Ribière et al. [11]
100	8.3	5.6	50	37
50	16	14	120	39
0	10	11	100	69

Extrapolation of our data to a larger battery pack size typically used in electrified vehicles gives an indication of the potential amount of released HF. A battery pack for an electrified vehicle, based on the tested EiG cell, could, for example, have 432 cells. This corresponds to 108 cells in series and four cells in parallel which results in a battery pack with 9.7 kWh and 346 V nominal voltage. The extrapolation factor is then 432/5 = 86.4, resulting in 400-1200 g HF depending on the SOC level. These values are in the same order of magnitude as those reported by Lecocq et al. [15] for fire tests on a complete electric vehicle.

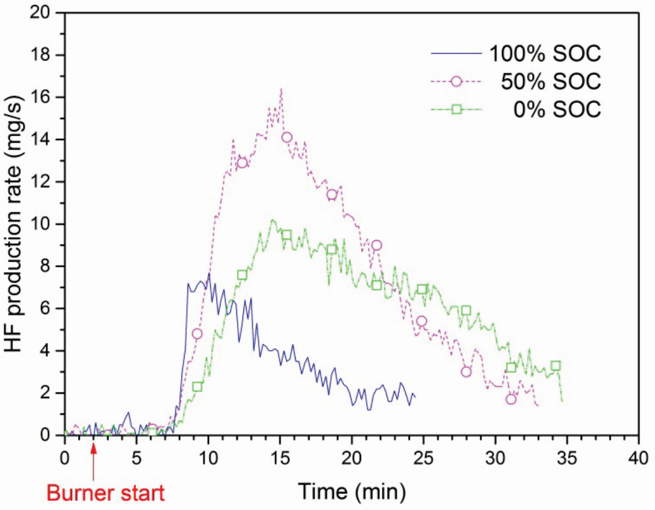

Figure 10 The rate of HF production for a EiG five-cell pack for 0%, 50% and 100% SOC.

CELL SAFETY MECHANISMS

Cylindrical 18650 cells for consumer products typically have a cobalt based cathode which is not as thermally stable as LFP [16]. A number of safety mechanisms [17] are often included in 18650 cells used in consumer products for low voltage systems. An example of such a safety mechanism is the current interrupture device (CID). The CID is a disc which is part of the current pathway. In case of overpressure in the cell, the CID is mechanically released due to the pressure, letting the cell go into open circuit mode. The CID is typically activated at a predesigned stage, before the cell can go into thermal runaway, by using shutdown additives [18]. PTC (positive temperature coefficient) is another safety mechanism, which protects the cell by rapidly increasing the resistance in the current pathway when trigged by an overtemperature, significantly lowering the current passing through the cell. Anyhow, the CID and PTC do not work that well in battery systems with multiple cells electrically connected in series and thereby a higher voltage [19] e.g. in batteries used in electrified vehicles. Figure 11 shows a cross-section X-ray photo of a 18650 cell where PTC and CID are shown.

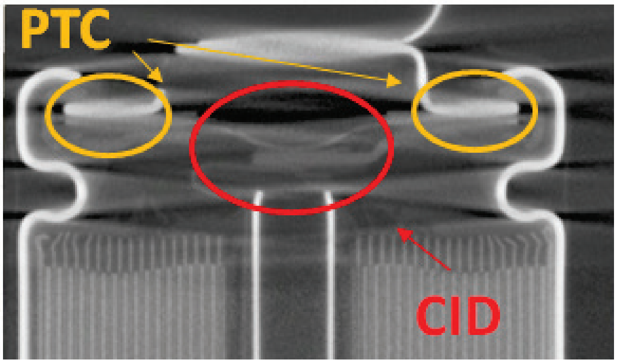

Figure 11 X-ray photo of a 18650 cell with the PTC and CID marked.

Shutdown separators are widely used in commercial Li-ion batteries as a safety protection for some abuse situations, e.g. overcharge and short circuit. The pores in the separator are closed at overtemperatures which lead to a hindered ion transport between cathode and anode and thus an open circuit. The shutdown separator usually consists of a layered structure where one layer has a lower melting temperature than the other layer. When the first layer melts the pores in the separator are closed, while the second layer sustains the cell integrity thereby prohibiting internal short circuit. Figure 12 shows DSC measurements of a polypropylene (PP) separator and of a shutdown separator with polyethylene (PE) and PP, the latter exhibits two melting temperatures, corresponding to the two materials. In case of e.g. an overcharge leading to an increased cell temperature, the PE will melt at around 130 °C, lowering the current and thereby the heating process. It may work less well in some situations e.g. when the current is interrupted too late or when the cooling is poor due to the battery system design. In those cases the melting temperature, around 160°C, of the second layer of PP can be reached leading to the total disintegration of the separator followed by an internal cell short circuit. The use of shutdown separators in large battery systems has shown not to have the same safety benefits as in small batteries. When many cells are electrical connected in series (forming a cell string) it causes the voltage to increase which in turn can also lead to separator breakdown [20].

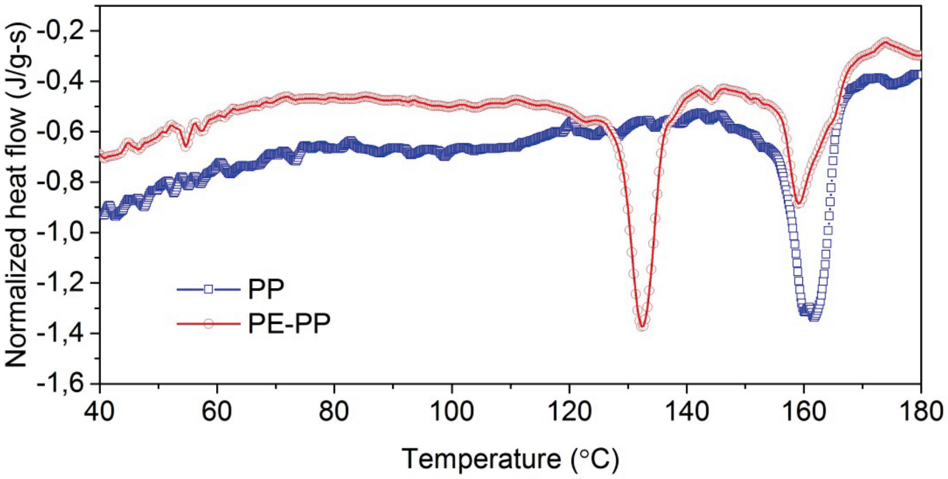

Figure 12 *DSC measurements of two different separator materials, one shutdown separator with PE-PP and one with only PP. The DSC measurements used a liquid N_2 cooled Mettler DSC-30, the samples were purged with N_2, and heated between 25 °C and 185 °C with a heating rate of 5 °C/min.*

In order to account for the drawback that some of the typical safety devices used in cells for consumer products cannot be used in Li-ion cells for electrified vehicles, other safety mechanisms such as special additives in the electrolyte are used. Li-ion cells for xEV typically uses cells which higher quality in manufacturing with more pure raw materials and safer chemistry like the LFP which can withstand abuse better. Figure 13 shows 2 C-rate overcharging of four LFP based cells with a capacity between 7-45 Ah. The GBS cell has a cathode of LFMP, i.e. LFP with manganese. The charger voltage was max 15.3 V and the charger was active during the complete test. The temperatures reached less than 80 °C, well below the onset temperature of the thermal runaway. However, the cells swell and gases are emitted. Four European battery cells were tested and the result from one of them is shown in Figure 13. Actually one of the European Battery cell unexpectedly caught fire. A situation of an overcharge abuse in the field might occur in case of a failure in the battery management system (BMS). High charge currents can occur e.g. during fast charging or during breaking (recuperation) of a xEV which makes those cases especially sensitive to errors in the overcharge protection. In principle, the consequences for overcharging of LFP cells are less dramatic than for other Li-ion chemistries but the temperature increase starts at a lower state of overcharge [16].

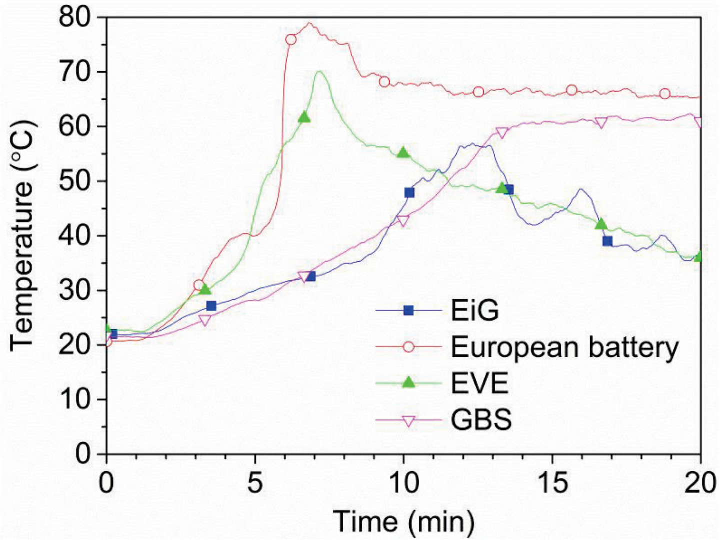

Figure 13 Overcharge tests of LFP and LFMP cells, with charge current of 2 C-rate.

In case of a short circuit of a Li-ion battery the current can be very high. Measurements of a low-ohmic short circuit on a single pouch cell from European Battery are shown in Figure 14. The voltage and current were measured with 1 kHz by an oscilloscope and cell surface temperatures (by eighteen type K thermocouples on both sides of the cell) by a data logger at 1 Hz. The short circuit peak current is close to 1100 A and then lowered to a plateau of about 700 A. High currents generates a lot of heat but for this cell the temperature increase is only about 5 °C since the short circuit is stopped when the positive terminal burns off from the cell. In case of a large battery pack with cell terminals that do not burn off, the current and the generated heat can be substantial and in case of burnt off terminal tabs the flames might ignite vented flammable battery gases or plastic parts inside a battery system.

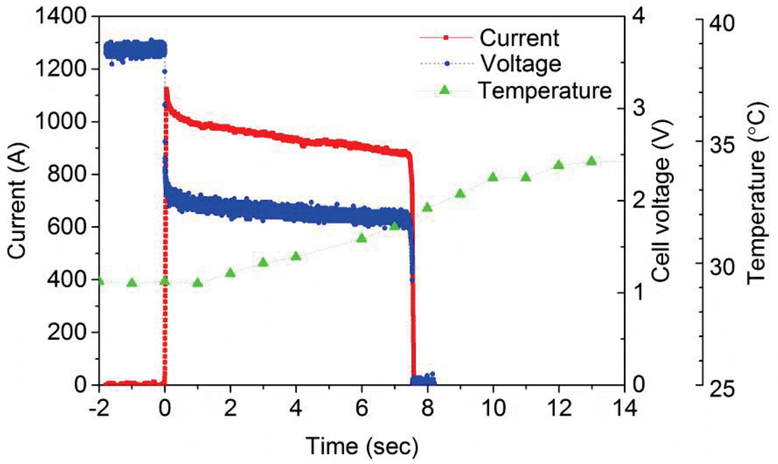

Figure 14 Short circuit of a European Battery pouch cell.

BATTERY SYSTEM AND ELECTRIFIED VEHICLE LEVEL

High battery safety is accomplished by using many layers of actions of various safety techniques. Figure 15 shows the safety-onion with examples of diverse safety actions used to ensure a low probability for fault and to minimize the consequences of a fault. Firstly, the cell chemistry is essential since this is the basis of the thermal stability. Secondly comes the cell design and packaging. In principle there are three main levels; cell, battery system and vehicle level.

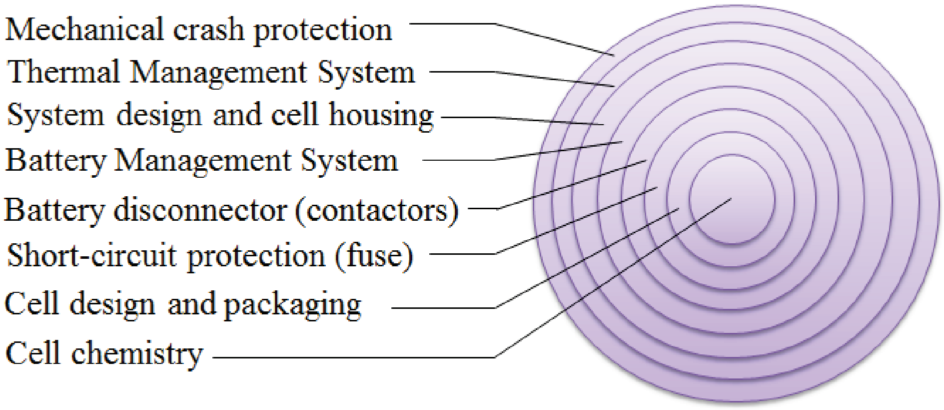

Figure 15 The safety-onion showing examples of layer by layer of different safety actions that can be used to establish a safe battery system in electrified vehicles.

CONCLUSIONS

There is a relatively good knowledge about the safety risks and safety devices used in consumer cells. Using Li-ion in the automotive sector puts higher demands on the battery since the batteries are significantly larger and with harsher environmental conditions, e.g. vibrations, humidity, larger temperature variations. The different Li-ion chemistries show diverse hazards where the LFP is less reactive but still safety measures are needed for all Li-ion batteries. High safety is achieved by adding several safety layers from cell to vehicle level, however the risk for a cascading fire in a complete battery pack starting from a single cell is not yet well studied and the knowledge about possible counteractions is thus also limited. Sometimes things go wrong even though smart safety strategies are used. The exploded cylindrical cell due to a cell vent malfunction showed this and this fact underlines the importance of using many safety layers.

The toxic gas emissions from Li-ion batteries, e.g. HF and POF_3, can pose a serious risk for persons. A replacement of the Li-salt $LiPF_6$ to a non-fluorine salt and change of fluorine binder could resolve this risk. Intense research is ongoing in this field but the required properties for a Li-ion battery in a xEVs are complex and demanding.

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