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Analysis of emitted gases from Li-ion LFP and NMC batteries at elevated temperatures

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Introduction

Aim:

Investigate constituent gases generated from venting Li-ion pouch cells to identify less known and well known chemical compounds with potential toxicity

Background:

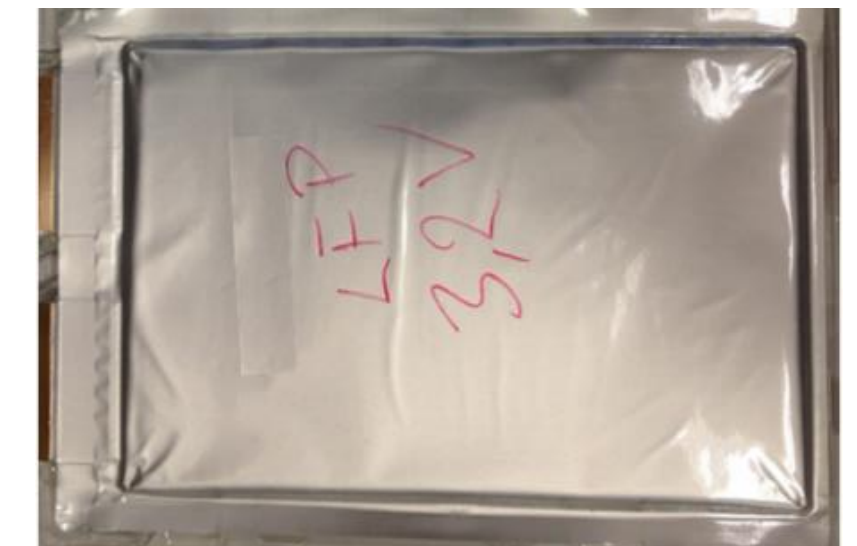
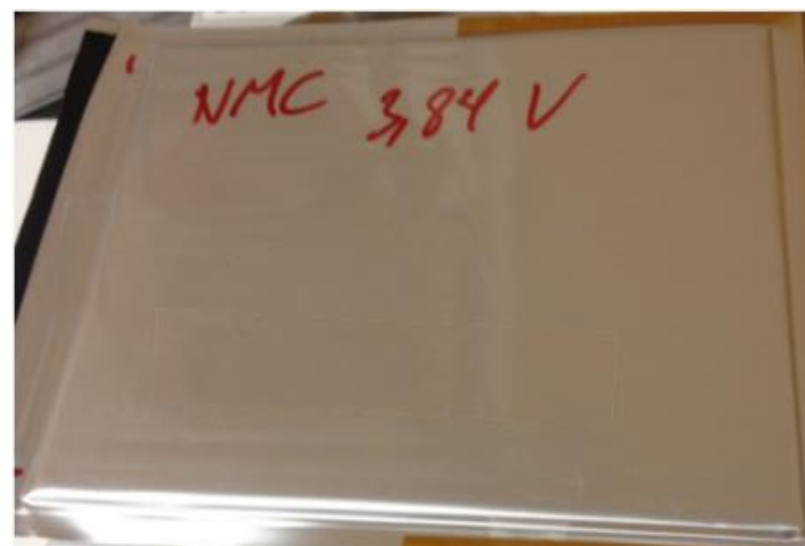
- Swedish Civil Contingencies Agency (MSB) funded this present study
 - Present study is intended to contribute to first responders education
- Previously "E-Vehicle Safe Rescue" (2012-2014) investigate burning cells, but constituent gases from cells venting without fire remained to be studied.



Test Material:

Automotive Li-ion pouch cells of two cathode chemistries

- NMC at 3,84 V with nom capacity 14 Ah, 386g
- LFP at 3,2 V with nom capacity 7 Ah, 236g



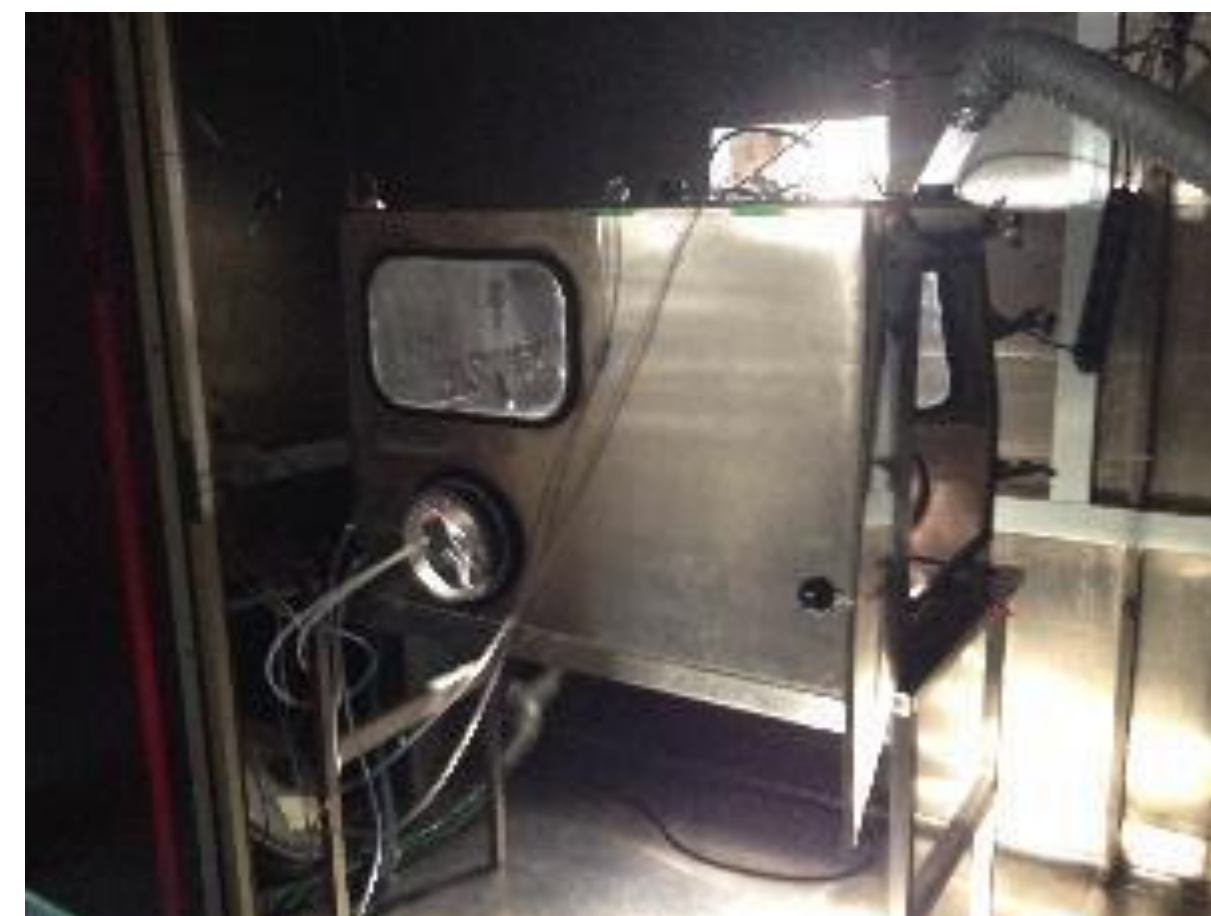
Method - Setup

Single cell



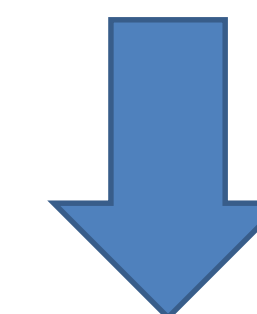
"Battery box"

Test chamber – outside

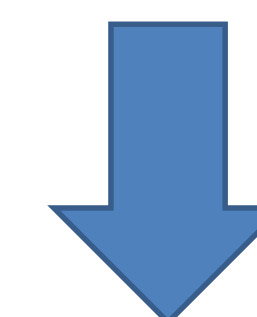


Test chamber – inside

Filters and adsorbents
(Tenax and Carbosieve)



ATD-GCMS
Thermal desorption gas
chromatography and mass
spectrometry



Toxicological assesment
Tox-Databases
TOXNET, ECHA



Method - Procedure

General

- Four experiments done on a single cell per test – Two LFP and two NMC
- Gas samplers in test chambers

Before test

- One cell placed in the battery box – swelling prevented
- Battery box and test chamber flushed with humidified N₂

During test

- Battery box heated until cell vents, while being flushed with humidified N₂
- Sampling started at instance of venting, and proceeded for 10 min

After test

- Dry nitrogen flushed the battery box and test chamber at 50 L/min
- After 10 min of flushing the test chamber was clear
- Filters and adsorbents collected for analysis by ATD-GCMS
- Test chamber and battery box was cleaned

Results – Toxicological Assessment

The selection criteria for a positive identification was a match factor above 90% in comparison to chemical structures in database NIST14

Tables available in related EVS29 article

Table 1 Emittants from LFP respectively NMC battery cells (GC-MS). Light grey table cells presents compounds found in tests of both chemistries. Yellow cells are compounds from LFP only; orange cells are compounds from NMC only. [12]

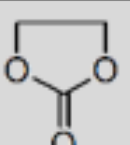
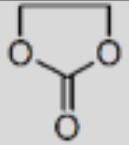
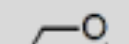
<u>LFP</u> Chem. compound	Structure	CAS#	Conc. (µg/m ³)	<u>NMC</u> Chem. compound	Structure	CAS#	Conc. (µg/m ³)
1,3-dioxolan-2-one		96-49-1	300	1,3-dioxolan-2-one		96-49-1	100
1,4-dioxane		123-91-1	0.2	1,4-oxathiane		15980	2

Table 2 Toxicological assessment summary of compounds identified by GC-MS, Dräger tubes and metal analysis [12]

Chemical compound	CAS no. ¹	TOXNET ² Skin eyes, respiratory tract	Hygienic limit values ³	Labelling of chemicals according to ECHA ⁴ : Hazard codes for chem-phys & human health
1,3-dioxolan-2-one	96-49-1	Irritating to eyes, skin and airways.	---	NA
1,4-dioxane	123-91-1	Very irritating to eyes, skin and airways. Possibly carcinogenic. LC ₅₀ mice inhalation. 37 g/m ³ /2 h LC ₅₀ rats inhalation. 46 g/m ³ /2 h	Limits (1996) LLV 35 mg/m ³ STV 90 mg/m ³ (H) The substance can	Highly flammable liquid and vapor (H225), Causes serious eye irritation (H319), May cause respiratory irritation (H335), Suspected of causing cancer (H351), May form explosive peroxides (E114019).



Results – Toxicological Assessment

Previously identified compounds detected in vented gases

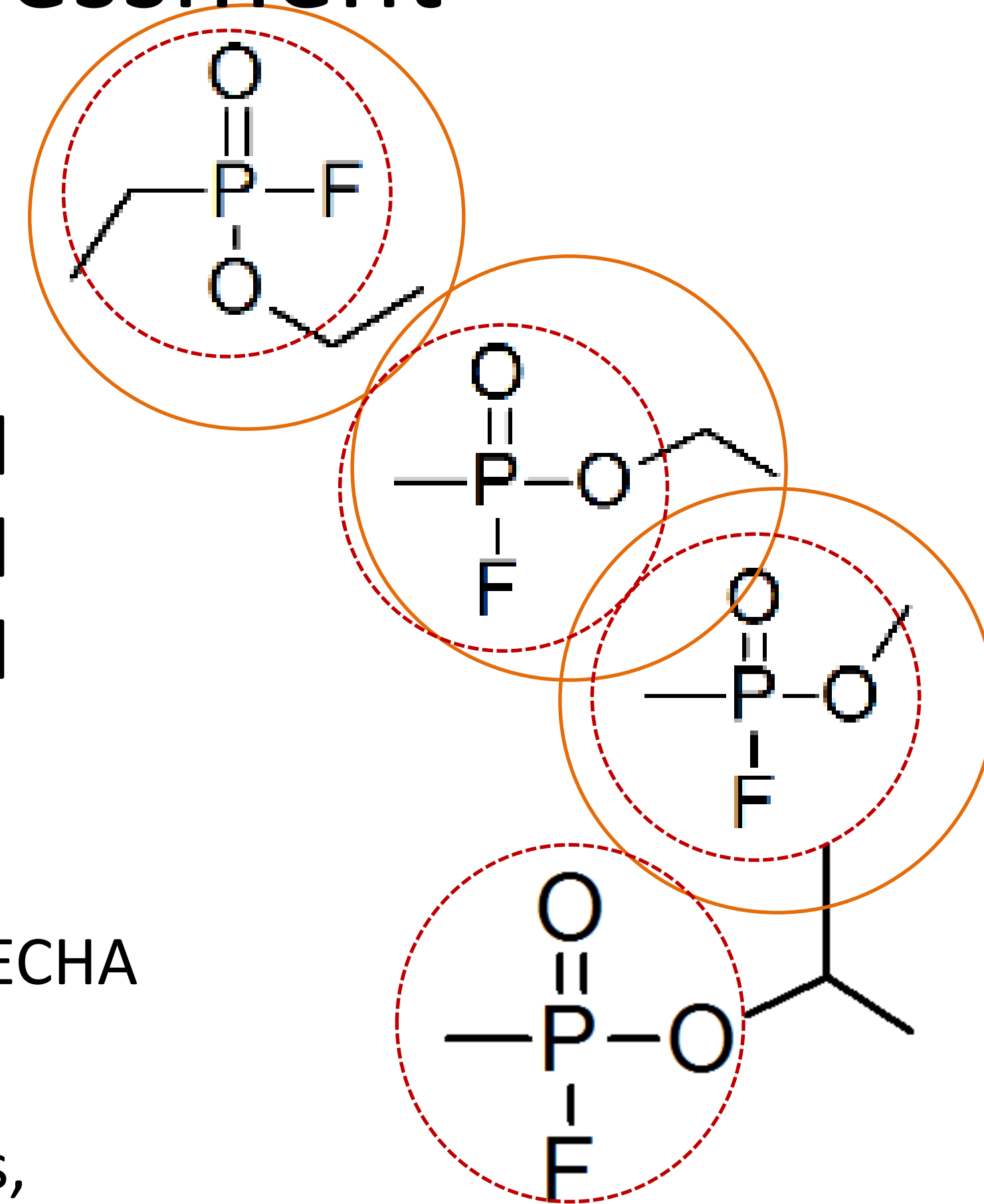
- **Organic species causing skin, eyes and/or respiratory irritation (*ref. to Table 2*)**
 - Electrolyte solvents (carbonates DEC, DMC, EMC); *Flammable liquid and vapor* (H225 and H226)
 - 1,4-dioxane [123-91-1]; *Suspected of causing cancer* (H351)
 - 1,4-oxathiane [15980-15-1]
 - 1-methylpyrrolidin-2-one [872-50-4]; *May damage fertility or the unborn child* (H360D)
 - 1-phenylethanone [98-86-2]; *Harmful if swallowed* (H302)
 - 2-methyl-1,3-dioxolane [497-26-7]
 - Benzoic acid [65-85-0]; *Causes damage to the lungs through prolonged exposure* (H372)
 - Ethyl prop-2-enyl carbonate [1469-70-1]
 - Ethylbenzene [100-41-4]; *May be fatal if swallowed and enters airways* (H304)
 - Styrene [100-42-5]; *Suspected of damaging fertility or unborn child* (H361d)
- **Inorganic species**
 - HF [7664-39-3]; *Fatal if swallowed/inhaled* (H300/H330), *Fatal in contact with skin* (H310)

Results – Toxicological Assessment

Phosphonofluoridates detected in vented gases

- **GC-MS screening of vented gases presented**
 - Ethyl ethylphosphonofluoridate, [650-20-4]
 - Ethyl methylphosphonofluoridate, [620-20-4]
 - Methyl methylphosphonofluoridate, [353-88-8]

- **Findings and considerations**
 - lack toxicological record in tox-databases TOXNET and ECHA
 - requires more research on their specific toxicity
 - have chemical structures similar to known toxic species, i.e. sarin gas [107-44-8]
 - Identification verified, but quantities remained very low





Discussion & Conclusion

- **Small test system; one cell per test**
- **This study identified the existence of chemical compounds**
 - Positive identification demanded a NIST14 match factor above 90%
 - Quantities were verified only when concentrations were high
- **Presence of HF confirmed**
- **Most interesting compounds were the Phosphonofluoridates:**
 - may present an unspecified health risk but tox-data is missing
 - chemical structures similar to Sarin
- **The presence of organo phosphonofluoridates call for continuing tox-research**
 - evaluate their potential to inhibit the enzyme acetylcholinesterase
 - provide further recommendations to first responder educations for E-Vehicle scenarios
- **Tests representing real world accident scenarios required**
 - clarify potential E-Vehicle occupant exposure levels in scenario with full size battery pack



Partners and Contact Information

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- Research center within Autoliv Inc. which is the world's largest automotive safety supplier.



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- Division of CBRN-Defense and Security. General lab inquires. FOI, conduct science for a safe and secure world



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- Academic national center working for a non-toxic environment





THANK YOU
FOR YOUR ATTENTION



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