

Experimental & Theoretical Study on the Solid, Liquid and Gaseous Residues after Fire Extinction of Lithium-Ion Batteries

Davide Palma^a, Sofia Ubaldi^a, Mario Quintero^b, Pierpaolo Gentile^b, Michele Mazzaro^b, Paola Russo^{a*}

^aDipartimento Ingegneria Chimica Materiali Ambiente, Sapienza Università di Roma, Via Eudossiana 18, Roma, Italy

^bDirezione Centrale per la Prevenzione e la Sicurezza Tecnica Antincendio ed Energetica. Corpo Nazionale dei Vigili del Fuoco, Largo S. Barbara 2, Roma, Italy.

paola.russo@uniroma1.it

The electric vehicles are a good option for aiming the Energy transition, in a such important sector such as the mobility. The use of a huge quantity of high energy and high power Lithium-Ion Batteries (LIBs) opens the discussion of many topics such as competitiveness compared to other technologies, recycling of the materials and the safety. This paper shows an experimental study based on fire extinguishing tests on NMC Lithium-Ion pouch cells, each with approximately 100 Wh energy stored. Different extinguishing agents were tested: Foam, Aqueous Vermiculite Dispersion (AVD). After tests, solid samples were taken from the burnt cell and the residue extinguishing liquid was collected. Gases produced from the combustion of the cell were also sampled during the test and collected in gas bags. Chemical analyses were performed on solid, liquid and gaseous residues in order to evaluate presence of hazardous compounds for health and environment. Gas Chromatography Mass Spectrometry and a Fourier-transform Infrared Spectroscopy were used to handle this type of analysis. The aim of this experimental work is to identify the hazardous compounds present in the residue of LIB after the fire is extinguished (i.e. electric vehicles) to evaluate their health and environmental impact and then to propose a methodology for their treatment or disposal. In particular, a comparison between different extinguishing agents is reported.

1. Introduction

To meet the emission limits imposed by the European Community the electric mobility will play an important role for the next 30 years. For supporting the required increasing electric vehicles (EVs) range a huge penetration of Lithium-Ion Batteries (LIBs) will take place. Incidents related to this technology should be investigated for a deep comprehension of the environmental impact that they may entail. In particular, the development of a fire from the LIBs stored in a EV might generate toxic and flammable gases. These gases are the product of several reactions occurring during the so called thermal runaway (TR), in which the chemical compounds within a cell react. Therefore, as consequence of TR fire and/or explosion may occur. Different agents were proposed in the literature for LIBs fires. Novec 1230 as extinguishing agent for LIBs fire was studied by Liu et al. (2018). Rao et al. (2015) showed that ABC powder extinguishing agent has low efficiency against LIBs fires. The efficiency of different water-based extinguishing agents, such as pure water, water + F500 (1%), water + Firesorb (1.8%) was studied by Egelhaalf et al. (2013). In our previous studies (Ubaldi et al., 2022; Palma et al., 2023), we demonstrated that water based agents (i.e., water mist, F500-water spray and F500-water mist) exhibited a higher extinction efficiency than CO₂, foam and AVD. After the extinction the solid and liquid residues may also cause and environmental contamination. Hence, in this paper an experimental work about the chemical analysis of gas, liquid and solid residues after fire extinction of LIBs is reported. In the literature, Golubkov et al. (2014) studied the production of gases of burning cells from three different cathode compositions such as lithium iron phosphate (LFP), lithium cobalt oxide (LCO), lithium nickel cobalt oxide (NMC). Ribière et al. (2012) analysed the combustion gases of pouch LIBs at different State of Charge (SOCs). Larsson et al. (2017) investigated HF

production and composition from fire of LIBs with different cathode chemistry such as LCO, LFP and lithium nickel cobalt aluminium oxide (NCA). They found that the amount of the HF produced increases with the higher SOCs. They also impute a higher HF concentration from pouch cells than cylindrical cells due to the lower venting pressure. Ubaldi et al. (2023) studied the key events, the gas and particulate emissions due to thermal abuse of NCA cells, evidencing the formation of toxic concentrations of HF and particle sizes of the order of PM2.5. Hynynen et al. (2023) performed a large scale fire test for measuring the fire behaviour of internal combustion engine vehicle (ICEV) and EV, highlighting the differential HF production between the two technologies. Jia et al. (2023) proposed a comparison between the gas composition of LIBs under overcharging and overheating conditions. Funk et al (2023) realized full scale EV fire tests, measuring the HF production. Andersson et al (2013) studied how the combustion gases composition (in terms of HF and POF_3) is influenced by the electrolyte composition, testing different solutions of electrolytes and lithium hexafluorophosphate (LiPF_6). But, far as the authors know, analytical studies on solid and liquid residues are not reported in the literature. The aim of these experimental tests is to compare how the extinguishing actions of the AVD and Foam (fire class 27A 233B 40F), certified for LIBs fires, influence the gas, liquid and solid residues composition. A theoretical calculation model has been developed to carry out the gas quantitative analysis.

2. Experimental

2.1 Materials

Cells used were pouch cells Kokam SLPB 25 Ah (Kokam), with a nominal energy of 92 Wh. Cells have square shape of 22 cm x 22 cm x 1 cm. The cathode chemistry is NMC and the anode is graphite. The layers of anode and cathode are immersed in an electrolyte made of a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and LiPF_6 .

2.2 Fire extinguishing tests & sampling

Experimental tests were performed to investigate the extinction efficiency of each extinguishing agent for a fire of a single cell. Each cell was placed horizontally on a metal grate and heated by two electric plates. 6 cm distance between the electric plates was set for ensuring enough space for the swelling of the cell (Figure 1). A portion of the combustion gases was sampled, filtered and collected in a gas bag (Figure 2). A gas pump set on $p^{\text{DISCHARGE}} = 1.15$ bar and $F^{\text{DISCHARGE}} = 2.5$ L/min was chosen and a sampling time of 110 s was set for a 5 L gas bag. A multi-layer gas bag (15 μm nylon, 7.62 μm aluminum and 50 μm Polyethylene) was used. For each test the liquid residues, the solid burnt cells, the Activated Carbon (A.C.) filters and the combustion gases were sampled for the subsequent chemical analysis. The liquids were collected within falcon test tubes (mL 50). The burnt cells were stored into high resistant plastic bag and preserved before solid sampling.

In the following a data elaboration of the chemical analysis carried out on the residues of test of Free burning cell without extinguishing agent (Test 16), of test with foam extinguishing agent (Test 19) and with AVD (Test 20) is reported. Foam composition is: EWAB15 (2 % SC 6 + 10 % Inilam AX + 88 % Water).

2.3 Analytical methods

A quantitative analysis of the combustion gases was performed through a Perkin Elmer Spectrum 3TM FT-IR Spectrometer with the following acquisition parameters: resolution 4 cm^{-1} , spectral range between 4500 and 650 cm^{-1} , 8 scans per spectrum and MCT as detector. Spectra were acquired continuously. A previous calibration obtained by standard gas was used for identifying and quantifying the species. A qualitative analysis of volatile organic compounds (VOCs) in the liquid, solid and A.C. filters was performed by Solid Phase micro Extraction Gas Chromatography-Mass Spectroscopy (SPME-GC-MS). Fiber Type: PK3, FFA SPME 100 μm PDMS, 23 Ga – RED. Column type: Agilent: HP – 5MS UI – 60 m x 0.250 mm x 0.25 μm .

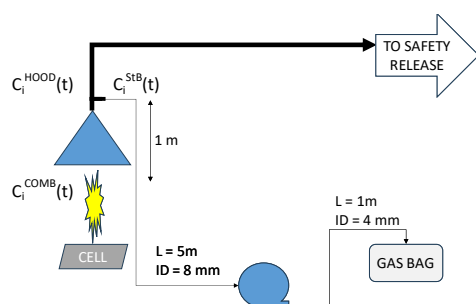


Figure 1: Scheme of the gas sampling system



Figure 2: Gas bag

Regarding the quantitative analyses, the gas stored in the gas bag is sent to the FT-IR with constant flow rate (F_G^B). Before it reaches the analysis cell, a dilution with N_2 is required for avoiding signal saturation. Once diluted, only a portion of the total flow, $(F_G^B + F_{N_2}) * \Phi = F_G^F + F_{N_2}^F$, is sent to the analysis.

3. Results

3.1 Gas Analysis results

The gas stored in the gas bag was analyzed by FT-IR. The quantifiable compounds were CH_4 , CO , CO_2 , DMC, DEC, EC, HCl and HF. H_2 is not detectable by this analysis. The results of free burning test, no extinction (Test 16), of test with foam as extinguishing agent (Test 19) and that with AVD agent (Test 20) are compared in order to understand how the different extinguishing agent influences the combustion gas composition. In table 1 are reported the concentration (C_i^B) and the mass (m_i^B) of the i -components in the gas collected in each test.

Table 1: Gas concentration and gas mass in the gas bag for Test 16, Test 19 and Test 20

Test	EXT		UOM	CH_4	CO_2	EC	HCl	HF	Σ
16	-	C_i^B	ppm(v)	10.9	141.1	0.0	20.9	4.0	176.8
19	Foam	C_i^B	ppm(v)	1.5	303.6	60.1	7.5	9.1	381.8
20	AVD	C_i^B	ppm(v)	32.8	2122.3	157	1.8	9.3	2323.2
16	-	m_i^B	g	$2.1 * 10^{-5}$	$7.6 * 10^{-4}$	0	$9.4 * 10^{-5}$	$9.8 * 10^{-6}$	$8.9 * 10^{-4}$
19	Foam	m_i^B	g	$3.0 * 10^{-6}$	$1.6 * 10^{-3}$	$6.5 * 10^{-4}$	$3.4 * 10^{-5}$	$2.2 * 10^{-5}$	$2.4 * 10^{-3}$
20	AVD	m_i^B	g	$6.5 * 10^{-5}$	$1.1 * 10^{-2}$	$1.7 * 10^{-3}$	$7.9 * 10^{-6}$	$2.3 * 10^{-5}$	$1.3 * 10^{-2}$

3.2 Gas results interpretation

Since FTIR analysis does not detect all the gas compounds produced during the fire, it is useful to write some definitions. Let's call m_c^B the mass of all the compounds sampled (i.e. not including the atmospheric air). Moreover, let's call $m_c^{B^{\circ}} = \sum m_i^B$ the total mass of the compounds detected and $m_c^{B^{\emptyset}} = \sum m_j^B$ the total mass of the not detected compounds such that $m_c^B = m_c^{B^{\circ}} + m_c^{B^{\emptyset}}$. The subscript "i" indicates a detected compound, while the subscript "j" indicates a not detected compound. The apex "°" refers to the total detected compounds (hence not including air), while apex "∅" to the total not detected compounds (no air). Figure 3a,b,c show the percentages of the i -th volumetric gas composition in the bag referred only to the detected compounds (C_i^B).

$$C_i^{B^{\circ}} \left(\% \frac{V}{V} \right) = \frac{V_i^B}{V_c^{B^{\circ}}} * 100 = \frac{V_i^B}{\sum V_i^B} * 100 = \frac{V_i^B / V_G^B}{\sum (V_i^B / V_G^B)} * 100 = \frac{C_i^B}{\sum C_i^B} * 100 \quad (1)$$

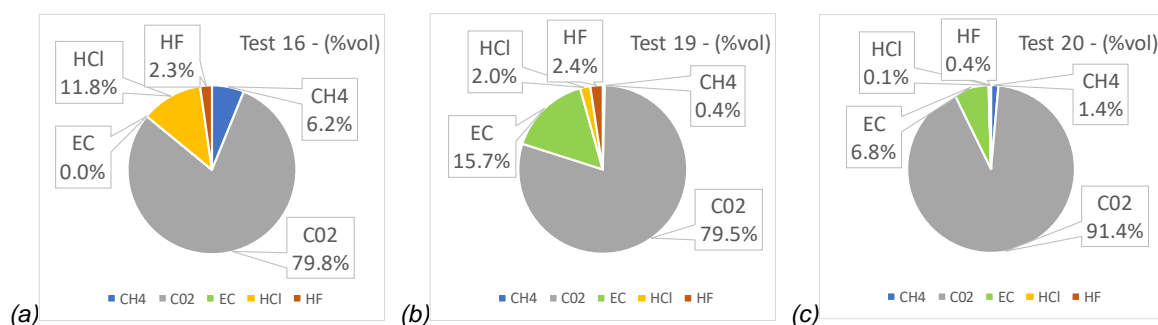


Figure 3: Gas composition (% V/V) of the total compounds detected in Test 16 (a), Test 19 (b) and Test 20 (c)

The concentrations of the sampled and detected gases referred to the total detected compounds ($C_i^{B^{\circ}}$) are comparable between the 3 tests. Figure 3a,b,c show that CO_2 is the main compound produced during the fire and the extinction phases. However, it can be highlighted how in the free burning test (Test 16) HCl is in a percentage of 11.8 %V/V with respect to the all the detected gases, while is 2.0 %V/V and 0.1 %V/V respectively for Test 19 and Test 20. On the contrary, the electrolyte EC is completely burnt in Test 16, while it is present in Test 19 as 15.7 %V/V and in Test 20 as 6.8 %V/V. It is likely that this evidence is related to the cooling effect provided by the extinguishing agents, which restrained the burning process.

3.3 A comparison between the Gas composition in the tests

This paragraph presents a physical model of the hood and the gas sampling system, which is intended to facilitate an understanding of the roles of all the parameters. It is assumed that, due to the hood aspiration velocity, the vertical diffusion characteristic time (τ_z) is much smaller than the horizontal diffusion characteristic time ($\tau_{x,y}$), for all the compounds. Thus, it is possible to assume that $C_i^{\text{HOOD}^\circ}$ only depends on z and time (see Figure 4). On the other hand, the total gas flowing through the hood (m_G^{HOOD}) is the sum of the total combustion compounds mass (m_C^{COMB}) and the atmospheric air mass (m_A^{ATM}), during aspiration. These considerations bring to Eq(2a) and Eq(2b):

$$\frac{\delta^2 C_i^{\text{HOOD}}(x,y,z,t)}{\delta x \delta y} \neq 0 \quad ; \quad \frac{\delta^2 C_i^{\text{HOOD}^\circ}(z,t)}{\delta x \delta y} = 0 \quad (2a) ; (2b)$$

$C_i^{\text{HOOD}^\circ}$ is the i -th gas compound concentration in the hood referred only to the detectable compounds. From Eq(2a), the concentration of the compounds in the gas through the hood (C_i^{HOOD}) is a function of the tridimensional space (x,y,z), depending on the random distribution of the combustion compounds in air across the horizontal section (see Figure 4), during the aspiration. Hence, the mass of the total compounds sampled in the gas bag (m_C^B) might be affected by a random error due to the sampling conditions. Consequentially, m_i^B might be affected too, such that Eq(3) can be written, where EA is the extinguishing agent action:

$$C_i^B \text{ function } (EA, C_i^{\text{HOOD}}) \quad (3)$$

On the other hand from Eq(2b), at the sampling point height (H_{SP}) Eq(4) can be assumed:

$$C_i^{\text{HOOD}^\circ}(t, z = H_{SP}) \equiv C_i^{\text{StB}^\circ}(t) \quad \forall x,y \in \text{hood section} \quad (4)$$

Because the distance between the gas source height (H_{GS}) and H_{SP} is small (1 m), Eq(5) can be assumed:

$$C_i^{\text{COMB}^\circ}(t) \simeq C_i^{\text{HOOD}^\circ}(t, z = H^{SP}) \quad \forall t \in \Delta t^{\text{SAMPLING}} \quad (5)$$

$$\text{Thus, } C_i^{\text{COMB}^\circ}(t) \simeq C_i^{\text{StB}^\circ}(t) \rightarrow C_i^{\text{COMB}^\circ} = \int C_i^{\text{COMB}^\circ}(t) dt = \int C_i^{\text{StB}^\circ}(t) dt = C_i^B \quad (6)$$

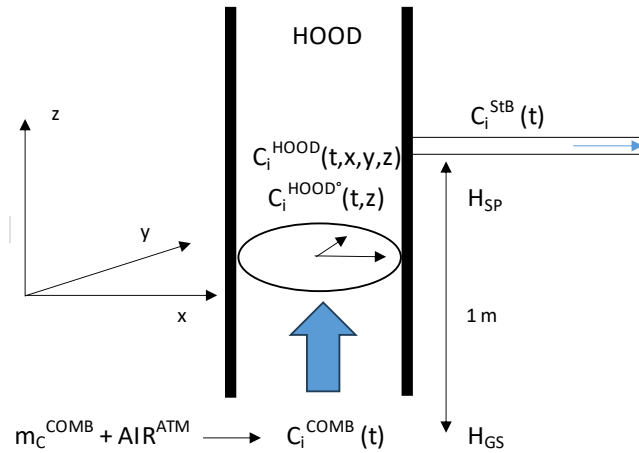


Figure 4: Hood & Aspiration Point physical model

For making the comparison between the gas composition of the two tests the ratio of the total produced masses of the i -th compound (Ω°) has to be considered. From Eq(6):

$$\Omega^\circ = \frac{m_i^{\text{COMB}}(\text{Test 19})}{m_i^{\text{COMB}}(\text{Test 20})} = \frac{C_i^{\text{B}^\circ}(19)}{C_i^{\text{B}^\circ}(20)} * \frac{m_C^{\text{COMB}^\circ}(19)}{m_C^{\text{COMB}^\circ}(20)} \quad \text{function } (C_i^{\text{B}^\circ}(EA), m_C^{\text{COMB}^\circ}(EA)) \quad (7a)$$

Due to the fact that $m_C^{\text{COMB}^\circ}$ is unknown from the tests, the calculation is expressed as ω° in Eq(9b):

$$\omega^\circ = \frac{m_i^{\text{COMB}}(19)/m_C^{\text{COMB}^\circ}(19)}{m_i^{\text{COMB}}(20)/m_C^{\text{COMB}^\circ}(20)} = \frac{m_i^B(19)/m_C^{B^\circ}(19)}{m_i^B(20)/m_C^{B^\circ}(20)} = \frac{C_i^{\text{B}^\circ}(19)}{C_i^{\text{B}^\circ}(20)} \quad \text{function } (C_i^{\text{B}^\circ}(EA)) \quad (7b)$$

With regard to Eq(3), C_i^B is a function of EA and the three-dimensional space ($C_i^{\text{HOOD}}(x,y,z)$), using $C_i^{\text{B}^\circ}$ in Eq(7a), instead of C_i^B (i.e. relating the calculation to the detectable compounds), allows Ω° to be decoupled from the random composition of the total gas flowing through the aspiration hood. This allows a comparison to be made

between different tests regardless of the mixing conditions between the compounds and the air across the hood section. Furthermore, since $m_c^{\text{COMB}^\circ}$ is unknown the calculation model is expressed as a normalized ratio in Eq(7b). This ratio (ω°) is calculated from known quantities (m_i^{B} and $m_c^{\text{B}^\circ}$). For clarity, since $m_c^{\text{COMB}^\circ}$ is a function of EA, the influence of EA on the formation and evolution of the detected combustion compounds mass ($m_c^{\text{COMB}^\circ}$) is lost when going from Ω° of Eq(7a) to ω° of Eq(7b).

Table 2: Ratio between the compound's emissions in the two extinction tests with foam (19) and AVD (20)

ω°	CH ₄	CO ₂	EC	HCl	HF
	0.3	0.8	2.2	24.0	5.5

From Table 2, when $\omega^\circ > 1 \rightarrow$ the AVD agent (Test 20) shot down more gas emission than the Foam agent (Test 19). Where $\omega^\circ < 1 \rightarrow$ the Foam agent shot down more gas emission than the AVD. This calculation shows that the Foam extinguishing agent is more efficient in inhibiting the production (and the evolution) of compounds as CH₄ and CO₂. On the other hand, AVD was more efficient in reducing the emissions of EC, HF and HCl.

3.4 Liquid, Solid, Filter Analysis results

In Table 3 and 4 the VOCs identified (yes) and searched, but not identified, (no) by SPME-GM-MS analysis in the solid, liquid and A.C. filter are reported.

Table 3: SPME-GC-MS analysis for the solid residues and the A.C. filter

Test	Solid residue				A.C. filter			
	DMC	EMC	DEC	EC	DMC	EMC	DEC	EC
Test 16	yes	yes	yes	no	no	yes	no	no
Test 19	yes	yes	yes	no	no	yes	no	no
Test 20	yes	yes	yes	no	no	yes	no	no

Table 4: SPME-GC-MS analysis of the liquid residues

Liquid residue	1-optanol	3-nonanol	4-nonanol	2-decanol	2-propil, eptanol	2-butyl, optanol	1-decanol
Test 16	LNA	LNA	LNA	LNA	LNA	LNA	LNA
Test 19	yes	yes	yes	yes	yes	yes	yes
Test 20	LNA	LNA	LNA	LNA	LNA	LNA	LNA

As Test 16 is a free burning test (no extinction), the liquid residue is not available: "LNA". Due to the extinction mode of the AVD in Test 20, no liquid was found after the fire. AVD agent is composed of 80 – 95 % water and 20 – 5 % exfoliated vermiculite flakes (other ingredients < 1%). When AVD is applied to the burning cell, the water evaporates and the Vermiculite forms a shell around the cell. After the extinction phase, only a dry solid film of Vermiculite remains. In the liquid residue of Test 19 with foam C8 – C10 alcohol molecules are present due to the Foam composition.

4. Conclusions

The aim of this work is to examine the impact of foam and AVD agents on the composition of gas, solid and liquid extinction residues. A theoretical calculation model was developed in order to describe the quantitative chemical analysis. This calculation model is based on the ratio of the masses of the i-th gas compound produced and developed by the cells during the fire and the extinction phases in the two tests normalized by the detectable compounds total combustion mass produced (ω°). The use of this model negates the sampling experimental error due to the mixing condition through the hood, but the EA influence on the total mass is lost. Consequentially, only a comparative result is obtained for each compound. The calculation model demonstrated that AVD agent was more effective than foam for reducing EC, HCl, HF emissions, but less effective for CH₄ and CO₂. In this calculation the non-detection of certain compounds (i.e. H₂) by the FTIR analysis does not introduce any error.

Nomenclature

F_G^B – gas flowrate from bag , L/min	EA – Extinguishing agent action
F_{N_2} – Nitrogen flowrate to analysis , L/min	C_i^{SiB} – i-th compound conc. sampled to bag, g
F_G^F – gas flowrate to FTIR , L/min	H^{SP} – Sampling point height, m
$F_{N_2}^F$ – Nitrogen flowrate to FTIR , L/min	H^{GS} – Gas source height, m
Φ - flux analysis fraction	$\Delta t^{SAMPLING}$ – Sampling time, sec
C_i^B – i-th conc. in bag, ppmv	C_i^{COMB} – i-th conc. in combustion gas, g/g
m_i^B – detect. i-th compound mass in gas bag, g	$C_i^{COMB^\circ}$ – i-th conc. in combustion gas referred to detected, g/g
m_j^B – not detect. j-th compound mass in gas bag, g	m_i^{COMB} – detect. i-th compound mass in combustion gas, g
m_C^B – compounds mass in gas bag, g	m_C^{COMB} – mass of compounds in combustion, g
$m_C^{B^\circ}$ – detect. compounds mass in gas bag, g	$m_C^{COMB^\circ}$ – mass of detect. compounds in combustion, g
$m_C^{B\emptyset}$ – not detect. compounds mass in bag, g	Ω° - Ratio of produced gas referred to detect., g/g
$C_i^{B^\circ}$ – i-th conc. in bag referred to detect., %V/V	ω° - Normalized ratio of produced gas referred to detected., g/g
V_i^B – detect. i-th compound volume in gas bag, L	ppmv – volumetric concentration (mL/m ³)
V_G^B – sampled gas volume in gas bag, L	
$V_C^{B^\circ}$ – detect. compounds volume in bag, L	
C_i^{HOOD} – i-th compound concentration in hood, g/g	
$C_i^{HOOD^\circ}$ – i-th conc. in hood referred to detect., g/g	

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