GAS DEVELOPMENT DURING THERMAL RUNAWAY
Work Package 1.4

ALBERO Project

Institut für Sicherheitstechnik/Schiffssicherheit e.V.

What gases can escape from a Li-Ion battery in the event of a thermal runaway?

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The release of gases from Li-Ion batteries has already been investigated on several occasions, including by BatteryUniversity. Flammable, toxic and carcinogenic substances have been found:

→ overcharge of a Samsung 60 Ah cell with blocked OSD (Overcharge Safety Device)

Results of gas analyses

	unit	Overcharge autoclave 60Ah SAMSUNG BMZ1307a_60Ah_GAS_02		thermal stability autoclave 60Ah SAMSUNG BMZ1307a_60Ah_GAS_04
kind of event		thermal runaway, venting, fire		cell opening, electrolyte evaporation, venting, no fire
volume of autoclave	l	45		45
p peak event	mbar	23700		13000
calculated total volume at normal pressure	l	1066.5		585
p final after event	mbar	8000		5390
volume of emitted gas	l	360		242.55
Fluorine concentration in the air of the autoclave	µg/l	353.3		90.2
O2	vol %	1.3		1.0
N2	vol %	13.7		19.1
H2	vol %	14.2		14.9
CO2	vol %	22.4		26.0
CO	vol %	15.2		16.9
Ar	vol %	0.1		0.2
Phosphin	mg/m3	0.1		0.07
Formaldehyde:	µg/m3	<2		<2
Acetaldehyde:	µg/m3	1720		1960
Propionaldehyde:	µg/m3	214		174
Butyraldehyde:	µg/m3	112		256
Valeraldehyd:	µg/m3	<2		<2
Methane:	vol%	8.70		7.4
Ethan:	vol%	4.5		1.8
Ethen:	ppm (vol)	34000		48000
Propane:	ppm (vol)	4900		2200
Propene:	ppm (vol)	17000		23000

calculatrion total amount = concentration * (volume autoclave + volume emitted gas)

→ rough gas volumina (360 L and 242 L)

→ flammable (e.g. propane), asphyxiating (N_2, CO_2), toxic (phosphine, HF, CO) and carcinogenic (aldehydes) reaction products

Figure 1: Gas release after a thermal runaway [1]

Additionally, it has been found that the release of gases depends on the very specific cell chemistry. If the mass percentage of various components of the batteries are differ from each other this also results in different amounts of released gases.

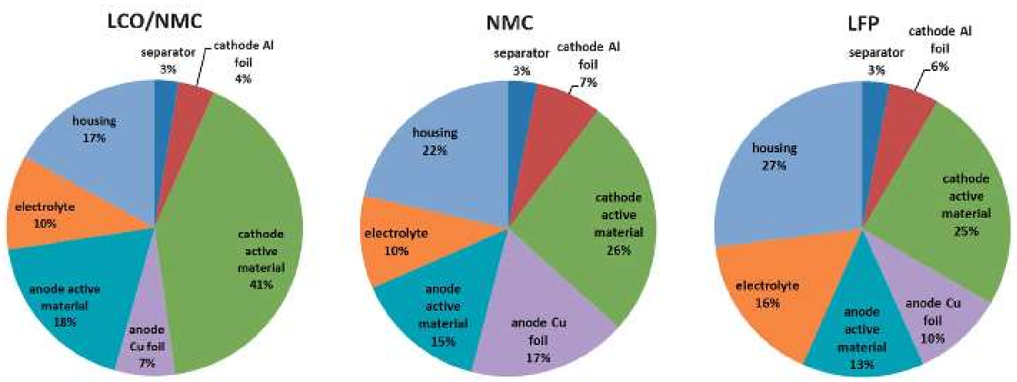


Figure 2: Mass percentages of the main components in different Li-Ion cells [2]. Thereby means LCO $LiCoO_2$, NMC Li-NiCoMn, LFP $LiFePO_4$.

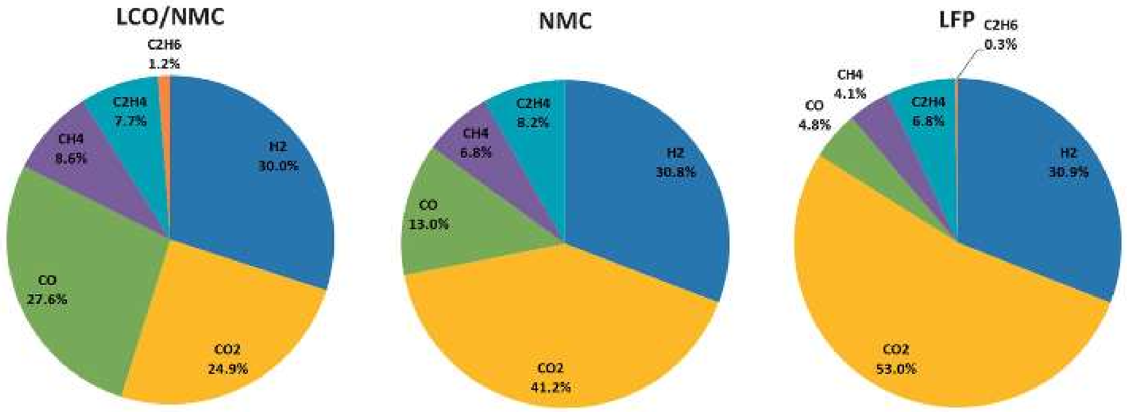


Figure 3: Proportions of gases released after a thermal runaway of various 18650 Li-Ion cells. [2] Thereby means LCO $LiCoO_2$, NMC Li-NiCoMn, LFP $LiFePO_4$.

In Figure 3 it can be seen that obviously especially the ratio of carbon dioxide / carbon monoxide strongly depends on the specific cell composition.

Other publications [3] list the following substances and decomposition products in case of fire:

- release of hydrogen, especially on contact with atmospheric moisture or extinguishing water after bursting of the battery housing.
- particularly at large batteries, sometimes a considerable release of graphite (up to the danger of graphite dust explosions).
- depending on the electrolyte, release of HF or phosphoric acid as well as phosphine.
- depending on the plastics used, hydrogen chloride and carbon dioxide/carbon monoxide.

It was also found [4] that the amount of gases released obviously depended on the state of charge! The gas composition was also partly dependent on the state of charge.

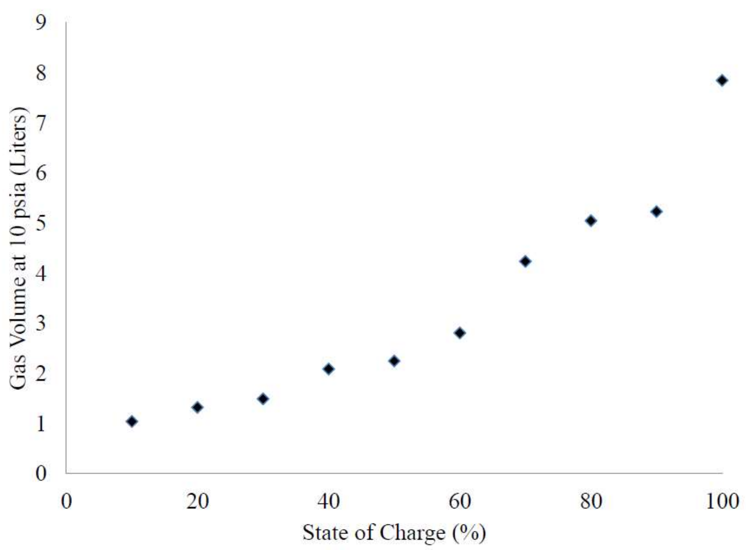


Figure 4: Released volume of a 18650 $LiCoO_2$-cell [4]

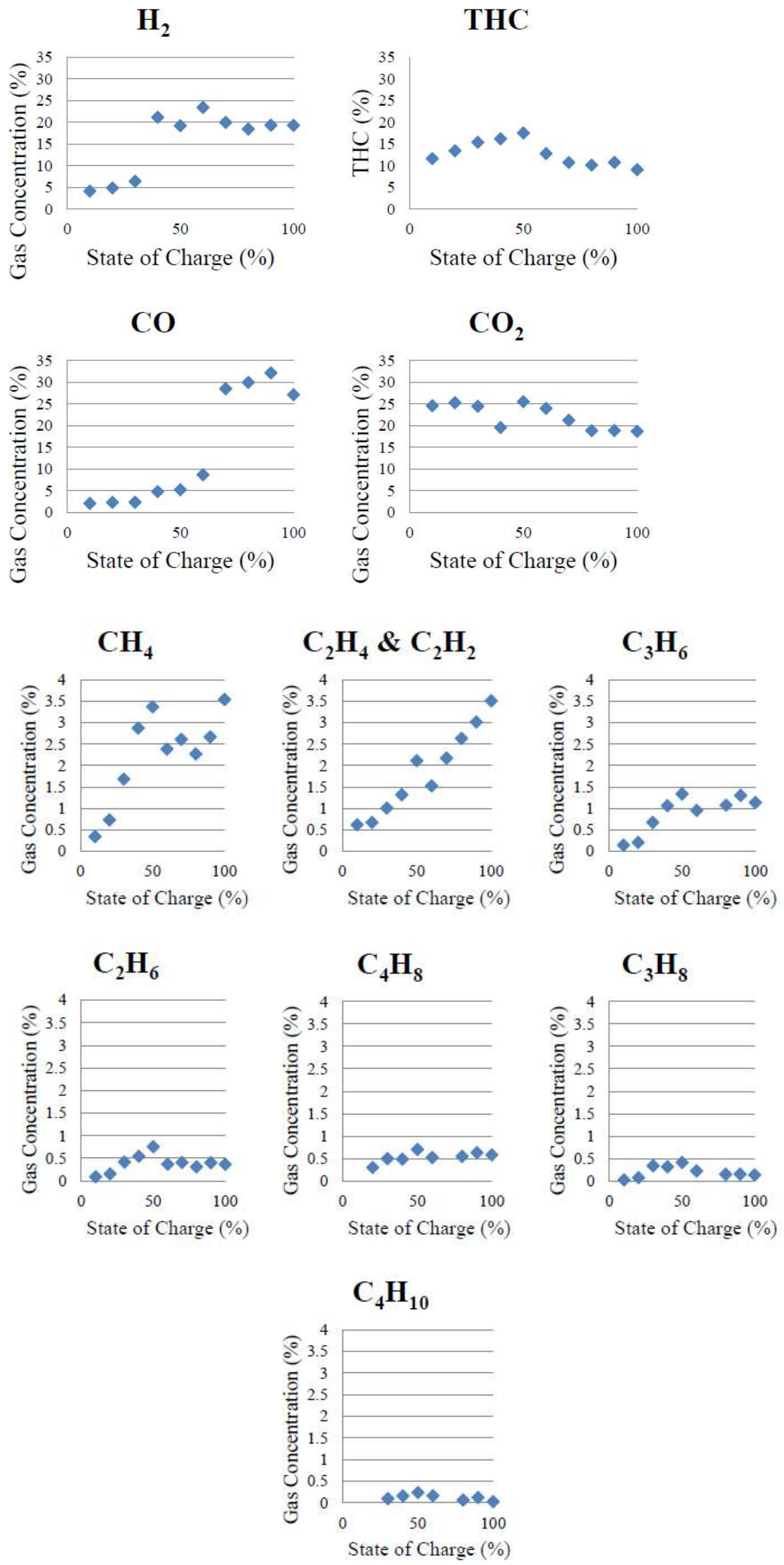


Figure 5: Gas release from 18650 $LiCoO_2$-cells, depending on the state of charge

The gas measurements were also performed for other cell chemistries:

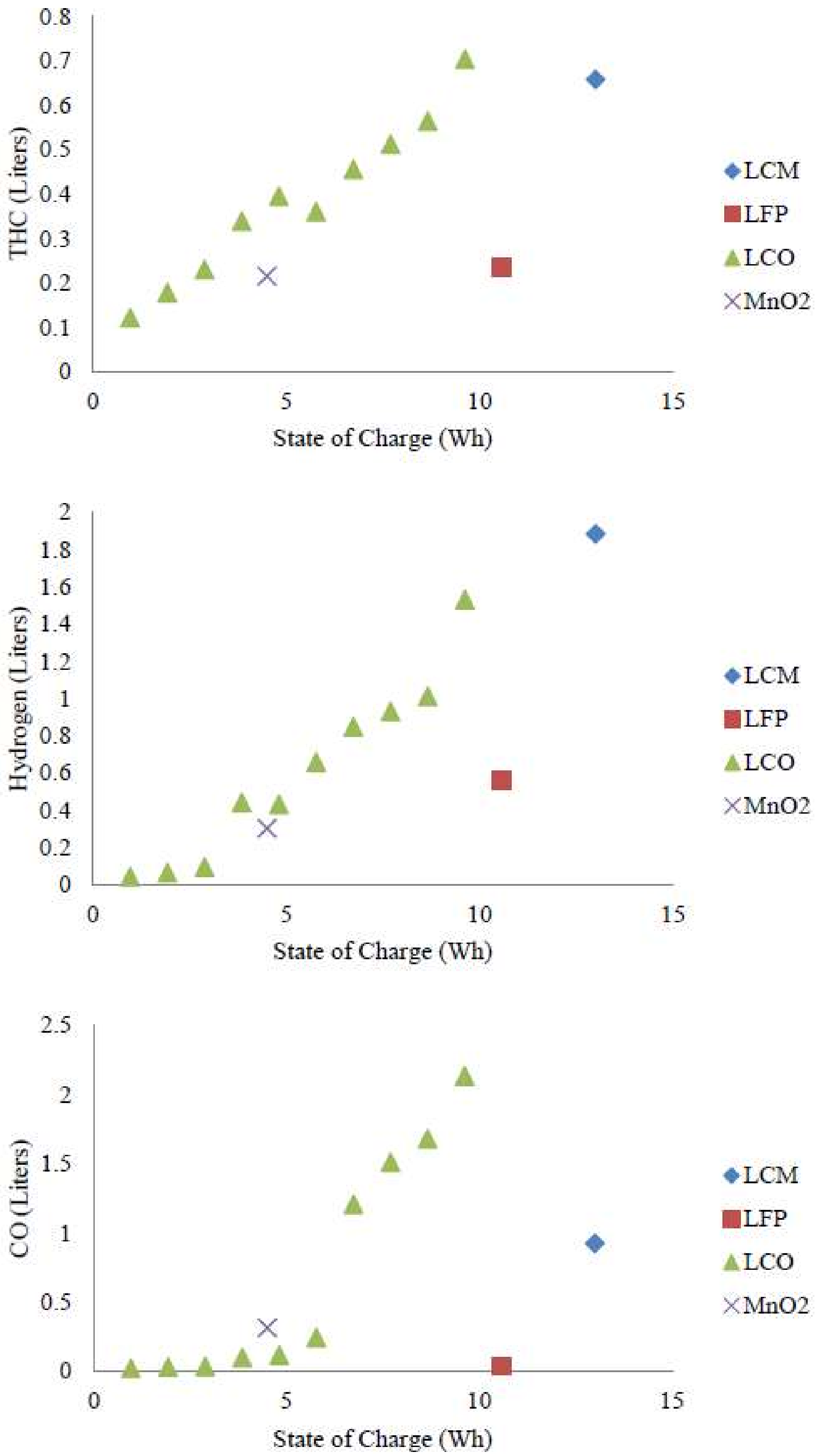


Figure 6: released gas for various cell chemistries [4] Thereby means LCM Li-NiCoMn, LFP $LiFePO_4$, LCO $LiCoO_2$ und MnO_2 $LiMnO_2$. According to the measurements from [2] presented above it is shown that hardly any CO is released for LFP cell chemistry.

Another work [5] considers the gas release as a function of time during a heating process. In a furnace, a cell was slowly heated from 80 to about 150 °. Thermocouples directly attached on the cell measured the temperatures due to thermal runaway.

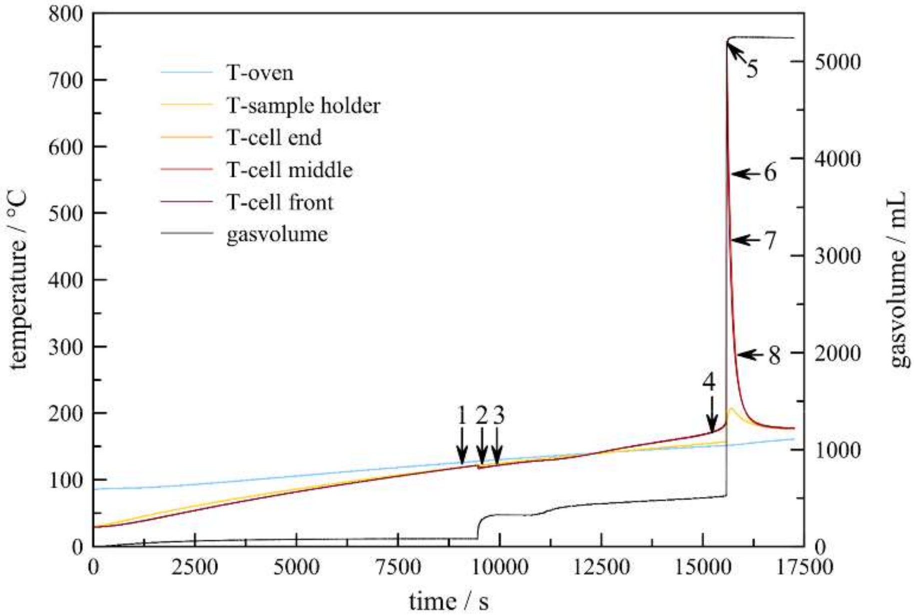
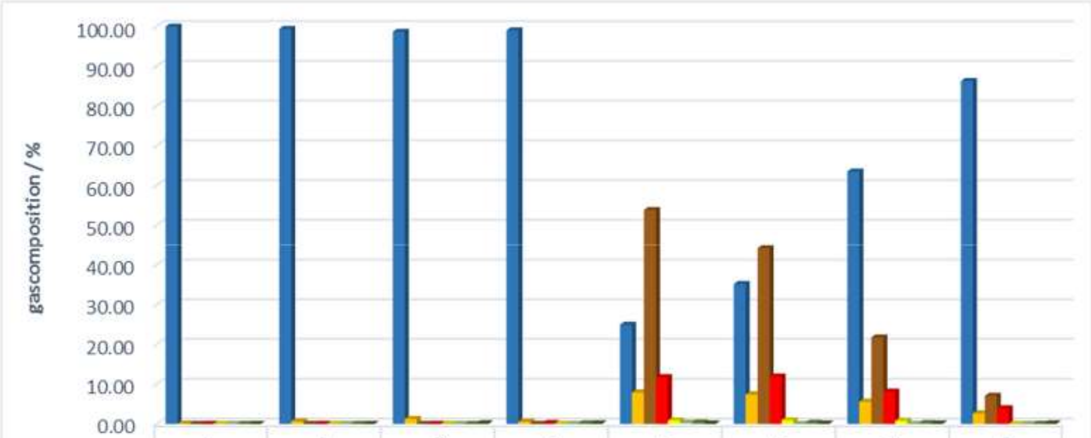


Figure 7: Heating up a Li-ion cell (Li(NiCoAl)O_2), the arrows indicate at which times gas samples were taken [5]



	1	2	3	4	5	6	7	8
N2 / %	99.95	99.39	98.64	99.00	24.95	35.20	63.49	86.25
CO2 / %	0.05	0.61	1.22	0.56	7.90	7.40	5.56	2.65
CO / %	0.00	0.00	0.00	0.00	53.81	44.22	21.75	7.05
H2 / %	0.00	0.00	0.00	0.20	11.77	11.92	8.13	3.91
CH4 / %	0.00	0.00	0.00	0.00	0.86	0.89	0.76	0.00
C2H2 / %	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00
C2H4 / %	0.00	0.00	0.00	0.11	0.33	0.28	0.20	0.01
C2H6 / %	0.00	0.00	0.15	0.12	0.10	0.10	0.11	0.13

Figure 8: Gas concentrations at the measuring points shown in Figure 7. [5]

Another investigation, in which the release of HF was also taken into account, came to the following results [6]. Here, the focus was specifically on the detection of toxic gases.

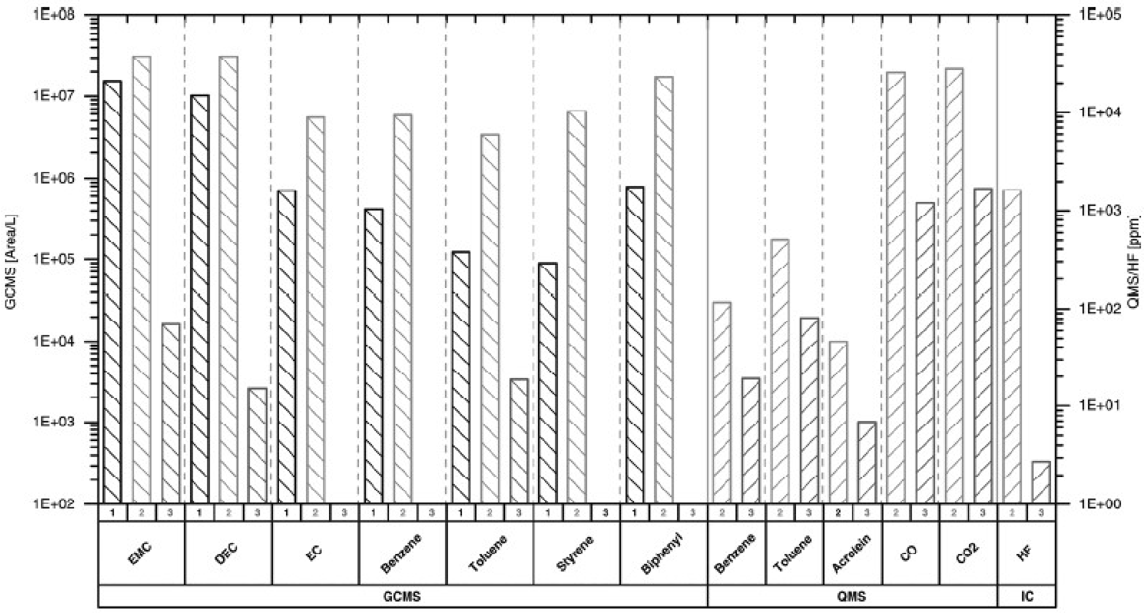


Figure 9: Gas release from a Li-NMC (Li-Nickel-Manganese-Cobalt)-cell, EMC: ethyl methyl carbonate; DEC: diethyl carbonate; EC: ethylene carbonate; CO: carbon monoxide; COS: carbonyl sulfide. [6]

The study [7] also specifically concentrates on the release of HF. For different cell chemistries and states of charge, the evolution of HF and (when expected) POF3 was determined. Significant amounts of HF between 20 and 200 mg / Wh of nominal battery energy capacity were detected with the burning Li-Ion batteries.

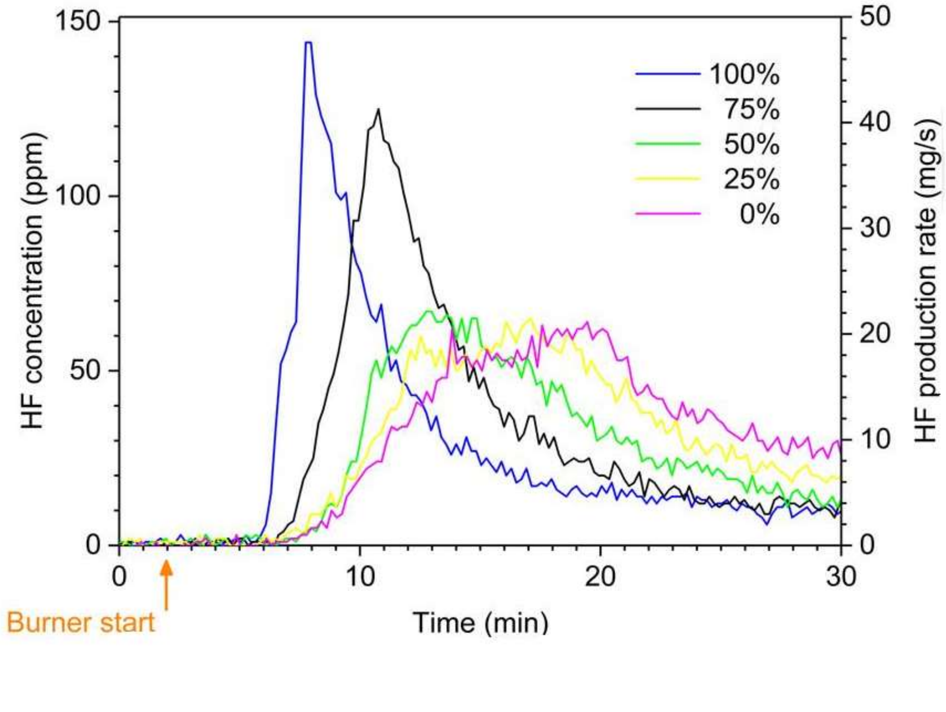


Figure 10: HF gas release of $LiFePO_4$-Zellen. These cells were flamed from the outside. [7]

A number of toxic (fluorine) compounds have also been detected [8].

Summary:

There are a large number of studies of the gases released during a thermal runaway of Li-ion batteries. In this summary by far not all found works were considered and read. Thereby it can be seen:

- The composition of the gases depends on the specific cell chemistry, but the main constituents are carbon dioxide, carbon monoxide, hydrogen and short-chain hydrocarbons. Additionally, various organic and fluor-organic compounds as well as inorganic phosphorus and fluorine compounds are released in smaller, but not entirely harmless, quantities.
- The quantity of gases released and also the composition of the gas mixture depends on the state of charge of the batteries. At a higher state of charge, the volume of gas released increases.

Literature:

[1] source: Dr. Jochen Mähliß, Li-Ionen-Batterietechnologie, Vortrag an der Hochschule RheinMain Rüsselsheim, Juni 2016 https://www.hs-rm.de/fileadmin/persons/khofmann/Gastvortraege/Vortragsfolien/20160603-Maehliss-Lithium-Ionen-Batterietechnologie.pdf

[2] Andrey W. Golubkov et. Al : Termal runaway experiments on consumer Li-ion batteries with metal-oxide and olivon-type cathodes, RSC Adv., 2014(4), 3633 - 3642 https://www.researchgate.net/publication/271378936_Thermal-runaway_experiments_on_consumer_Li-ion_batteries_with_metal-oxide_and_olivin-type_cathodes

[3] Michael Buser, Jochen Mähliß: Lithiumbatterien Brandgefahren und Sicherheitsrisiken https://www.riskexperts.at/fileadmin/downloads/Publikationen/Lithiumbatterien__Sicherheitsratgeber__BUSER__Maehliss__2016.pdf

[4] Federal Aviation Administration, William J. Hughes Technical Center, Aviation Research Division: Lithium Battery Thermal Runaway Vent Gas Analysis, Final Report, 2016 https://www.fire.tc.faa.gov/pdf/TC-15-59.pdf

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[6] Antonio Nedjalkov et.al.: Toxic Gas Emissions from Damaged Lithium Ion Batteries—Analysis and Safety Enhancement Solution, Batteries 2016, 2, 5

[7] Fredrik Larsson et. al.: Toxic fluoride gas emissions from lithium-ion battery fires https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5577247/

[8] Ulrika Bergström et.al. Vented Gases and Aerosol of Automotive Li-ion LFP and NMC Batteries in Humidified Nitrogen under Thermal Load, Dezember 2015 https://www.msb.se/RibData/Filer/pdf/27998.pdf