

Cite this: *Energy Environ. Sci.*, 2012, **5**, 5271

www.rsc.org/ees

PAPER

Investigation on the fire-induced hazards of Li-ion battery cells by fire calorimetry

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Received 26th July 2011, Accepted 15th August 2011

DOI: 10.1039/c1ee02218k

The use of the high energy Li-ion battery technology for emerging markets like electromobility requires precise appraisal of their safety levels in abuse conditions. Combustion tests were performed on commercial pouch cells by means of the *Fire Propagation Apparatus* also called Tewarson calorimeter in the EU, so far used to study flammability parameters of polymers and chemicals. Well-controlled conditions for cell combustion are created in such an apparatus with the opportunity to analyse standard decomposition/combustion gases and therefore to quantify thermal and toxic threat parameters governing the fire risk namely the rate of heat release and the effective heat of combustion as well as the toxic product releases. Using the method of O₂ consumption, total combustion heats and its kinetic of production were determined as a function of the cell state of charge unveiling an explosion risk in the case of a charged cell. 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. The first order evaluation of the dangerousness of toxic gases resulting from fire induced combustion such as HF, CO, NO, SO₂ and HCl was undertaken and stressed the fact that HF is the most critical gas originating from F-containing cell components in our test conditions.

1. Introduction

Today, it is crucial to find a source of alternative energy respecting the environment through the use of renewable

energies. The Li-ion battery is one of the emerging new systems of electric storage^{1–3} proposed in industries for innovative application (automobile, solar and wind energy, ...) according to its high energy density (approximately three times that of the Ni-MH battery). However, although these batteries have become quite common for consumer market applications like cell-phones or laptops, the widespread use of this technology for emerging markets like electromobility or smart grids requiring stronger energy and power capacities must be examined from a safety point of view. In general, most of the inherent hazards trigger

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Broader context

Safety and safety management could remain for some time the hurdles to overcome before a sustainable development of lithium type electric storage systems is seen worldwide. Therefore, numerous initiatives have been launched by various organizations in the EU (CENELEC, UN Sub-Committee of experts on TDG in Geneva, Recharge, ...), and overseas (SAE, NFPA, ISO, ...) to learn more on technical aspects of safety issues and to improve—through testing and modelling—the resistance of such batteries to abuse conditions. However, fire, as rare an event it may become, remains a possibility. Therefore the consequences of fire scenarios involving lithium batteries need to be fully appraised for fire safety engineering purposes. This work is one of the earlier contributions in that direction, relying on the use of the so-called “*Fire propagation apparatus*”, internationally recognized as one of the most outstanding pieces of test equipment ever made available to fire scientists to produce scientifically sound data that can be extrapolated and in turn serve risk analysis in various contexts. Basic data allowing pertinent estimates of thermal and chemical threats following a burning Li-ion cell of the “pouch type” have been achieved and are discussed in a way that allows further evaluations regarding fire safety issues on the full value chain of electric energy storage.

accidental scenarios when batteries are misused or facing abnormal environmental conditions. In such a case, the contact of highly energetic active materials with flammable organic solvent-based electrolytes can lead to situations out of control. When working out of the stability domain of the system (in terms of temperature or voltage), a series of undesirable reactions (varying according to the type of electrochemistry involved) may occur such as electrolyte reduction at the negative electrolyte interfaces,⁴⁻⁶ lithium metal plating,^{7,8} oxidation of electrolyte at high potential *versus* Li⁺/Li⁰,^{9,10} These side reactions can lead to release of heat and gases, then subsequently cause thermal runaway¹¹ that entails significant threats such as explosion or fire phenomena such as the combustion of the electrolyte after rupture of battery confinement. Currently, tests are proposed to characterize the safety performance of the cell constituents of the batteries and appraise their safety levels in abuse conditions. They are determined from technical guidance documents and emerging standards are often under a revision process (UL,¹² ANSI, SEA, ISO and IEC, UN Manual of tests and criteria, ...). A recent compilation of these tests was recently proposed by Doughty.¹³ These tests can be classified into electrical (overcharge, internal short circuit, external short circuit, overdischarge, ...), mechanical (shock, nail penetration, crush, ...) or environmental (thermal cycling, ...) but hardly ever take account of fire conditions either resulting from a thermal runaway process or induced by external environment.

In particular, a fire event resulting from those abuse tests is considered as severe (rated as level 5 to 6) according to hazards rating schemes (level rating from 0 to 7) developed by various organisations (Table 1). However, severity may or may not be critical according to potential adverse effects of such a fire event in a given context, and this consideration has received so far little attention.

From a general survey of past fires that occurred in the last decades, it can be stated that a large proportion of fire injuries and fatalities can be attributed to the inhalation of smoke and toxic gases, so the identification and quantification of the released gases are of major interest as well as the determination of heat produced or onset temperature for thermal runaway. Researchers mainly focused so far on collecting the thermodynamic data, indeed the thermal abuse response of Li-ion cells has been studied at both the component and cell levels using differential scanning calorimetry (DSC)^{11,14-16} and accelerating rate calorimetry (ARC).¹⁷ In this paper, we report thermal tests performed with a fire calorimeter, namely the Fire Propagation Apparatus (ASTM E2058 & NFPA 287), also called the

Tewarson Apparatus in Europe.¹⁸⁻²⁰ This very versatile device originally developed by FM Global can give access to the most important fire parameters that are needed for qualifying actual accidental scenarios, such as the heat release rate (governing the thermal threat) and products release rate (governing the toxic threat). This calorimeter is routinely used to study the flammability parameters of polymers,²⁰⁻²² but is also relevant to learn on the fire behaviour of chemicals²³⁻²⁵ and electrical components.²⁶ The collected combustion thermal and chemical data are the basic input data required for performing thermal and toxic impact calculation to estimate the consequences of industrial fires. In particular, the on-line gas analysis instrumentation (including Fourier-Transform Infra Red equipment) conjugated to flow rate and mass loss rate measurements provides chemical data allowing the determination of the nature and the relating yields of toxic combustion or decomposition products.

In this article, a description of the Tewarson calorimeter and the heat rate calculation method is presented. Tests performed on commercial batteries with different states of charge are reported, supplemented by a discussion on possible mechanisms leading to the formation of the detected gases along with an evaluation of the human toxicity.

2. Experimental

Pretesting

First of all, to prevent the Tewarson calorimeter from being damaged by extreme fire scenarios, a preliminary test is performed to evaluate the explosion risk and relating effects. Hence, a sample of each battery to be studied in fire conditions in the Tewarson calorimeter was placed at first inside a concrete test chamber to undergo the impact of a pool fire of ethanol. In such conditions, no serious explosion risk was observed and adequate testing procedures were established according to further investigations making use of the Tewarson calorimeter.

The fire propagation apparatus (Tewarson calorimeter)

The working principle of the Tewarson apparatus is illustrated in Fig. 1. This apparatus comprises two main subsystems. The lower part of the equipment is used to set the sample in combustion configuration under well controlled conditions. The upper part conveys the smoke gases into the exhaust system through a ducting section where critical measurements are made. In particular, the set of instruments allows the quantification of main thermal and toxic threat parameters such as the rate of heat

Table 1 Toxicity threat and overall battery hazard rating according to various approaches (adapted from ref. 32)

Overall hazard level	EUCAR description	SAE J2464 description	IEC description	Toxicity issue
0	No effect	No effect	No effect	
1	Passive protection activated	Passive protection activated	Deformation	
2	Defect/damage	Defect/damage	Venting	Yes
3	Leakage ($\Delta\text{mass} < 50\%$)	Minor leakage/venting	Leakage	Yes
4	Venting ($\Delta\text{mass} \geq 50\%$)	Major leakage/venting	Leakage	Yes
5	Fire or flame	Rupture	Rupture	Yes
6	Rupture	Fire or flame	Fire	Yes
7	Explosion	Explosion	Explosion	Yes

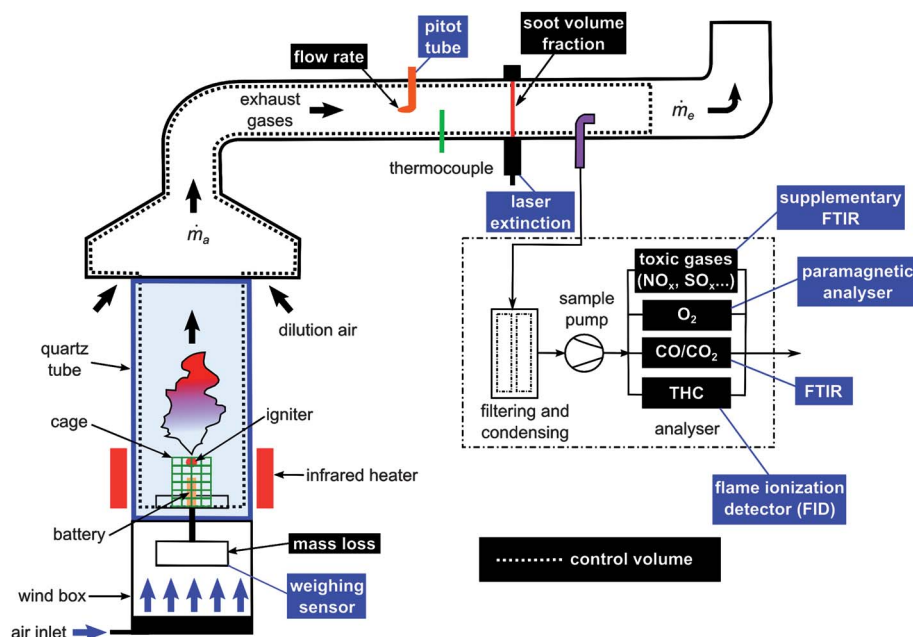


Fig. 1 Schematic of the INERIS fire propagation apparatus (Tewarson calorimeter).

release, the effective heat of combustion and the yields (or generation efficiencies) of the combustion products.

(i) Lower part details. The battery is placed in a tailored stainless steel cage which is laid onto a sample holder in the central axis of the system. The sample holder and its content are connected to a weighing sensor located inside the wind box, distributing evenly the combustion air (or any other oxidizing stream) in the combustor chamber delimited by a quartz tube. The oxidizing agent is injected at the bottom of the wind box. From this configuration, a well delimited area of combustion is thus created; it allows easy control of the degree of ventilation. The experiments were carried out under controlled air flow (350 L min^{-1}) simulating outside fire conditions.

An external heat flux is applied to the combustion chamber by four infrared heaters using tungsten filament quartz lamps inserted in both air-cooled and water-cooled reflectors (irradiance level impacting the sample in the order of 35 kW m^{-2}) placed around the battery (at around 10 cm) and whose efficiency depends on the matching between the emitted wavelength and the absorption spectrum of the material to be heated. The resulting flammable gas released from the battery can be ignited thanks to a pilot-flame placed at 30 mm above. Such infra-red heaters are desirable as they provide thermal aggression comparable to a fire environment and do not bring any additional fuel source needed to set fire conditions that would otherwise interfere with emissions of gases from the item under testing.

(ii) Upper part details. Fire products are totally captured and mixed with dilution ambient air, in the sampling duct, where the gas temperature and the product–air mixture flow rate are measured. The online analysis of the diluted smoke includes the quantification of O_2 by paramagnetic analyzer, CO and CO_2 by FTIR analyzer, soot using optical measurement and total

hydrocarbons by means of flame ionization detector. The volume fractions of these molecules will be utilized hereafter as input data to calculate thermodynamic and kinetic magnitudes. Note that these analyses are performed after preconditioning the gases by filtration and dewatering.

A supplementary FTIR Instrument was also implemented to provide data on “standard” toxic gases such as hydrogen halides, HCN, NO_x , SO_x , and aldehydes. Herein are reported the most significant concentrations detected with a Nicolet 6700 spectrometer using a 2 m gas cell ($V = 200 \text{ mL}$). It is worth noting that this fire calorimeter was recently listed as one of the rare lab-scale “fire physical models” capable of producing pertinent fire toxicity data at ISO level.²⁷

Determination of the heat release rate (HRR)

The rate at which energy is released from a fire is the most important factor which governs its behavior.²⁸ It is possible to determine the HRR experimentally in a convenient way using the method of oxygen consumption. During a combustion process that has gone to completion, it can be estimated by

$$\dot{q} = E(\dot{m}_{\text{O}_2}^0 - \dot{m}_{\text{O}_2}) \quad (1)$$

where $\dot{q}$ is the heat release rate (kW), $\dot{m}_{\text{O}_2}$ and $\dot{m}_{\text{O}_2}^0$ are the mass flow rates of oxygen from the entrained air when a combustion occurs or not, respectively (kg s^{-1}). E is the energy released per mass unit of O_2 consumed for a given fuel (kJ g^{-1} of O_2). For a large number of organic solids and liquids or gaseous compounds, this energy appears to be approximately constant (this is known as the Thornton principle). After having checked the values for all possible battery compounds that are able to burn, we took the averaged energy “ E ” of 13.1 kJ g^{-1} of O_2 . In most cases however, combustion in fire conditions is found to be incomplete implying carbon monoxide and soot particles

formation. This leads to an overestimation of the HRR calculated from eqn (1) that therefore requires the following corrections:

$$\dot{q} = E(\dot{m}_{\text{O}_2}^0 - \dot{m}_{\text{O}_2} + \Delta \dot{m}_{\text{O}_2(\text{CO} \rightarrow \text{CO}_2) + (\text{soot} \rightarrow \text{CO}_2)}) - \dot{q}_{\text{CO} \rightarrow \text{CO}_2} - \dot{q}_{\text{soot} \rightarrow \text{CO}_2} \quad (2)$$

where $\dot{q}_{\text{CO} \rightarrow \text{CO}_2}$ and $\dot{q}_{\text{soot} \rightarrow \text{CO}_2}$ are the HRR accounting for the CO and soot combustion respectively. They are defined as $\dot{q}_{\text{CO} \rightarrow \text{CO}_2} = \dot{m}_{\text{CO}} E_{\text{CO}}$ with $E_{\text{CO}} = 17.6 \text{ kJ g}^{-1}$ of O_2 required to convert CO to CO_2 , $\dot{q}_{\text{soot} \rightarrow \text{CO}_2} = \dot{m}_{\text{soot}} E_{\text{soot}}$ with $E_{\text{soot}} = 12.62 \text{ kJ g}^{-1}$ of O_2 required to convert soot to CO_2 .²⁹ The interested readers may refer to ref. 22,30 and 31 to learn about the applicability of these fire calorimetry equations which remain a complex issue according to actual material burning, gases measured and inherent limitations of the technique.

Batteries composition

For this study, 2.9 Ah (11 Wh) commercial pouch-type batteries were tested. Prior to being subject to the Tewarson test, a battery mass distribution (Fig. 2) has been established to subsequently compare with the combustion data resulting from the gas quantification. This mass distribution was assessed partially by support of physicochemical analysis of fully discharged battery components and by estimation from an industrial database. This battery was dismantled in an argon-filled glove box. The length, width, thickness and weight of the electrode and the separator were measured (Table 2). The electrode materials composition was determined by X-ray diffractometry (Bruker D8 with a PSD detector Cu $K\alpha$). To do so, a fragment of electrode was cut and then examined without washing. The separator was rinsed in acetonitrile to recover the electrolyte whose composition was analyzed by ElectroSpray Ionisation High Resolution Mass Spectrometry (ESI-HRMS) and GC/MS techniques. The

conductive carbon content was estimated as representing 10% of the calculated electrodes weight and binder quantities were estimated at 10 and 5% of the negative and positive electrode mass respectively. The weight of the electrolyte was assessed by considering a density of 1.2 and a volume porosity of 50% for the separator and 30% for the electrodes.

Batteries state of charge

The calorimetric tests were undertaken at three different states of charge (100% SOC, 50% SOC and 0% SOC) and reproduced three times. All batteries were electrically preconfigured by initial cycling consisting of a galvanostatic charge/discharge cycle (C/10) between 2.0 and 4.1 V and then were brought to the wanted SOC (Fig. 2). In order to prevent self-discharge and storage effects, the cycling was carried out less than 24 hours before the calorimetric test. These cycling tests were performed with a VMP system (Biologic, Claix, France) equipped with an amplifier.

3. Results and discussion

From the physicochemical analysis, graphite carbon and LiMn_2O_4 materials were identified at the negative and positive electrode respectively and the ethylene, diethyl and dimethyl carbonate solvents (EC : DEC : DMC) with LiPF_6 salt were analyzed as electrolyte. The battery mass distribution is shown in Fig. 2. The active material represents 36% of the battery total mass while the current collectors weight percentage accounts for 30%. Other compounds namely the electrolyte, separator, binder and packaging materials that are mostly constituted of organic or polymers represent 27% (wt) in total.

a. Calorimetric and kinetic analysis

During testing, all batteries behave globally the same way; starting to swell around 90 seconds after the starting point of the external radiant heating process, then opening from the tabs, similar to the movement of an accordion.

(i) **Loss of mass.** Whatever the battery SOC was, the measured mass loss was found to be nearly identical (17, 17 and 16%) whereas the associated kinetics were quite different. As shown in Fig. 3, the discharged battery combustion process lasted longer than that of the fully charged battery (8 min vs. 3 min) and the half charged battery disclosed an intermediate behavior.

A visual observation of the cells after combustion clearly showed the exfoliated coiled copper foil and the presence of aluminium droplets due to Al melting. This observation indicates that the maximum temperature reached during the combustion test within the battery could be estimated between 660 and 1083 °C. At such temperature, all the organic and polymer compounds from separator, binder, packaging and electrolyte should have obviously burnt.

The packaging is comprised of an aluminium foil covered by polymer layers which can be roughly estimated at half the weight. So, the weight percentage of all organics and polymers deduced from this approximation and Fig. 2 data is about 23% which is comparable with the 17% mass lost during experiments. Visual observation of the battery after the test revealed that only the

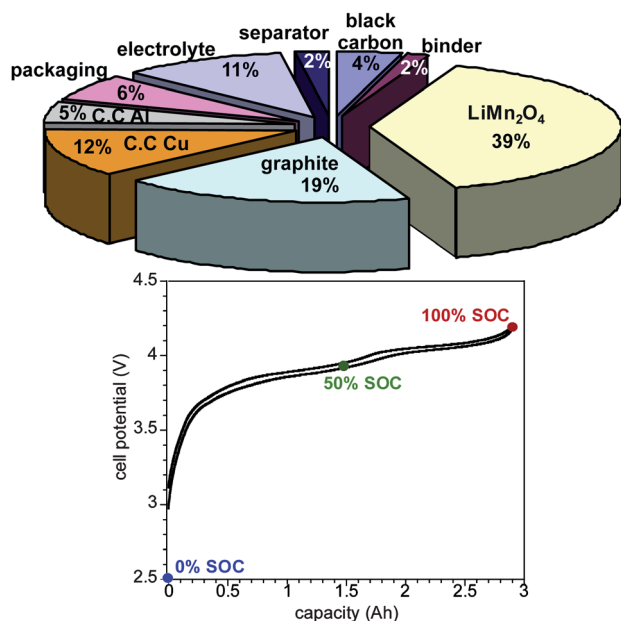
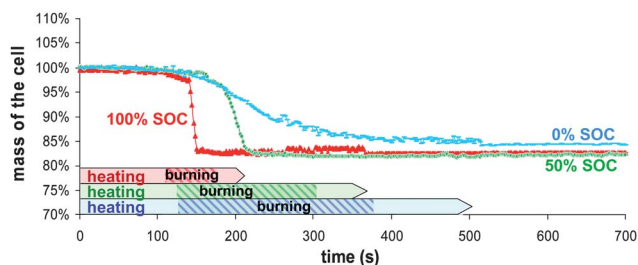


Fig. 2 Mass distribution ($m = 95 \text{ g}$) and potential–capacity curve (2.9 Ah) of the Li-ion battery.

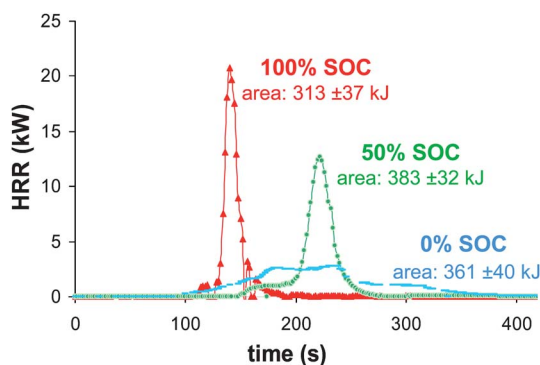
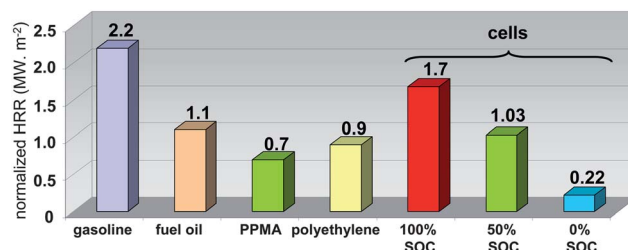
Table 2 Component dimensions measured after 2.9 Ah pouch cell opening

	Cathode	Al current collector	Anode	Cu current collector	Separator
Length/cm	11.9		12.3		12.3
Width/cm	6.5		6.9		6.9
Thickness/cm	2×0.007	0.04	2×0.0065	0.02	0.0031
Number of electrodes	11		12		

**Fig. 3** Samples mass loss during combustion as a function of time for different battery SOC.

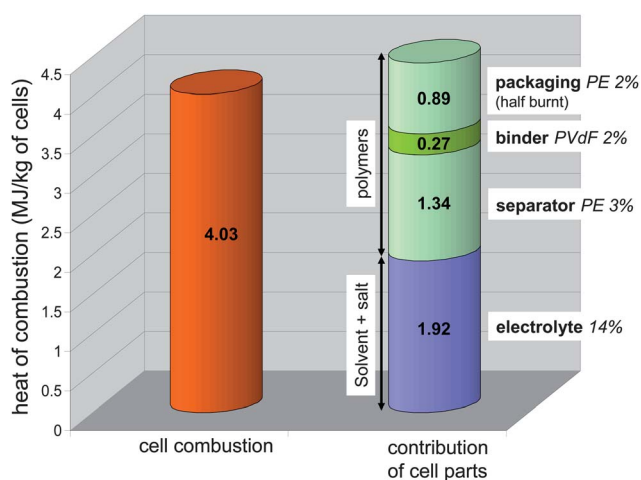
upper part of the packaging burnt that slightly decreases the organic compounds percentage to roughly 21%. Therefore, the decomposition and combustion of polymers and electrolytes are responsible for practically all the mass loss indicating such combustion conditions are optimal.

(ii) **Heat released rate (HRR).** The key data to consider are not only the energy value of the combustion but also the way this energy is released with time and the overall information can be extracted from the HRR profile (Fig. 4). In our case, HRR calculation is based on O_2 consumption, corrected for CO and soot production. Fig. 4 shows that the maximum HRR value increases with the SOC. This was found to reach approximately 21, 13 and 2.6 kW for 100, 50 and 0% SOC, respectively. Divided by the battery surface area, the resulting normalized HRR value ($kW m^{-2}$) can be compared with those of other combustible compounds such as standard fuels and polymers that were previously tested using the same Tewarson calorimeter. The normalized HRR value for the 100% SOC batteries is slightly lower than that of gasoline (Fig. 5). For the 50% SOC battery, this is equivalent to that of fuel oil while the 0% SOC battery

**Fig. 4** Comparison of 100, 50 and 0% SOC batteries heat release rates measured from oxygen consumption calorimetry.**Fig. 5** Comparison of 100, 50 and 0% SOC batteries normalized HRR ($MW m^{-2}$) with that of different combustibles.

presents the lowest value. Another point to consider is the kinetics of the combustion heat release. Fig. 4 clearly shows that the fully charged battery discloses the highest reaction rate; the combustion heat is very shortly released that could entail a potential risk of explosion. The 0% SOC battery is safer with a lower reaction rate. These kinetic changes may be explained either by exothermic redox processes occurring at the interface electrolyte/lithiated negative electrode upon heating or by a fire-induced short which may imply quite rapidly dissipation (by Joule effect) of the electric energy.³² Note that fire calorimetry techniques relying on mass balance (O_2 consumption) cannot, by principle, account for energy simply liberated by the Joule effect.

The HRR profile integration allows the estimation of the overall dissipated combustion heat. The calculated average values were 313 ± 37 , 383 ± 32 and 361 ± 40 kJ for 100, 50 and 0% SOC, respectively, corresponding to a maximum effective combustion heat of 4.03 ± 0.34 MJ kg^{-1} of cells (Fig. 6).

**Fig. 6** Maximum experimental combustion heat (HRR integration) of the battery compared with cumulated contribution values pertaining to its organic parts calculated from thermodynamic data.

Compared to gasoline, the maximum volumetric energy of the battery (50% SOC) is three-fold lower (10 vs. 33.1 MJ L⁻¹). It can be noted that although the fully charged battery has the highest HRR values and reaction rates, the combustion energy displays the lowest value.

Thanks to the mass distribution of the battery that was previously estimated, we could predict the contribution of the combustion heat for organics namely the electrolyte and the polymers from separator, binder and packaging. The heat of combustion for PVdF as well as PE were found in the literature,^{33,34} and the heat of combustion of electrolyte was calculated using the heat of formation of solvents and salt^{35–37} and its assumed combustion products such as HF, Li₂O, P₄O₁₀, CO₂ and H₂O.³⁸ As shown in Fig. 6, the sum of these contributions compares well (91%) with the actual cell combustion heat deduced from Tewarson calorimeter data. The slightly higher value may indicate the yield of combustion is not quite complete as usually observed in fire conditions. It can be noticed the overall heat of combustion calculated for the polymers represents at least half the total heat.

Further discussion on uncertainties in HRR measurements. Apart from usual sources of uncertainties well described in the fire science literature (e.g. ref. 22,30, and 31), the brand new question here is the importance of energy that may be liberated through erratic electric discharge through external/internal shorts during the experiments (Joule effect), and that cannot indeed be related to O₂ consumption. Our estimate of the maximum contribution of such a process is about 10% of the overall energy content of a fully charged cell. This calculation confirms that the use of the oxygen consumption technique is reasonably relevant for the estimation of HRR in support of related fire safety engineering objectives.

b. Gas analysis and the toxic threat in abuse conditions leading to fire

The production of volatiles from the battery combustion could come from solids involving for the most part, thermal decomposition processes, or from liquids by a simple evaporation process. Also, as the temperature of a burning solid tends to be high, chemical reactions between the battery compounds or/and volatiles should be considered implying that the composition of gases which are ignited tends to be extremely complex. In this study, the gases we focused on allowed the assessment of the combustion overall efficiency (CO, THC), the HRR value (O₂, CO₂, CO) and the toxic risk (CO, HF, HCl, NO_x, SO₂).

(i) CO, CO₂ and total hydrocarbons (THC). CO and CO₂ productions plotted in Fig. 7a and b reveal the combustion overall efficiency. Note that the CO production increases with the SOC of the battery; the combustion efficiency is reflected by $n_{\text{CO}_2}/n_{\text{C}_{\text{total}}}$ molar ratio that reached 90, 98 and 99.5% for 100, 50 and 0% SOC of the tested batteries respectively. These values show that the more the battery stores energy the less the combustion goes to completion in our test conditions. This statement is also highlighted by the production of the total hydrocarbons (Fig. 7c) due to the fuel that has not burnt. Unlike

the 100% SOC case, the yield of THC for the two other batteries SOC is close to zero.

(ii) SO₂, HCl, CO, NO and HF. Uncontrolled combustion energy can cause material damage and thermal threat to people (burns), but attention has also to be paid to the reaction products, some of them having deleterious effects on humans, beyond the CO hazard.

During the experiments, “standard” toxic gases production was followed by means of the Infra-Red technique. The analysis revealed consequent yield for five of them: SO₂, HCl, CO, NO and HF.

In Fig. 8a, nitrogen oxide production is reported during combustion. This production depends on the SOC; when the SOC increases, the NO concentration increases and the production time is shortened. The origin of the nitrogen source was checked by testing different parts of the battery (packaging, separator, positive and negative electrodes) but no such source was identified. The nitrogen oxide might be produced as a reaction product of nitrogen (originating from air or fuel-bound N₂) and oxygen from air within the flame (thermal route of NO_x production). Usually, temperatures as high as 2500 K are necessary and radical processes as below are involved:



Visual observation of the combustion (video recording) confirms an apparent relationship between the flame intensity and the NO production measured: highly intense in a short time for the 100% SOC, less intense in a longer time for the 50% SOC and a dim flame for around 3 minutes in the case of 0% SOC. As far as the N₂ presence is concerned, further testing at larger scale would be needed to clarify its origin.

The yield of SO₂ was analyzed (Fig. 8b) and, surprisingly, was found to be in a higher concentration in the case of the fully charged battery. The origin of sulfur containing molecules arises from battery additives. Indeed, sulfur-based compounds are known to be used as additives for their property in facilitating SEI formation.^{39–41} The heat release reaches a threshold for which the temperature is enough to initiate the degradation of the additive to form sulfur oxide. Unlike fully charged batteries, 50% and 0% SOC HRR values seem to be too low to allow such reaction.

Chlorine was detected through halide production (Fig. 8c). Polymers are chlorine potential sources and may be found in three components of the battery: binder, separator and packaging. The common binders used for commercial batteries, PVdF or CMC,⁴² do not contain chlorine; the sole halogen element which can be found is fluorine in PVdF. Combustion experiments on separator and packaging were undertaken and only the separator revealed the presence of chlorine. The HCl production kinetic for the 100% SOC batteries was different from the others for which the production spans at least two minutes. The quantity of this rejected halide has no SOC dependence and remains low (~25 mg).

From the gas effluents, hydrofluoric acid (HF) was also detected (Fig. 8d). The preliminary analyses of the battery components revealed that the major sources of fluorine were the

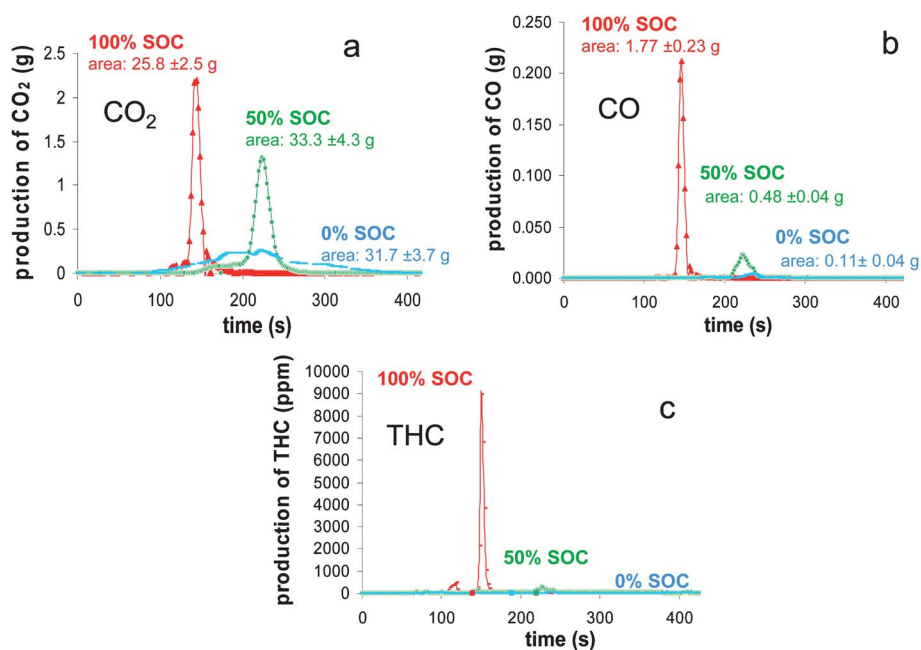


Fig. 7 Mass flux of CO₂ (a), CO (b) and THC (c) as a function of time during the combustion of the batteries at different SOC.

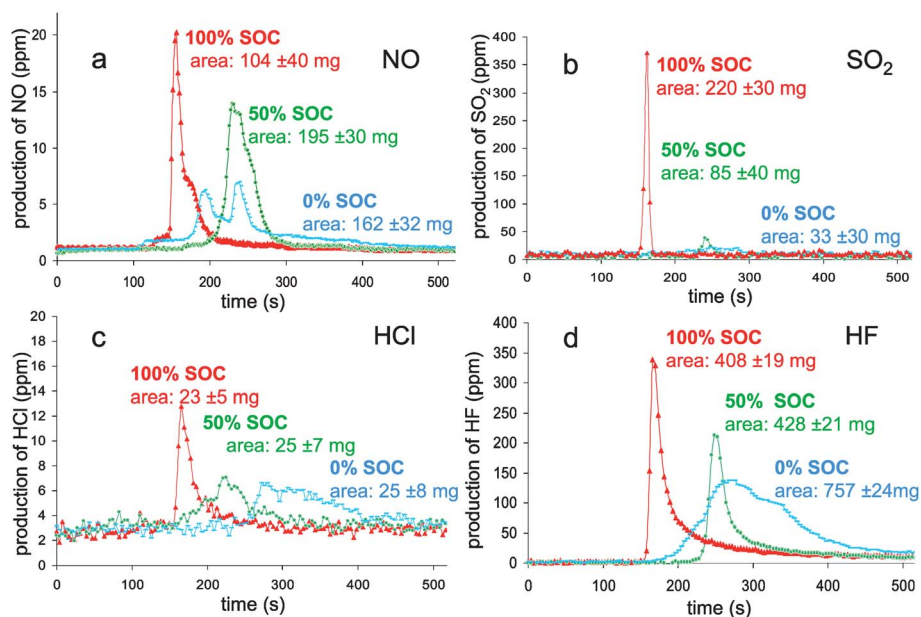


Fig. 8 Mass flux of NO (a), SO₂ (b), HCl (c) and HF (d) as a function of time during the combustion of the batteries at different SOC.

electrolyte salt (LiPF₆) and the binder (PVdF). Its production kinetic turned out to be different according to the battery SOC and followed the HRR profiles. Consequently, HF emission extends over a longer time (200 seconds) for a 0% SOC compared to 50 seconds for a 100% SOC. In accordance with the reaction rate, half-charged batteries behaved as an intermediate case.

Surprisingly, the HF cumulative masses calculated from the peak integration indicated quite different values; the higher one corresponding to the discharged batteries. From the mass distribution analysis, the HF equivalent mass could be estimated to be 1.21 g from the electrolyte and 1.23 g from the binder.

Hence, the detected maximum value (0.757 mg) only represents a third of the total equivalent mass of fluorine contained in the battery. It is worth noting here that, unlike the batteries, the combustion of a EC : DMC : DEC (1 : 1 : 1 wt) LiPF₆ (1 M) electrolyte tested alone in a pool burning mode by means of the same PFA apparatus entailed the release of nearly the total equivalent mass of HF (~98%). Hence, in the case of battery combustion, either a large part of HF is absorbed on battery components or fluorine is involved in complex chemistry^{43,44} so that other fluorine based compounds, not detected here, might be released.

c. Toxicity evaluation

A judicious question is the significance of toxic gas data from these combustion tests. A series of national and international standards give general guidance regarding the toxicity of gas as carbon dioxide, carbon monoxide, hydrogen halides (HCl, HBr, and HF), sulfur dioxide, hydrogen cyanide, nitrogen oxides, formaldehyde (CH₂O) and acrolein (C₃H₄O) gases. Based on the French standard,⁴⁵ the evaluation of the dangerousness⁴⁶ of the combustion gas products was undertaken. Two toxicity limit values were taken into account: the Irreversible Effects Threshold (IET) and the First Lethal Effects Threshold (FLET), as defined in the French regulatory context to perform toxic hazard studies in industrial environment. For a first order toxic hazard evaluation, we have considered the maximum quantity of gas released during all the combustion experiments in a fictive scenario where these gases are evenly distributed in a room of 50 m³ to compare experimental values with the mentioned thresholds.

From the experiments, the maximum values used were 0.22 g (4.4×10^{-3} g m⁻³), 0.025 g (5×10^{-4} g m⁻³), 1.77 g (3.54×10^{-2} g m⁻³), 0.195 g (3.9×10^{-3} g m⁻³) and 0.757 g (1.5×10^{-2} g m⁻³) for SO₂, HCl, CO, NO and HF, respectively. Fig. 9 plots the FLET and IET values as a function of both the exposure time and the maximum concentration of gas released from

the battery combustion tests. Whatever the exposure time, experimental values are far from IET limits. By basic extrapolation not taking account any scale-up effect on toxic species yields (which is indeed a very questionable assumption), we have evaluated the electrical energy of the batteries required for reaching the individual IET and FLET (Table 3) at a 60 minutes exposure time. Energies as high as 60 to 1320 Wh and 110 to 7880 Wh are announced to approach both the IET and FLET toxicity limits respectively, indicating that the hazard driven by those toxics would require full combustion of relatively large batteries to become critical. From this viewpoint, emerging e-mobility applications (hybrid electric vehicles, plug-in hybrid electric vehicles, full electric vehicles...) that require embarked electric energy storage systems in the range of 15 to 30 kWh would actually deserve dedicated studies focusing on toxicity impacts in the case of EV related fire scenarios. This is true in

Table 3 Estimated battery energy to reach the IET and FLET values for the NO, CO, HCl, SO₂ and HF toxic gases (exposure time of 60 minutes, fire occurring in a 50 m³ room)

(Wh)	HF	CO	NO	SO ₂	HCl
IET	60	290	280	530	1320
FLET	110	1140	2080	4710	7880

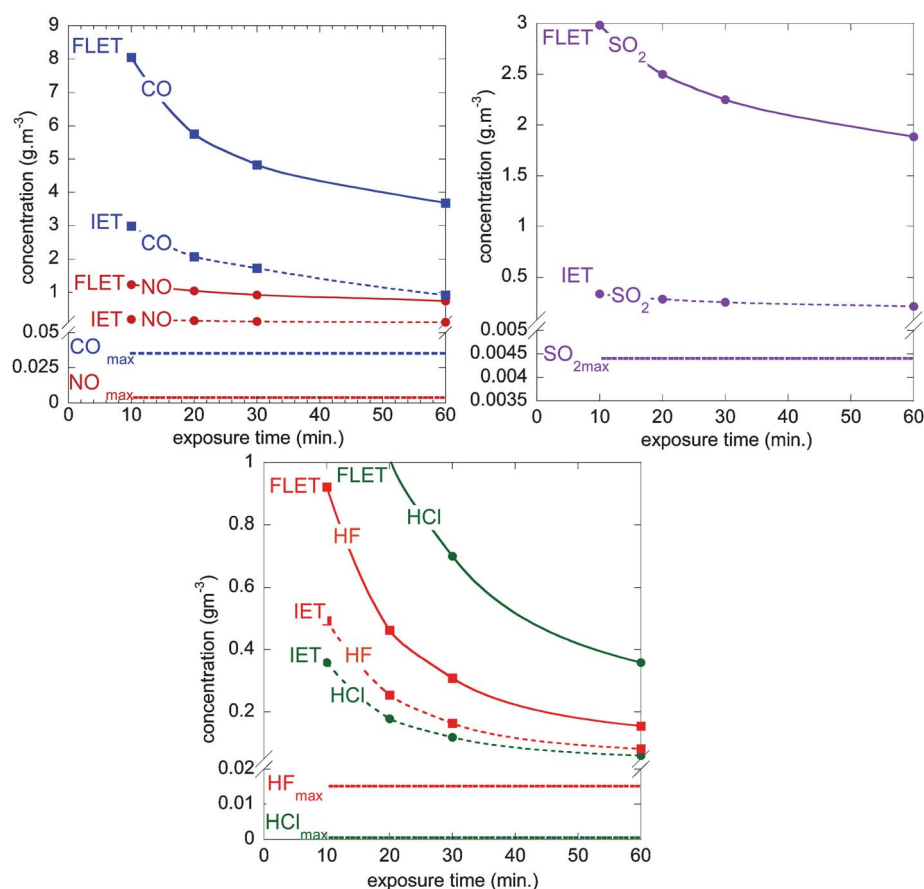


Fig. 9 FLET and IET concentration values as a function of exposure time with maximum concentration of CO, NO, SO₂, HCl and HF gases released from the batteries combustion (2.9 Ah pouch cell burning in a 50 m³ room). These graphs allow first-order evaluation of their dangerousness (see Table 3).

particular for storage fires and EV car fires, all the more in the latter case than the volume in which toxic smoke may be trapped could be far less than 50 m³ (e.g. car interior), or in case multiple car burning may be feared depending on the confinement taken into consideration (e.g. garage, underground park place, ...).

Note that CO toxicity is a common threat of any fire burning any carbon containing material. The actual threat being clearly related to the amount of material burning, combined (often additive) actions of individual gases, temperature and confinement conditions. More attention might be paid for hydrofluoric acid, since energies of 60 and 110 Wh (roughly equivalent to that of a laptop) are necessary to achieve the IET and FLET limits in these conditions. So, it can be deduced that fluorine based molecules are one of the key points for the battery security field. As it was mentioned above, fluorine sources are coming from the binder and the electrolyte. The removal of fluorine from the binder is conceivable and already exists with the use of binders such as carboxymethyl cellulose but replacement of fluorine containing salts in the electrolyte is a challenging situation for most applications. Reducing flammability of solvents might possibly serve fire toxicity management.

4. Conclusion

The calorimeter implementation for battery safety application was undertaken to add to the existing techniques, equipment able to provide more insight into the fire battery behaviour. This study has demonstrated the interest of the Tewarson calorimeter in the scope of battery safety field. This apparatus permits on-line analysis of mass loss and combustion gases production such as O₂, CO, CO₂, hydrogen halides, HCN, NO_x, SO_x, aldehydes, and THC. From these data, the heat released rate, the heat of combustion and the mass of burnt products from the combustion tests can be deduced. These data could be of great help for fire simulation. Moreover, the identification and quantification of toxic emissions from combustion gases can also be estimated. As a result, the whole data could have a part in the improvement of battery from safety point of view.

2.9 Ah pouch type batteries were tested at 100, 50 and 0% state of charge. Results showed that the masses lost during all the fire experiments were practically identical and roughly corresponded to the mass of organics. Nevertheless, depending on the SOC, the way of losing mass was different revealing the major role of the accumulated electrochemical energy.³¹ Upon heating (radiation of infrared heaters), this energy is released through different reaction pathways, leading to thermal runaway within the materials and production of fuel gas. The exact nature of these extra-reactions is beyond the scope of this paper but could be reactions of electrode materials with the electrolyte, electrolyte decomposition or positive active material decomposition. In the case of the fully charged batteries, the energy is rapidly released verging on explosion, and the phenomenon suddenness restricts the oxygen consumption leading to incomplete combustion. This can be noticed by the hydrocarbons detection, the highest carbon monoxide production and the lowest heat energy value. When the battery is half-charged, the thermal runaway is less important allowing the combustion to go nearly to completion. For the fully discharged case, the burning of the battery is relatively slow (8 minutes) leading to the complete combustion condition.

Quantification of O₂, CO and CO₂ gases allowed estimation of the cell combustion heat either by O₂ consumption or by CO and CO₂ releases. The maximum value (~4 MJ kg⁻¹ of the tested pouch 2.9 Ah batteries) was found to be close to the one calculated from thermodynamic data (combustion and formation heat of the organics). This quite good correlation brings to light that a battery heat of combustion can be estimated through simple addition of the contributions of all polymers and electrolyte combustion heats. Note that for the tested pouch cells, at least 50% of the combustion heat originates from polymers.

From the online analysis, significant concentrations of toxic gases are detected as HF, CO, NO, SO₂ and HCl. The production of these gases also depends on the cell SOC; carbon oxides and nitrogen oxide are the direct products of combustion and their kinetics follow the HRR profile. SO₂ is probably the reaction product of sulfur-based additive added into the electrolyte and its formation requires high heat that the fully charged battery is only able to release. The yield of HCl remains low and seems to have no SOC dependence. In contrast, HF results indicate a SOC dependence and the maximum concentration is achieved with the fully discharged battery. The evaluation of the dangerousness of the gaseous combustion products was undertaken by a simple extrapolation of the toxicity thresholds. The results stress the problem of fluorine-based compounds from a safety point of view and more precisely in the case of EV and HEV large-scale application. Despite the fact that experiments were conducted under high air flow and with high heat flux applied to the battery, it seems that future works have to be focussed on the replacement of LiPF₆ by a less fluorine-containing salt^{47,48} and by the removal of fluorine in the binder.

Acknowledgements

This work was supported by “Région de Picardie” through the BatteryNanosafe project. The authors are grateful to Jean-Pierre Bertrand for his technical assistance and to Alexandra Paillart and Michel Armand for helpful discussions.

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