Battery Safety Science Webinar Series

Advancing safer energy storage through science

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Gas Emissions at Fire, Overheating and Overcharging Events for Lithium-Ion Batteries

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GAS EMISSIONS AT FIRE, OVERHEATING AND OVERCHARGING EVENTS FOR LITHIUM-ION BATTERIES

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With the widespread use of lithium-ion batteries incidents involving gas and smoke emissions are occurring for different battery installations, in small and large scale, examples:

October 10-11, 2019 Hybrid ferry Ytterøyningen, Norway Fire followed by explosion next day

Shanghai car fire April 21, 2019

June 8, 2020 — The National Transportation Safety Board called for a change in air cargo shipping requirements for some types of lithium-ion batteries.

An explosion occurred in a solar energy battery facility in Arizona on April 19, 2019

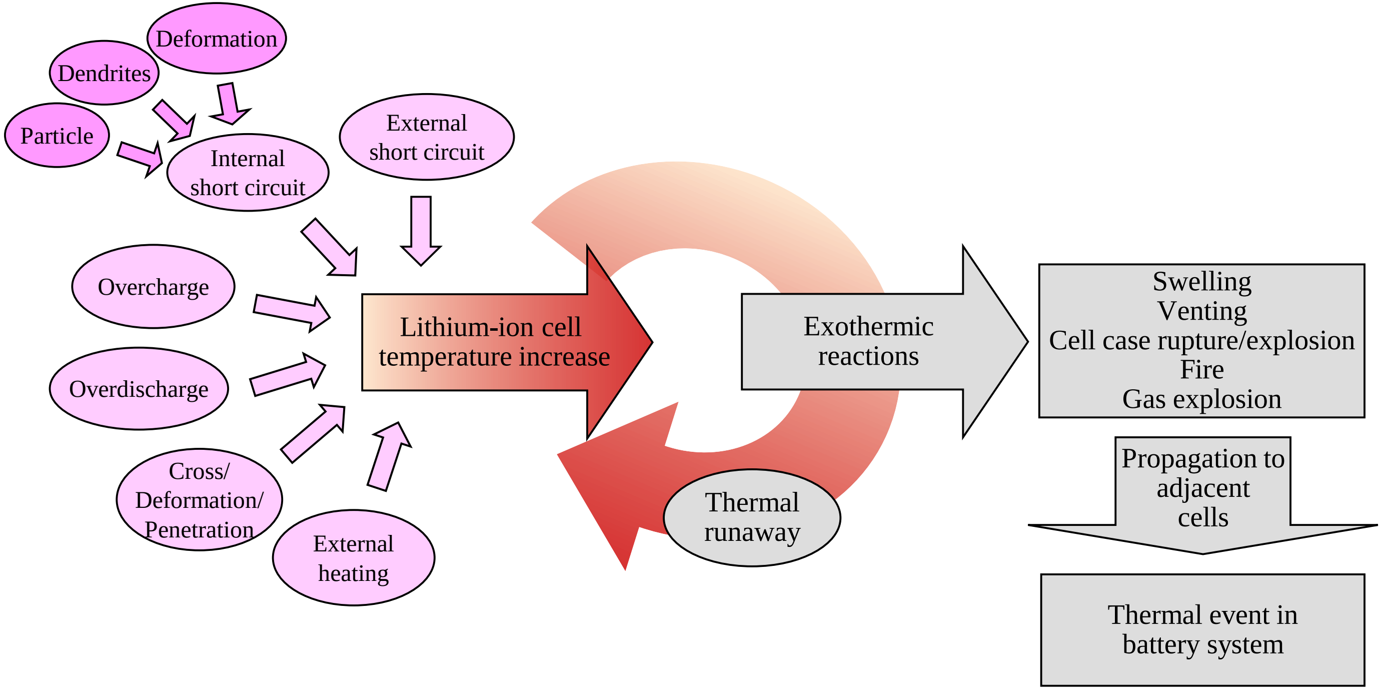
Firefighters were called to a fire at Arizona Public Service’s 2 MWh energy storage facility in West Valley, Arizona. When entering, two firefighters were seriously injured, the final report was published late July 2020.

https://edocket.azcc.gov/Docket/DocketDetailSearch?docketId=22496#docket-detail-container1

Issues to be addressed

- Type of risks are associated with gas and smoke emissions from Li-ion batteries – delayed ignition of combustible gas, toxic gases
- The content of the emissions
- Under what conditions are the emissions formed and what could be done to decrease or eliminate these risks
- Could there be smoke without fire?
- The gas emission does not need to be primarily due to a battery cell failure; external incidents such as external fire, control problems, cooling problems etc. may cause a serious event in the battery system

Thermal runaway initiation



Overcharge abuse with a 2 C-rate current of a 30 Ah cell with LATP/NCA. ($LiAlTiPO_4$ - $LiNiCoAlO_2$)

Gases can be emitted with or without thermal runaway, we will here discuss mainly three cases, emissions where the battery cells are exposed to external fire, overheating or overcharging.

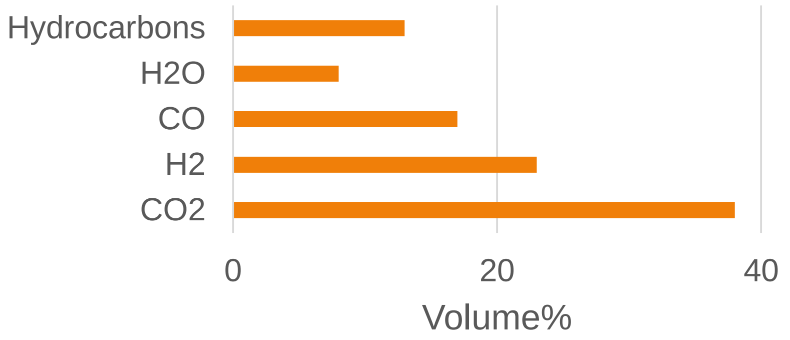
Two risks that will be discussed

- Emitted gases are not initially ignited but collects in a closed volume, mixed with air. Ignition at a later stage can cause a rapid combustion, deflagration (subsonic flame propagation, moderate overpressures) or detonation (supersonic flame propagation, high overpressures), both commonly referred to as “explosion”.

- Emitted gases are in general toxic, with composition dependent on a number of factors also including whether the gas has been ignited or not.

Composition of gas emissions

Gas emissions depend on many parameters, cell chemistry, type of incident, state-of-charge, cell age and temperature, etc. Measured amounts of gas in test situations also depend on test conditions, ambient etc. Common gases emitted in hot venting and thermal runaway events are CO_2, CO, H_2, hydrocarbons as well as minor amounts of other gases.



An example: Venting of an overheated automotive cell. Source: C. Essl et al. Batteries 6, 30 2020.

The gases originates from thermal decomposition and reactions of electrolyte, binder and electrode materials. If the gases ignite the composition of the resulting gas may differ as in battery fires.

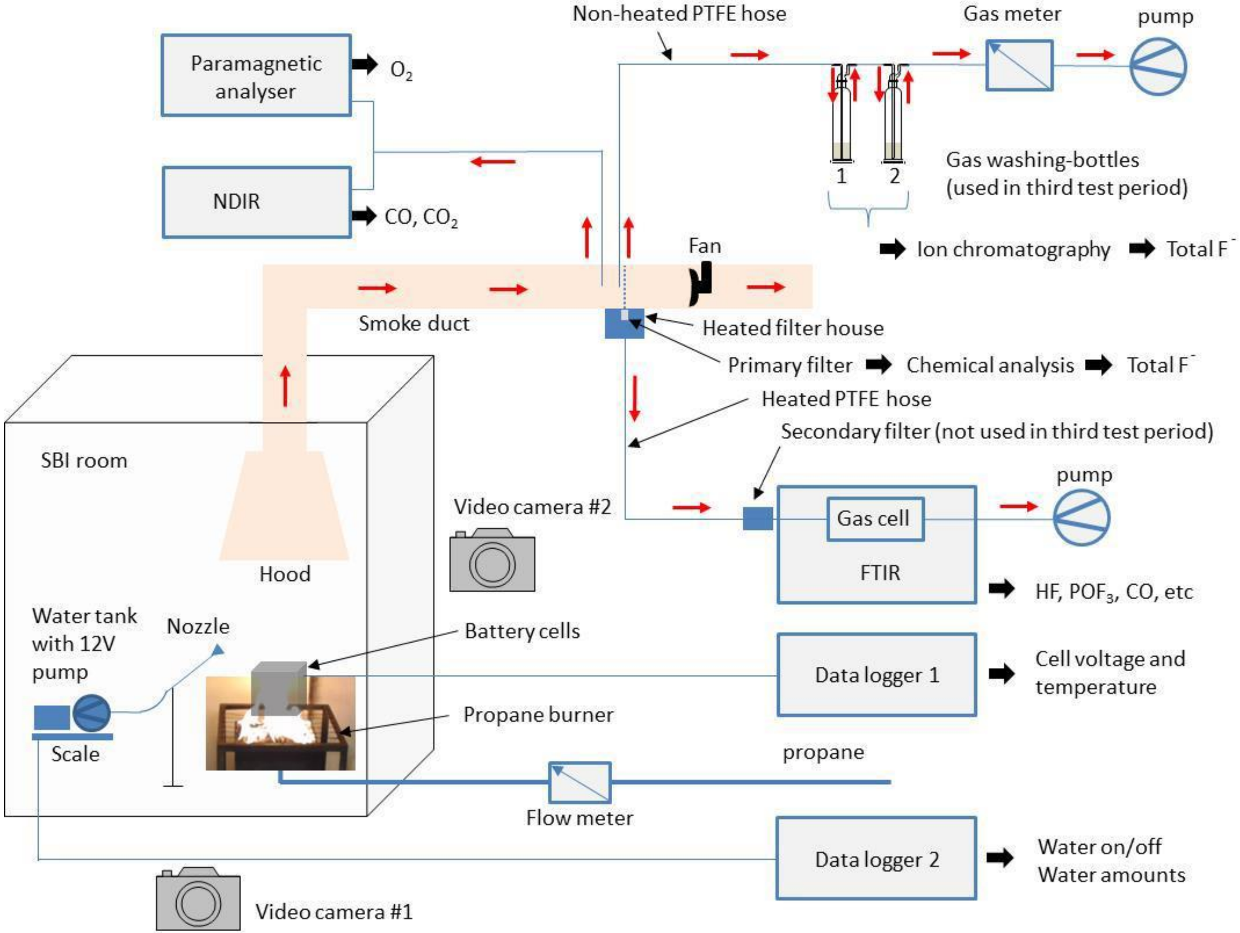
Gas measurements with FTIR – some examples of gas emissions during abuse tests

External fire

External heating

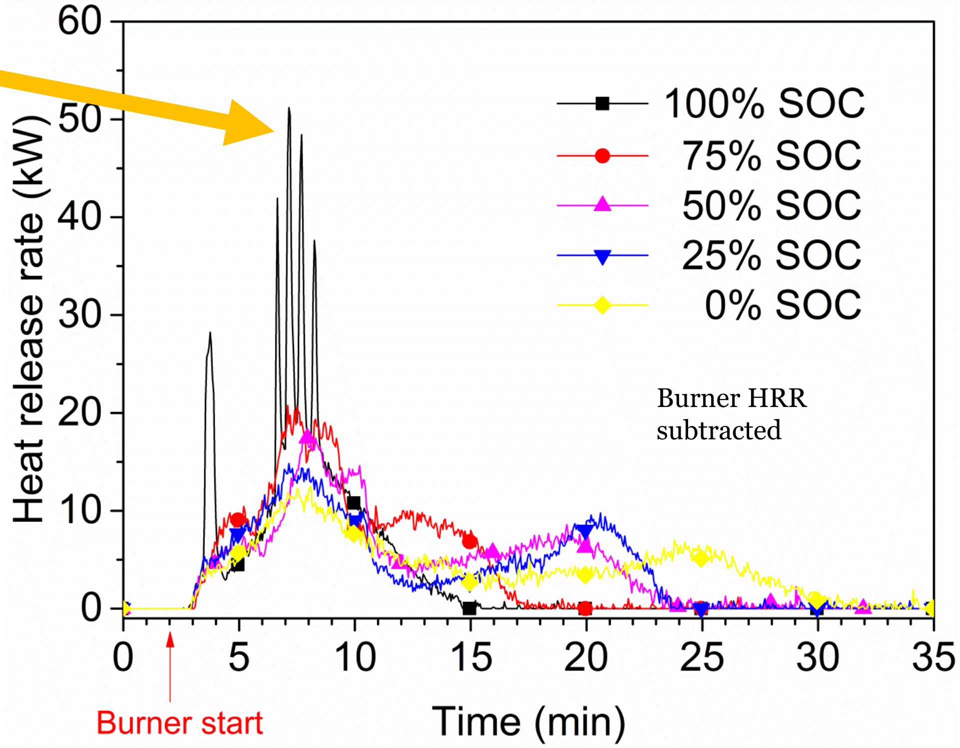
Overcharge

Fire test measurement setup



Heat release rate (HRR)
Fire test with external propane burner – 5x7 Ah LFP pouch

Outbursts

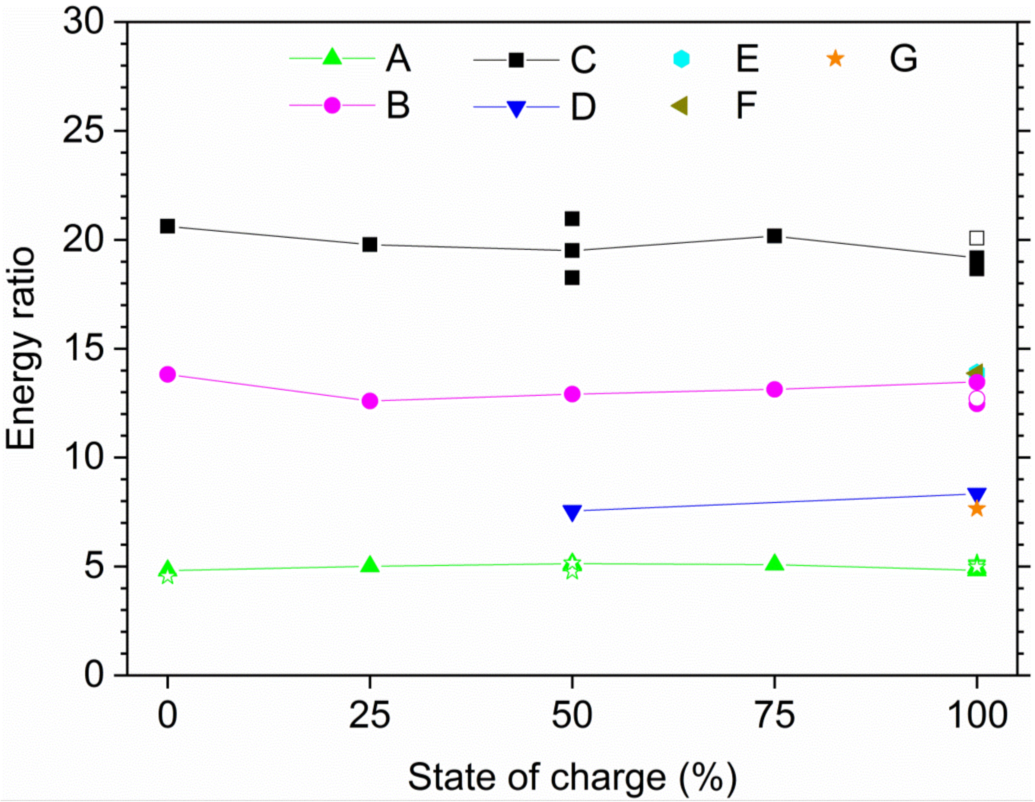


- Fire calorimetry:
  Oxygen consumption method,
  corrected for CO_2
  → HRR
- Integration of HRR = Total heat release (THR)

Combustion energy ~ 5-20 x electrical energy

Values for fire tests (full combustion)

	Type	Capacity per cell (Ah)	Form
A	LCO	6.8	Prismatic
B	LFP	20	Pouch
C	LFP	7	Pouch
D	LFP	3.2	Cylindrical
E	LFP	8.0	Cylindrical
F	NCA-LATP	30	Pouch
G	Laptop pack	5.6	Cylindrical



THR = 17-75 kJ/Wh

https://www.nature.com/articles/s41598-017-09784-z

Smoke and gas emission

- In general, large amounts of smoke and gas are released when a cell overheats
- Nobody wants to have fire or flames…
- But to what costs in terms of gas and smoke?
- **Fire/flames may sometimes be preferred – to reduce severe gas risks.**

Generally for fires:
without flame/ignition – typically worse gas compositions

The degree of combustion influences the smoke/gas composition

FTIR gas measurement method

- Well-defined ventilation flow –
  needed for quantitative measurements (0.4 m^3/s)
- Well-defined partial flow to FTIR (3.5 l/min)
- Heated gas sampling system to avoid condensation (180 ºC)
- HF is absorbed in sampling system (tube, filter, gas cell)
- Filter analysed for every test
- Calibration: HF (2 ppm detection limit), POF_3 (6 ppm),
  PF_5 (qualitatively)
- Delay times - Synchronization FTIR to other data (O_2 overlay)
- Fast sampling updates – real-time measurements (every 12 sec)
- For detection of H_2 e.g. GC is needed (not included in this setup)

F. Larsson, P. Andersson, P. Blomqvist, A. Lorén, B.-E. Mellander,
”Characteristics of Lithium-ion batteries during fire tests”, *J Power Sources*,
271, 414-420, 2014.

Vent gases are flammable, toxic & corrosive

- Gas emissions typically start before thermal runaway
- Gases are produced with and without thermal runaway
- Volatile electrolyte, release of excessive pressure before cell case explosion
- Cells are often designed with safety vent/weakening
- Examples of emitted gases:
  - CO_2, CO, H_2, CH_4, C_2H_4, C_2H_6, ….
  - Solvents in liquid/gas phase: DEC, DMC, EMC, EC, ...
  - Fluoride gases: HF, POF_3, ….
- Gas emissions in confined spaces are extra problematic; tunnels, underground car parks, …

Sun et al., Nano Energy, 27, 313, 2016, reported > 100 gaseous compounds in vent gases

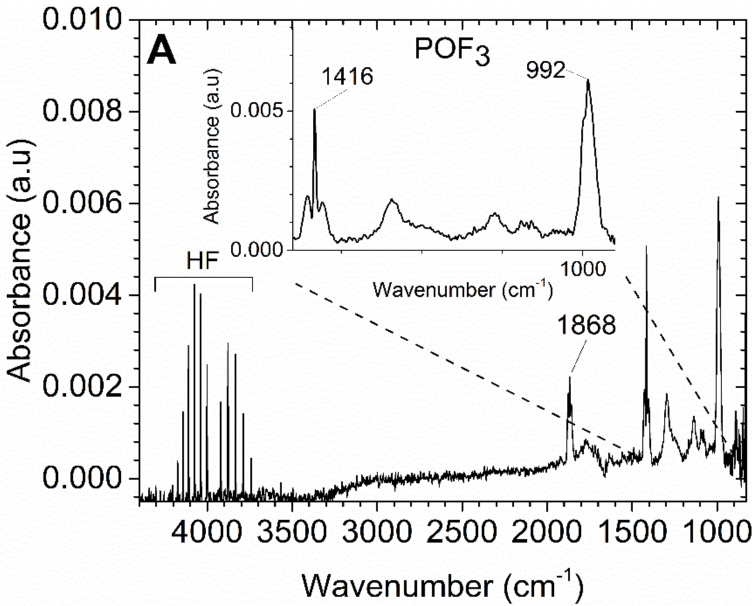
Gas detection

Toxic gases of special concern:

- $LiPF_6 \rightarrow LiF + PF_5$
- $PF_5 + H_2O \rightarrow POF_3 + 2HF$
- $POF_3 + 3H_2O \rightarrow H_3PO_4 + 3HF$

PF_5 was not detected in our measurements

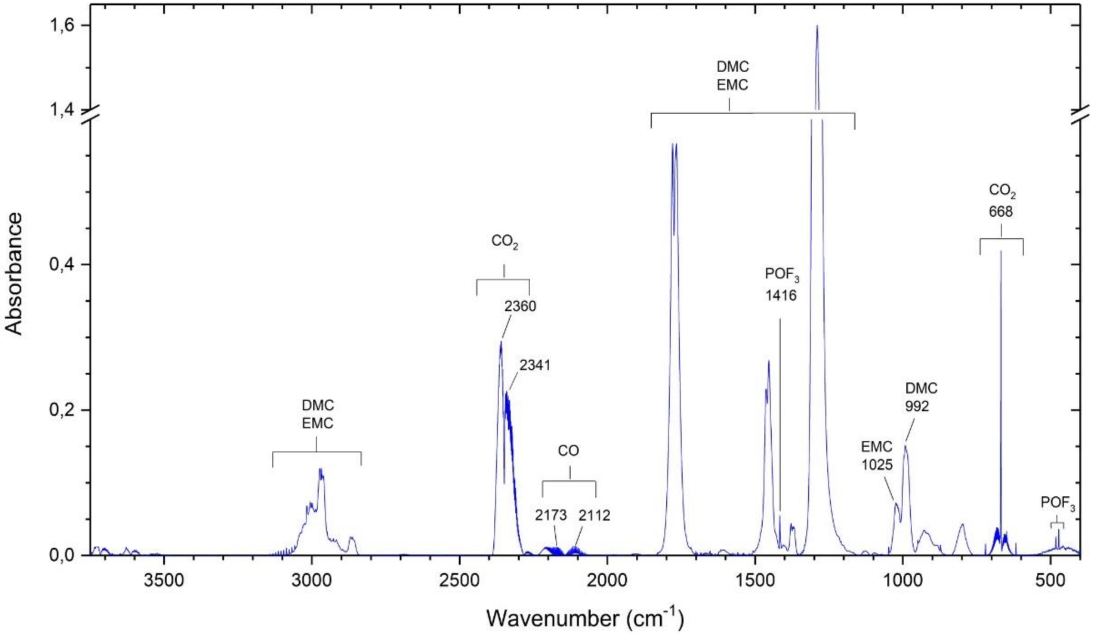
The toxicity of HF is well known but the toxicity of POF_3 is currently unknown.
Critical limits of exposure might be lower for POF_3 than for HF as in the chlorine analog POCl3/HCl.



FTIR spectral bands used for POF_3 and HF identification and monitoring

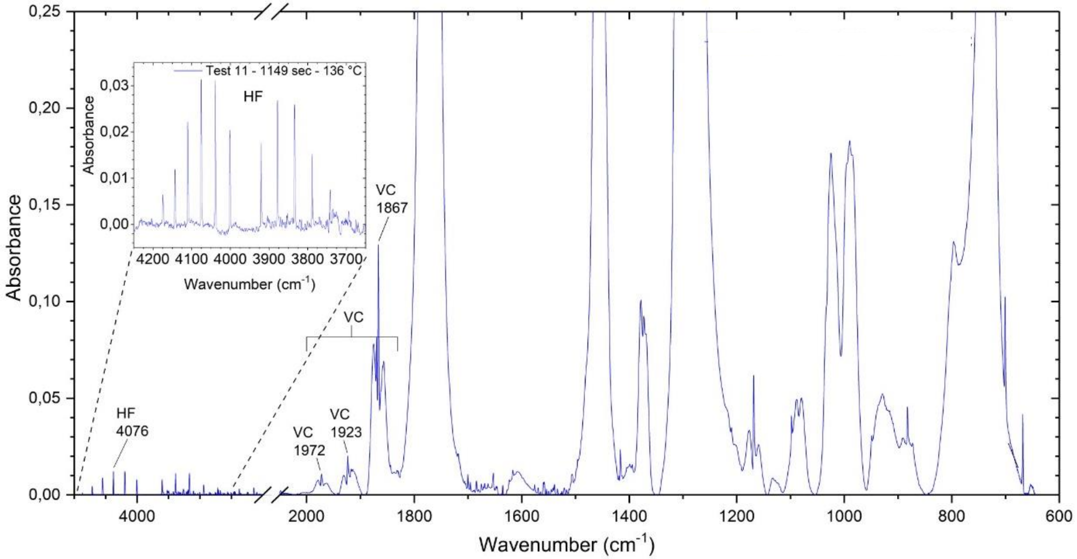
Substance	Wavenumber (cm^{-1})	Assignment
POF_3	992	P-F asymmetric stretching
POF_3	1416	P=O stretching
HF	3878	H-F stretching

Example of gas emission during overcharge of a LFP cell.



At a battery cell surface temperature of 74.7 °C a number of gases are detected, mainly electrolyte solvents , CO and CO_2 but also small amounts of POF_3. The DMC band overlaps with one of the POF_3 bands. The battery vent was in this case manipulated to allow the measurement of gaseous emissions without interruption of the current interrupt device.

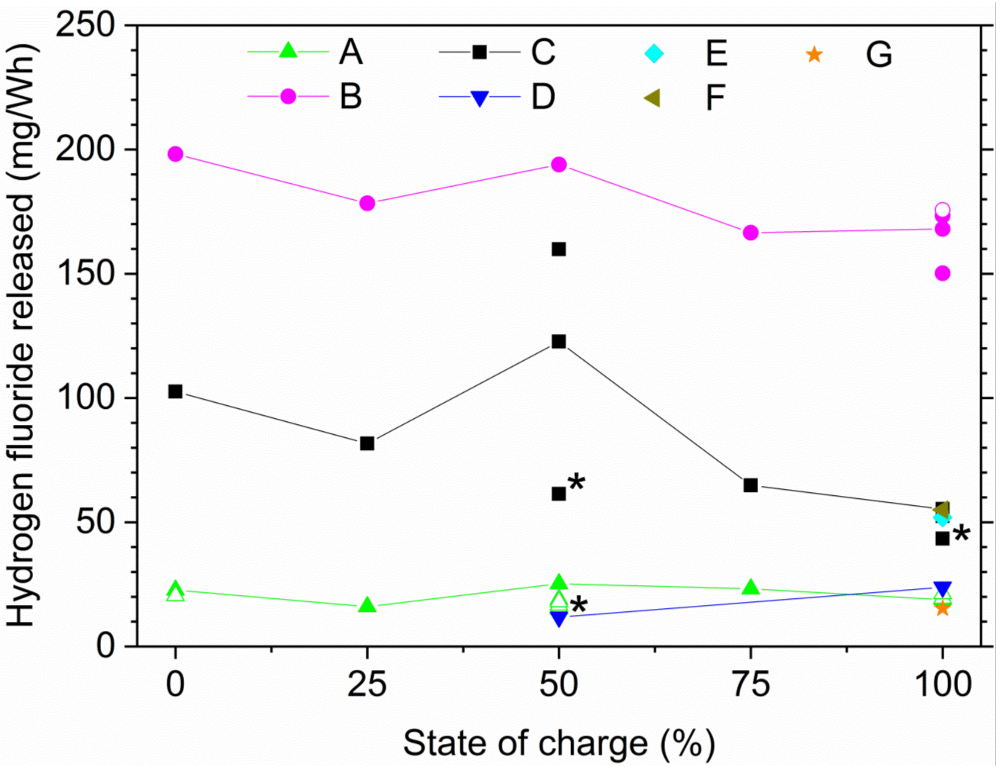
…a little later…



Gas emissions at 122 °C (battery cell surface temperature) and 136 °C. HF emission is detected. The development of the emissions can be followed as a function of time.

External fire tests - 7 commercial Li-ion cells

	Type	Capacity per cell (Ah)	Form
A	LCO	6.8	Prismatic
B	LFP	20	Pouch
C	LFP	7	Pouch
D	LFP	3.2	Cylindrical
E	LFP	8.0	Cylindrical
F	NCA-LATP	30	Pouch
G	Laptop pack	5.6	Cylindrical

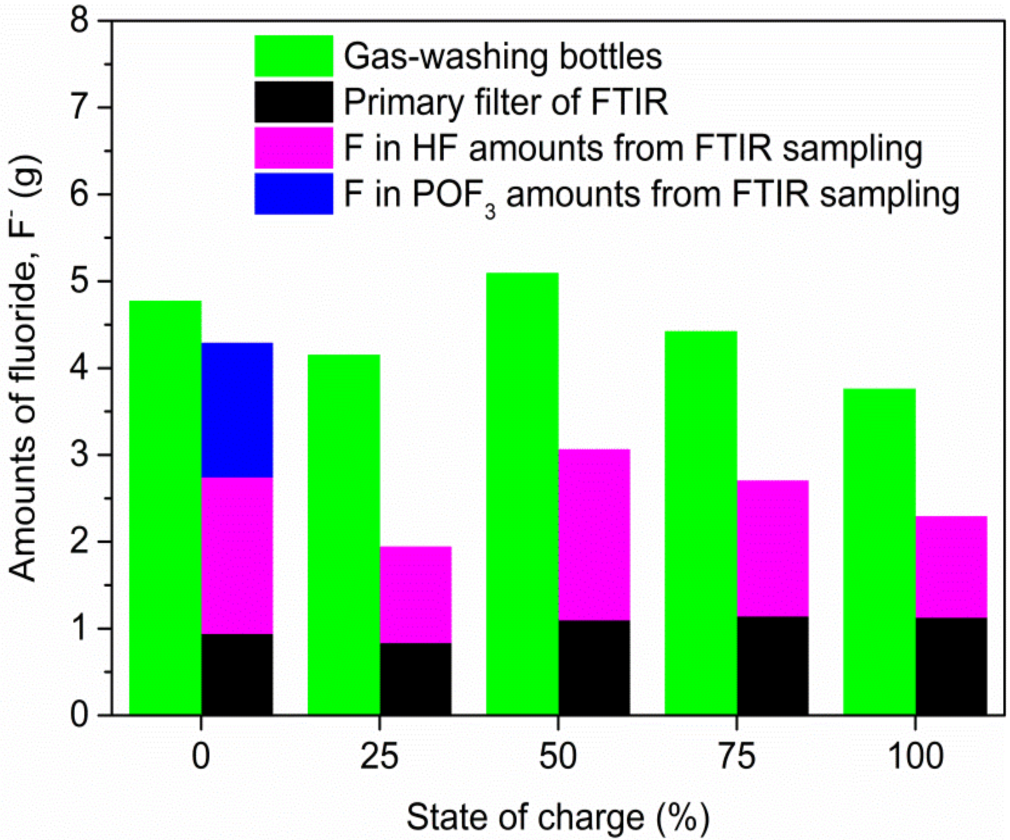


Total HF amount released:
20 to 200 mg/Wh

https://www.nature.com/articles/s41598-017-09784-z

Amounts of fluoride

- Two independent and parallel measurement techniques
  - FTIR
  - Gas-washing bottles



https://www.nature.com/articles/s41598-017-09784-z

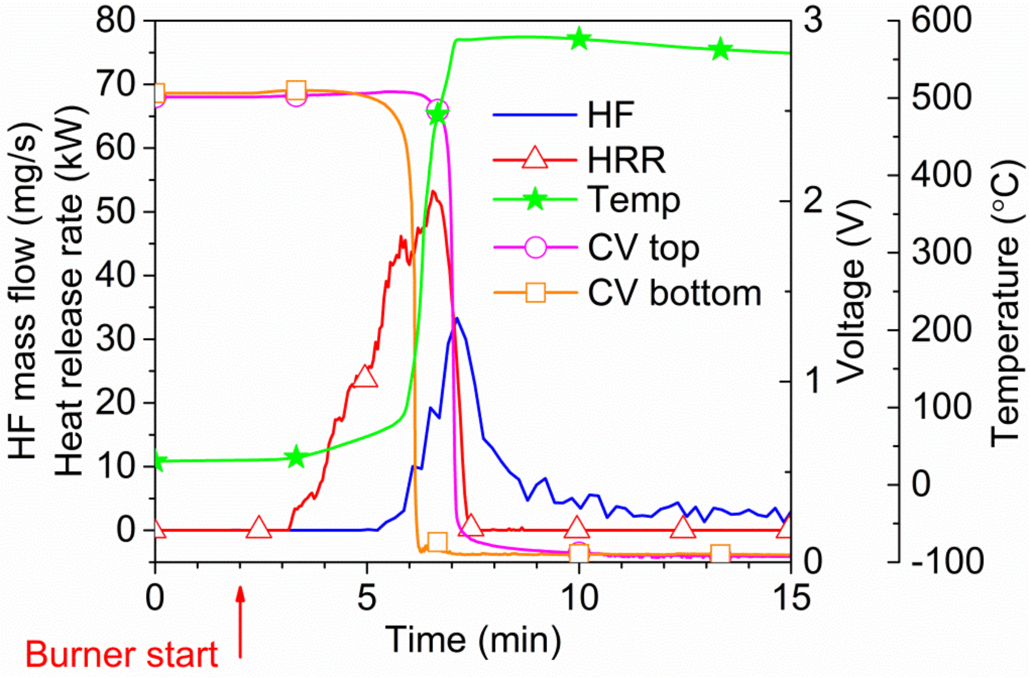
Fire test: Two 30 Ah LTO-NCO pouch cells, 100% SOC

FTIR:

- HF peak 100 ppm
- 4.8 g (FTIR)
  1.6 g (filter)
- = 6.4 g HF

Gas-washing bottle:

- 11.2 g HF



F. Larsson, P. Andersson, P. Blomqvist, B.-E. Mellander, **"Gas emissions from Lithium-ion battery cells undergoing abuse from external fire"**, Conference proceedings of Fires in vehicles (FIVE) 2016, Baltimore, 5-6 October 2016, edited by P. Andersson, B. Sundstrom, *SP Technical Research Institute of Sweden*, Boras, Sweden, p. 253-256, 2016.

Toxicity of hydrogen fluoride

1.7 mg/m^3 Allowed exposure level at work in Sweden, e.g. for firefighters
25 mg/m^3 IDLH = Immediately Dangerous to Life or Health (30 min)
139 mg/m^3 The lethal 10-minute value (AEGL-3)

Our results extrapolated for a fire where a 100 kWh Li-ion battery (typical for a large electric car) is fully combusted correspond to an emission of 2 - 20 kg HF.

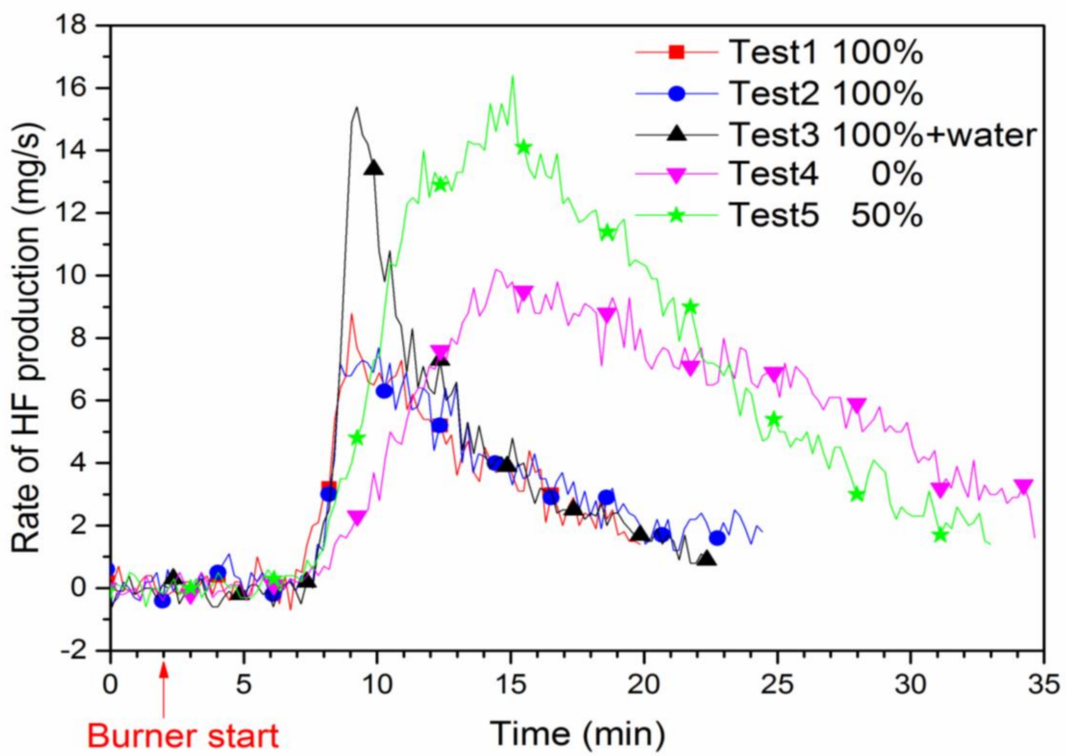
Symtoms of HF inhalation: Upper airway irritation; muscle pain and cardiac arrhythmia may occur with delayed onset up to about two days after exposure.

On site treatment: Upper airway – similar as for astma, ev intubation to prevent swelling. Antidote to HF – calcium tablets

”Emergency prepardness and response guidelines for anhydrous hydrogen fluoride and hydrofluoric acid”, American Chemistry Council, Washington DC, October 2018, https://www.americanchemistry.com/ProductsTechnology/Hydrogen-Fluoride-2/Emergency-Response-Guidelines-for-AHF.pdf

Fire test: Five-cell-pack of 7 Ah LFP pouch cells
Fluoride gas emissions and water mist as fire extinguishing medium

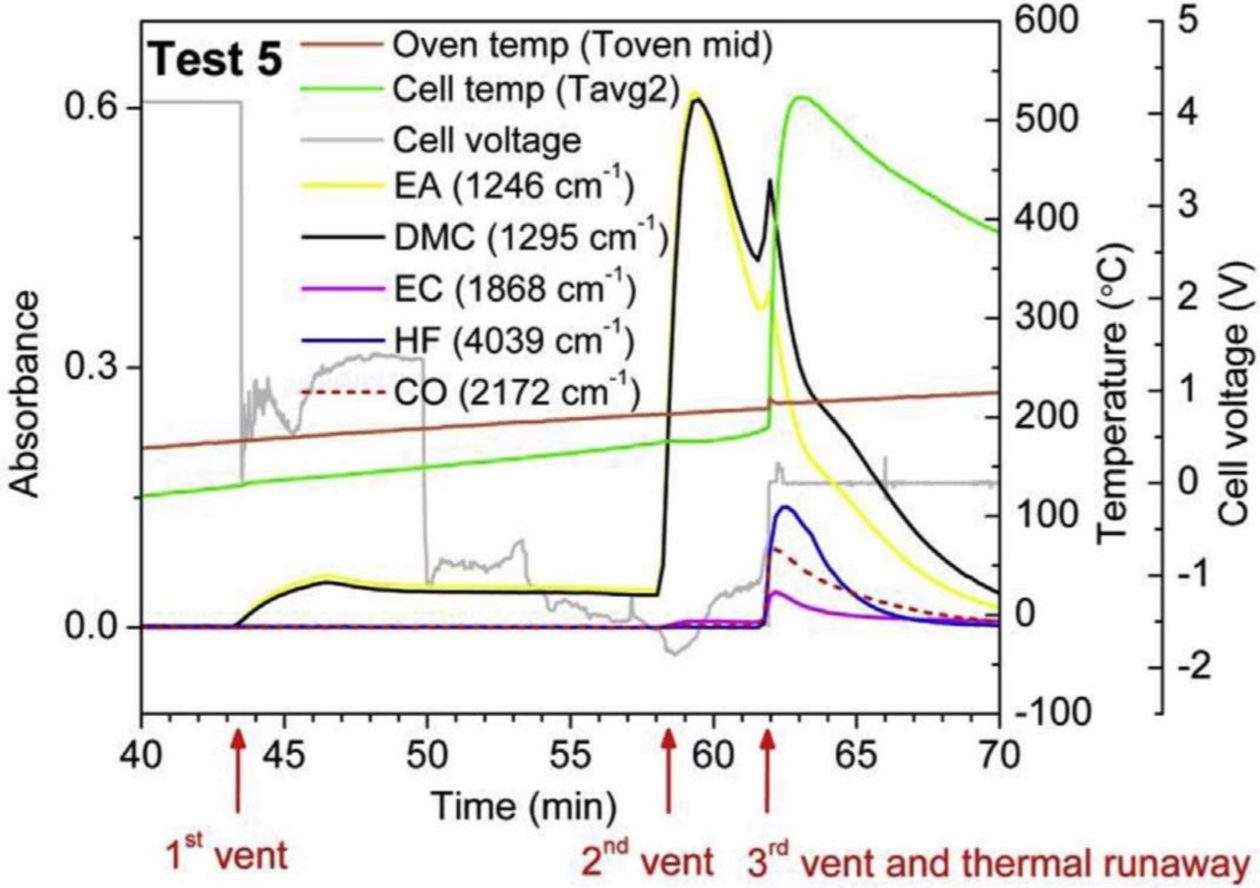
- HF found
- POF_3 not detected but was likely present
- PF_5 not detected (highly reactive)
- HF production rate increases temporarily by about 100% when water mist is applied but the total amount is more or less unchanged



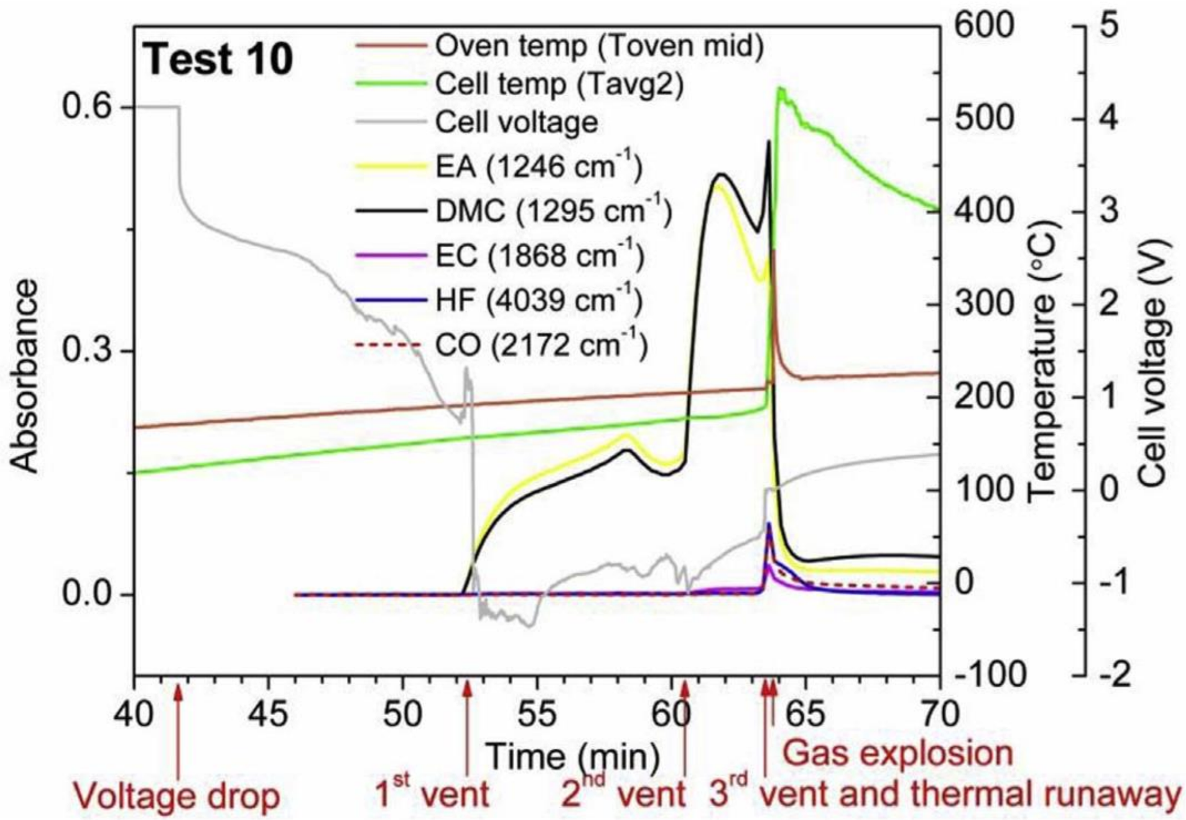
F. Larsson, P. Andersson, P. Blomqvist, A. Lorén, B.-E. Mellander, **"Characteristics of Lithium-ion batteries during fire tests"**, *J Power Sources*, 271, 414-420, 2014.

Overheating

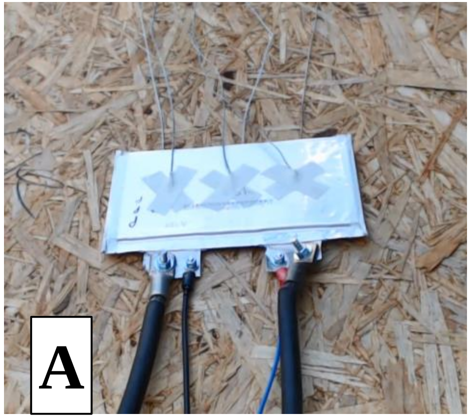
- LCO cell 6.8 Ah



Overheating LCO cell 6.8 Ah



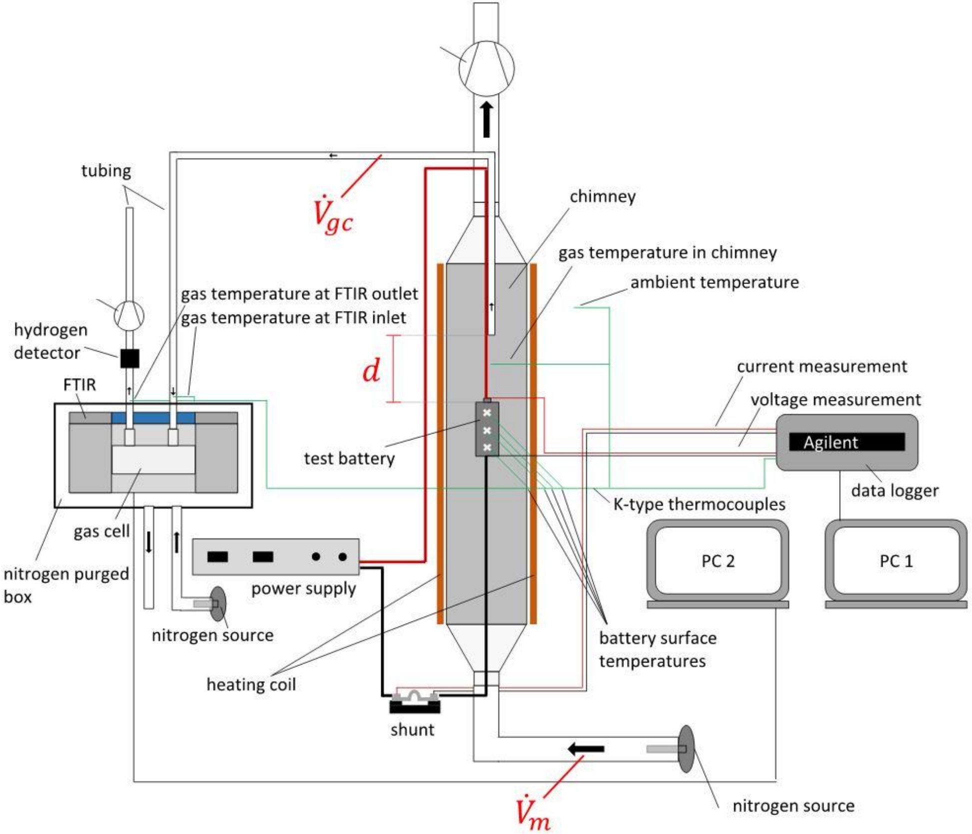
Overcharging:



Overcharge abuse tests of 13 Ah LTO/NMC pouch cells. (**A**) before overcharge (**B**) shows gas release during overcharge with a current of 2 C-rate (26 A) and (**C**) for another cell during overcharge with a current of 7 C-rate (91 A) that ignited after gas release. (LTO - Lithium titanium oxide, NMC - Lithium nickel manganese cobalt oxide)

Cell setup for gas detection at overcharging

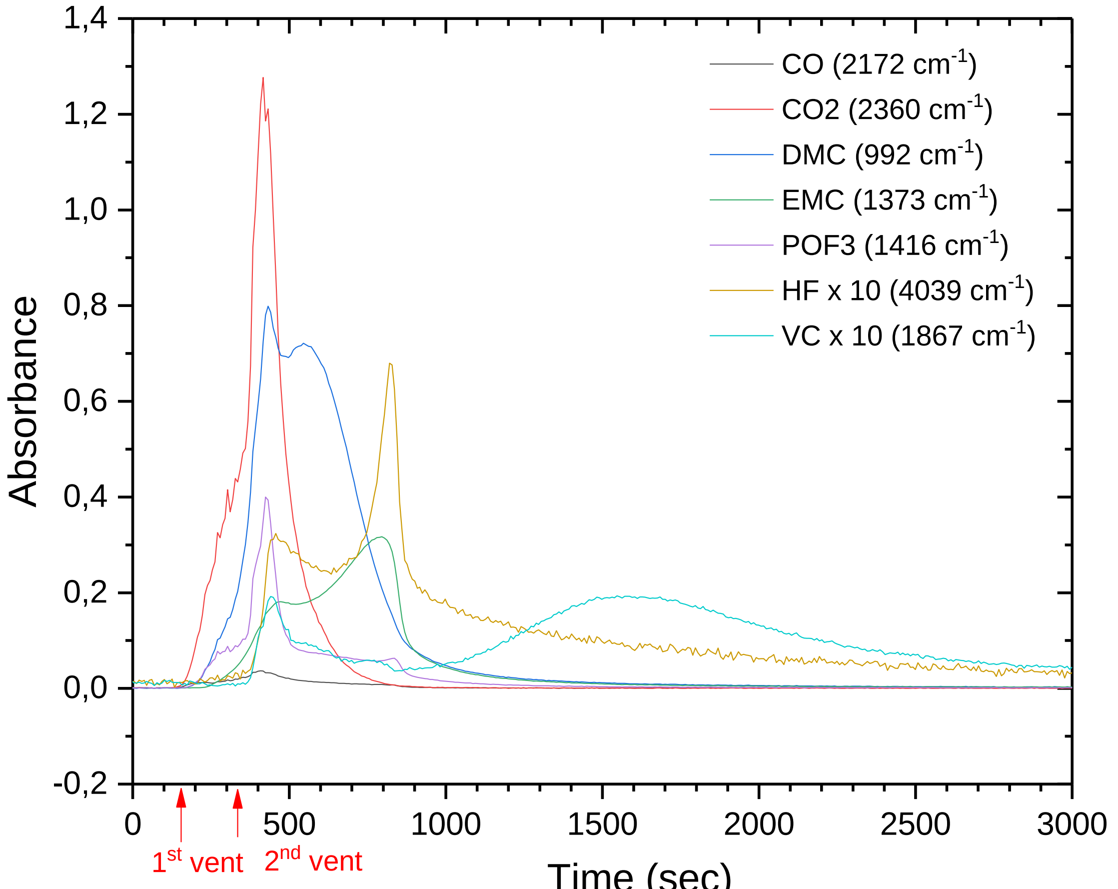
- For example during overcharging the following gases have been observed overcharging LFP:
  - Carbon dioxide (CO_2)
  - Carbon monoxide (CO)
  - Ethylene carbonate (EC)
  - Dimethyl carbonate (DMC)
  - Ethyl methyl carbonate (EMC)
  - Vinylene carbonate (VC)
  - Phosphoryl fluoride (POF_3)
  - Hydrogen fluoride (HF)
  - Hydrogen (H_2)



Some gas emissions are invisible to the eye

Overcharge 2C rate

LFP 3.2 Ah



Onset HF 84 °C battery surface temperature

Gas release and ignition

Can occur:

- Before and without thermal runaway
- Multiple vents may occur, some not visible by eye
- If gases are mixed with air and confined – a gas explosion can occur in case of ignition
- Ignition via: autoignition due to hot parts/electrical connections, sparks, external source, etc.

Battery explosions

Two types:

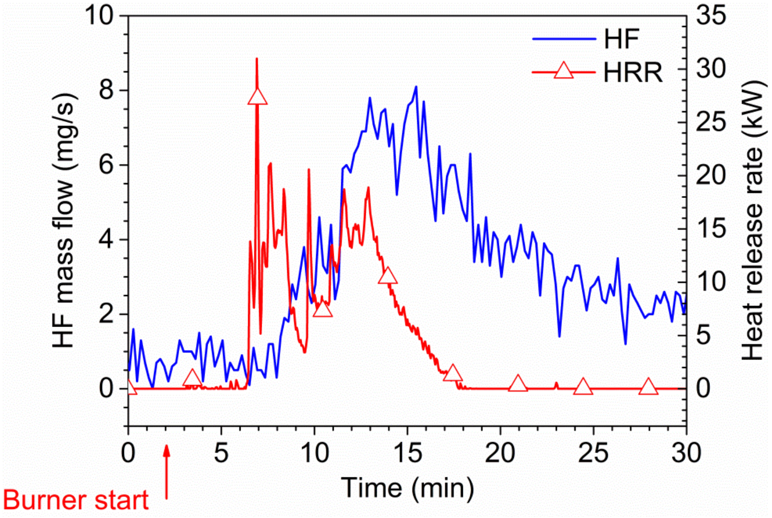
Cell case explosion


Gas explosion

Delayed ignition of released gases mixed with air in a confined/semi-confined space

Can cause more severe damage

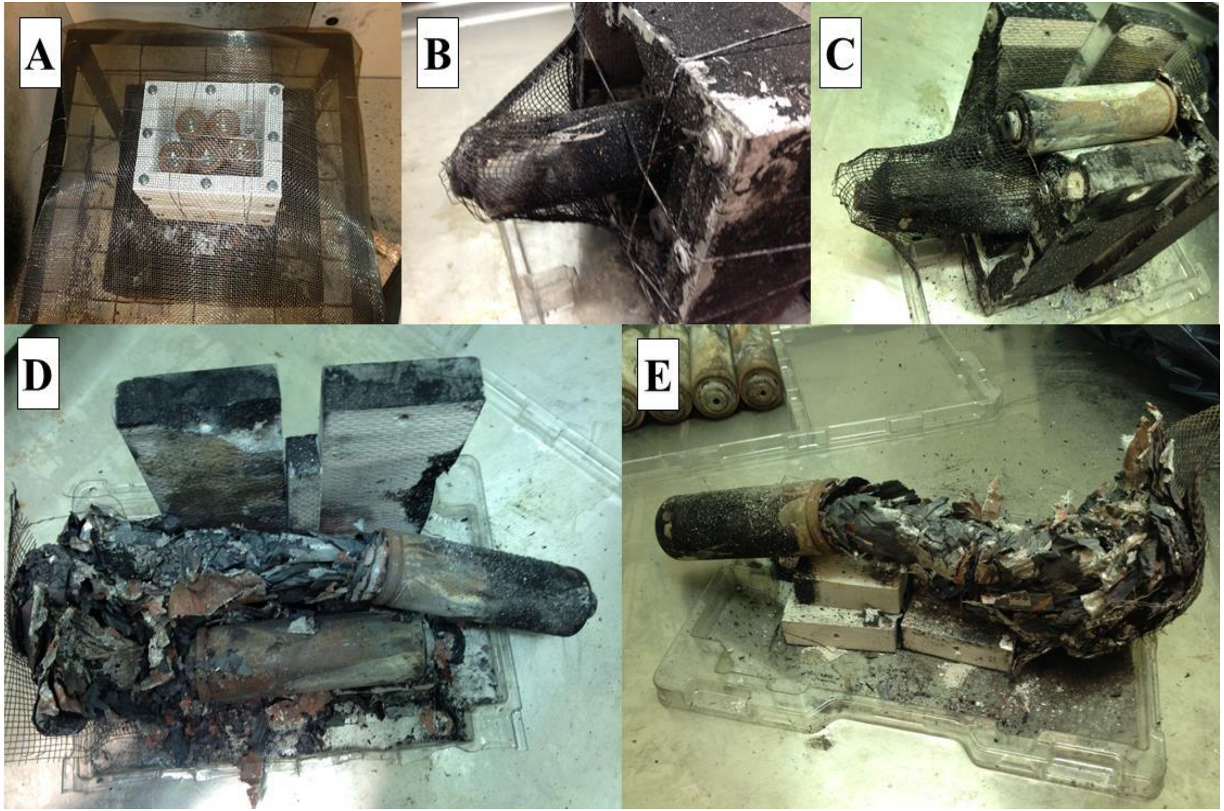
Fire test: Five cylindrical cells of 8 Ah LFP, 100% SOC



- 1 out of 5 cells exploded
- Safety vent did not work

F. Larsson, P. Andersson, P. Blomqvist, B.-E. Mellander, **"Gas emissions from Lithium-ion battery cells undergoing abuse from external fire"**, Conference proceedings of Fires in vehicles (FIVE) 2016, Baltimore, 5-6 October 2016, edited by P. Andersson, B. Sundstrom, *SP Technical Research Institute of Sweden*, Boras, Sweden, p. 253-256, 2016.

Details on the battery explosion



Prevention and mitigation

In addition to regular efforts to limit the propagation of a cell event to a cascading failure extendig from cell to cell and from module to module…

- Ventilation – key to avoid collection of flammable and toxic gases. Including modelling of gas distribution and spread in case of a gas release. Will gases affect areas with humans? Eventual filtering.
- Explosion (deflagration) protection. In enclosed geometries, include a ”weak wall” that will give way in case of a rapid increase of pressure. Predikt the possible consequences of an explosion.
- Detection – gas detection to get an early warning of gassing

Note that risks are not only due to events that start inside a cell – external triggering of gas emissions e.g. through external fire might be a more common risk.

Lithium-ion Batteries used in Electrified Vehicles – General Risk Assessment and Construction Guidelines from a Fire and Gas Release Perspective , Carl Fredrik Larsson, Bengt-Erik Mellander Report (2017): https://www.diva-portal.org/smash/get/diva2:1146859/FULLTEXT01.pdf

Conclusions

- Large batteries can produce large amounts of gas in adverse situations, for example external fire.
- Gas emissions are flammable and toxic, in confined areas that may create risks for explosions and danger to persons.
- There are limited number of studies on gas emissions for aging batteries, for example for large scale second use of automotive batteries. Measurements are complex and more knowledge is needed.

VIDEO

External heating abuse test

Videos of gas explosions can be found at:
https://www.sciencedirect.com/science/article/abs/pii/S0378775317314398

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RI. SE

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Some of our published papers

- Gas explosions and thermal runaways during external heating abuse of commercial lithium-ion graphite-$LiCoO_2$ cells at different levels of ageing, Fredrik Larsson, Simon Bertilsson, Maurizio Furlani et al, Journal of Power Sources. Vol. 373, p. 220-231 (2018)
- Lithium-ion battery electrolyte emissions analyzed by coupled thermogravimetric/Fourier-transform infrared spectroscopy, Simon Bertilsson, Fredrik Larsson, Maurizio Furlani et al Journal of Power Sources. Vol. 365, p. 446-455 (2017)
- Lithium-ion Batteries used in Electrified Vehicles – General Risk Assessment and Construction Guidelines from a Fire and Gas Release Perspective , Fredrik Larsson, Bengt-Erik Mellander Report, https://www.diva-portal.org/smash/get/diva2:1146859/FULLTEXT01.pdf (2017)
- Are electric vehicles safer than combustion engine vehicles? Fredrik Larsson, Petra Andersson, Bengt-Erik Mellander in: Systems Perspectives on Electromobility 2017, p. 34-48
- Overcurrent Abuse of Primary Prismatic Zinc–Air Battery Cells Studying Air Supply Effects on Performance and Safety Shut-Down, Carl Fredrik Larsson, Antti Rytinki, Istaq Ahmed et al, Batteries. Vol. 3 (1) (2017)
- Toxic fluoride gas emissions from lithium-ion battery fires, Fredrik Larsson, Petra Andersson, P. Blomqvist et al, Scientific Reports. Vol. 7 (10018), p. 1-13 (2017)
- Lithium-Ion Battery Aspects on Fires in Electrified Vehicles on the Basis of Experimental Abuse Tests, Fredrik Larsson, Petra Andersson, Bengt-Erik Mellander, Batteries. Vol. 2 (9) (2016)
- Safer battery systems in electrified vehicles – an electrified bus perspective, Fredrik Larsson, Johan Anderson, Petra Andersson et al, Eurotransport. Vol. 14 (3), p. 50-53 (2016)
- Thermal Modelling of Cell-to-Cell Fire Propagation and Cascading Thermal Runaway Failure Effects for Lithium-Ion Battery Cells and Modules Using Fire Walls, Fredrik Larsson, Johan Anderson, Petra Andersson et al, Journal of the Electrochemical Society. Vol. 163 (14), p. A2854-A2865 (2016)

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Thank you for your time.

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