Li-ion batteries in submarines: Gas monitoring & handling

Current knowledge and outlook

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Introduction

- Viola Nilsson, 27, Malmö, Sweden
- Submarine Systems Engineer at Saab Kockums(2021-now)
    - Air Purification
    - Air Monitoring
    - Oxygen

Aim

Summarize current research:

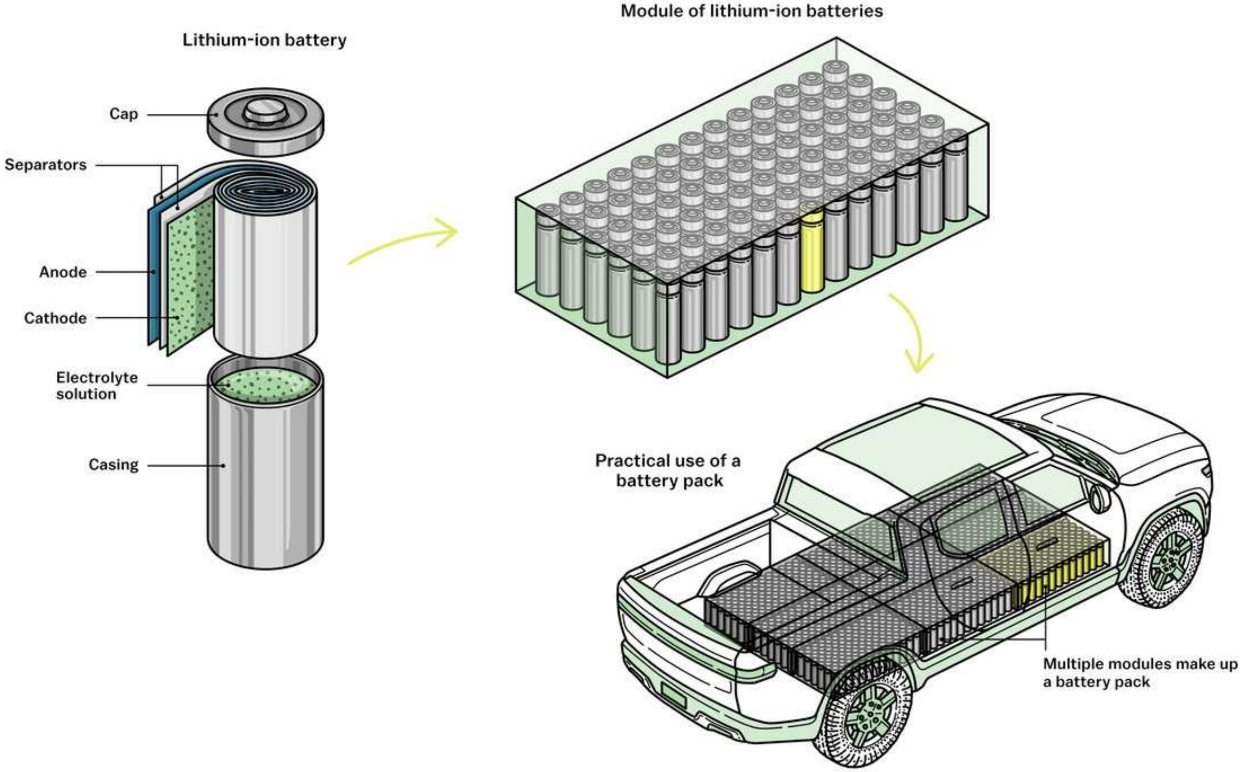
- Factors impacting thermal runaway gas composition (battery chemistry, state of charge, trigger method, atmosphere)
- How early signs of thermal runaway can be detected with a gas monitoring system (target gases, sensing methods)
- Handling of gases expelled in thermal runaway

Discussion

- How can we monitor to prevent TR on submarines?
- What gases should we monitor?
- How should we handle gases produced in TR?

Lithium-ion batteries

- In Electrical Vehicles
- Submarines next?
- High energy density
- Fast development, constantly new research



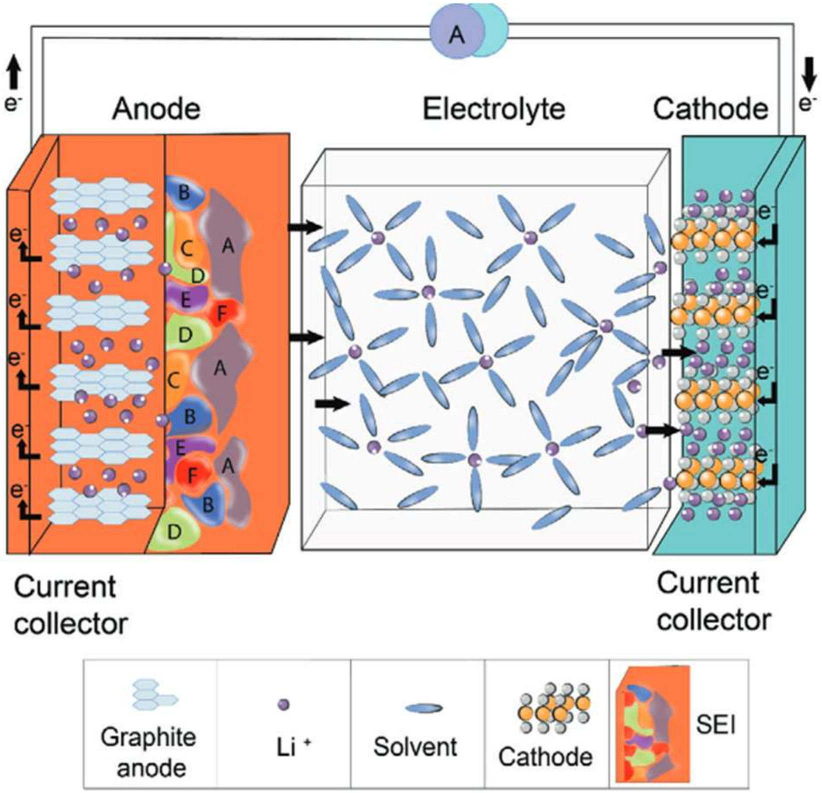

Cylindrical


Pouch


Prismatic

Sources: [17], [34]

Lithium-ion batteries



Model of Li-ion battery [5]

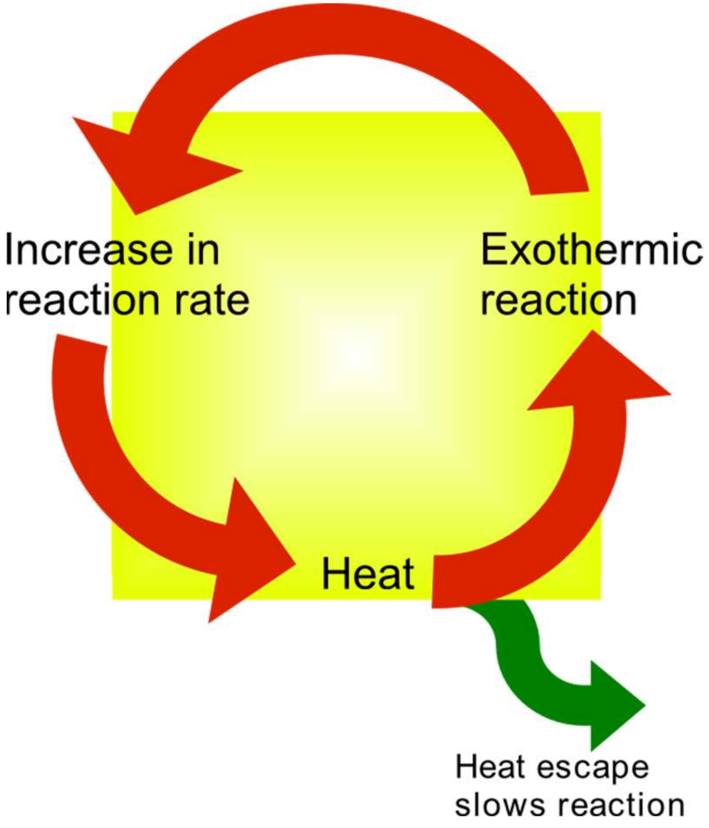
- **Anode** – carbon based
- **Cathode** – metal oxide
- **Electrolyte** – liquid

Thermal Runaway

Tesla Li-ion car suspected Thermal Runaway fire. Switzerland, May 10 2018 (Reuters)

Thermal Runaway (TR)

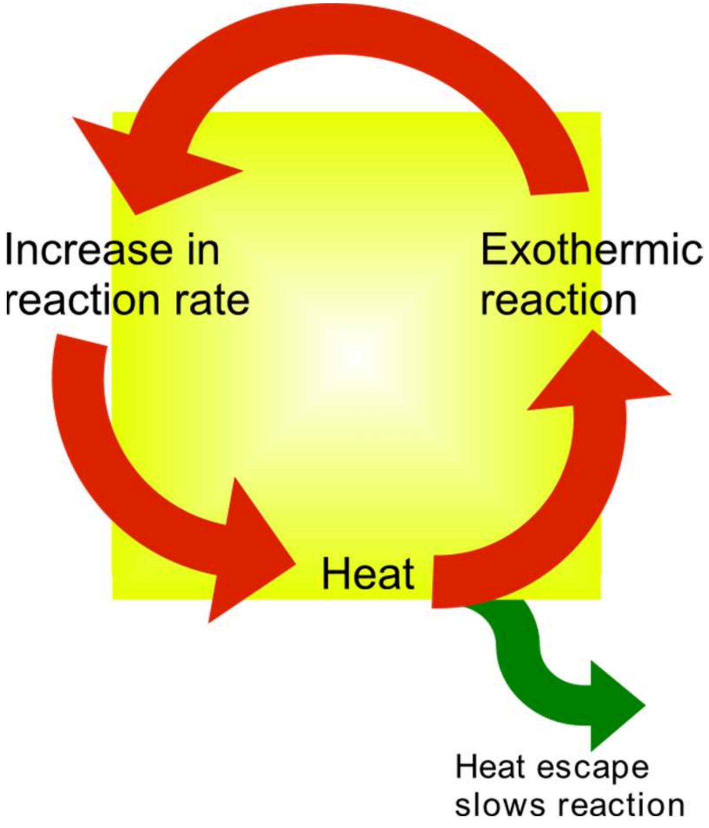
- Exothermic reaction
- Self-heating
- Cause:
  - Mechanical
  - Electrical
  - Outside temperature



Sources: [11], [12], [13], [14], [15],[16]

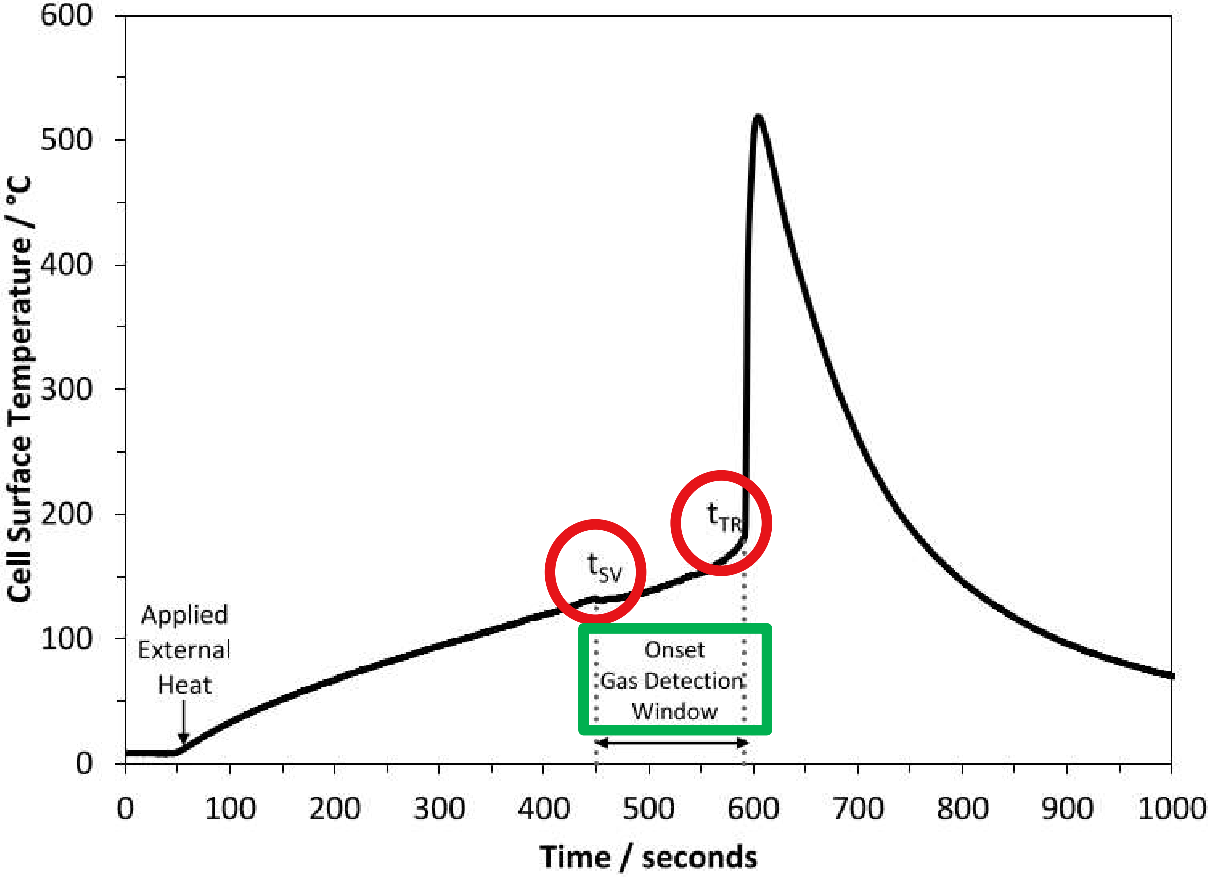
Thermal Runaway (TR)

- Toxic & flammable gases produced
- Could lead to DISSUB (Distressed submarine) situation
- *UN global technical regulation:* Electrical vehicles should send alarm to user 5 minutes before hazardous conditions caused by TR



Sources: [11], [12], [13], [14], [15],[16]

TR process



Cell temperature over time. [14]

- t_{SV} = safety venting
- t_{TR} = thermal runaway
- Onset gas detection window.

- Safety venting – the first sign of TR! Bursting disc on cylindrical batteries.

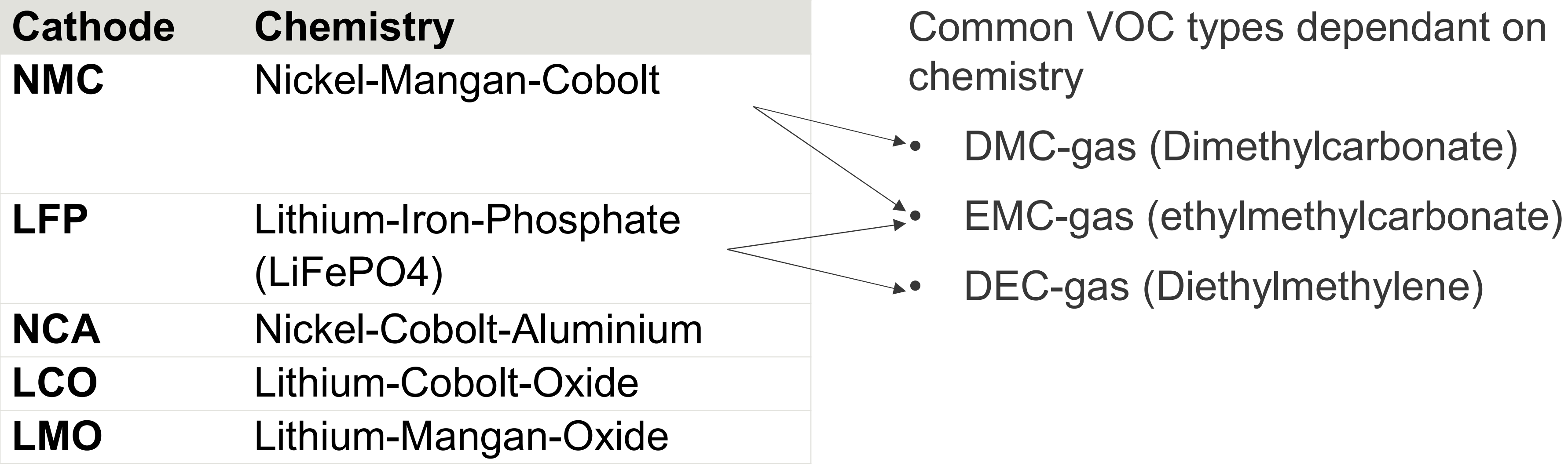
TR factors

- Which gases forms in TR?
- How much gas forms?

Depends on:

- Battery chemistry
- State of Charge
- Trigger Method
- Atmosphere

TR: Battery chemistry



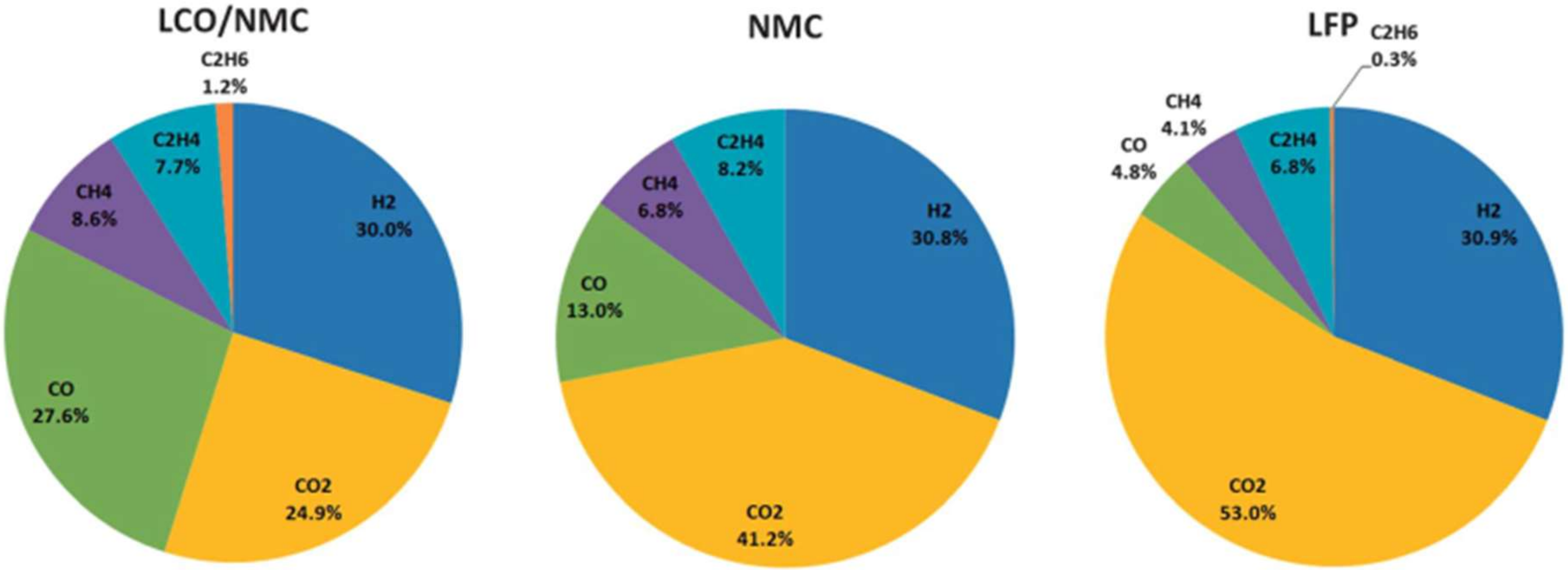
Cathode	Chemistry
NMC	Nickel-Mangan-Cobolt
LFP	Lithium-Iron-Phosphate (LiFePO4)
NCA	Nickel-Cobolt-Aluminium
LCO	Lithium-Cobolt-Oxide
LMO	Lithium-Mangan-Oxide

Common VOC types dependant on chemistry

- DMC-gas (Dimethylcarbonate)
- EMC-gas (ethylmethylcarbonate)
- DEC-gas (Diethylmethylene)

Sources: [18], [19], [20]

TR: Battery chemistry



Sources: [31]

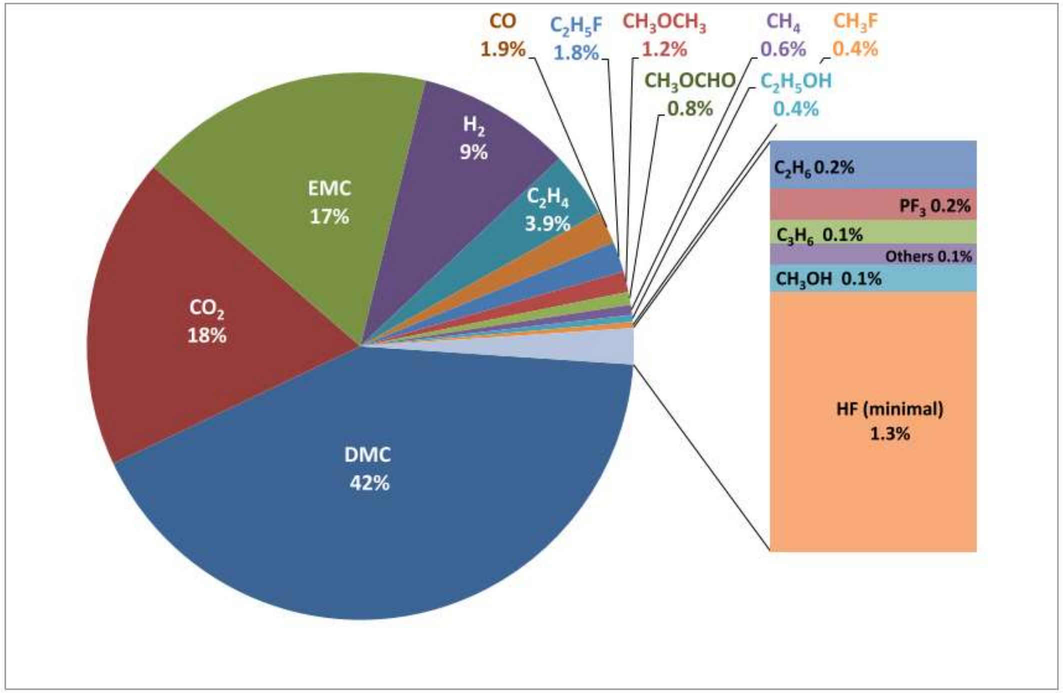
TR: Battery chemistry: example

LFP battery:

Composition of gases generated from TR.

Example: small amounts of HF!

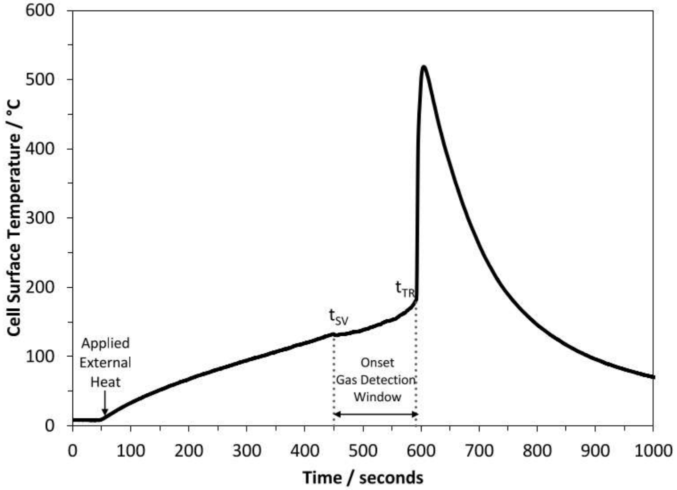
Sometimes fluorides used in solvent in electrolyte.



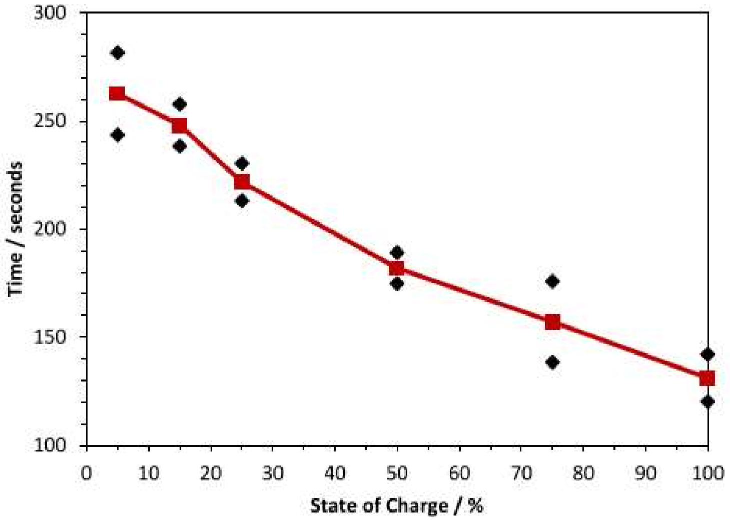
Sources[19]

TR: State of Charge (SOC)

- How charged the battery is (0-100%)
- Higher SOC -> more violent TR
- Temperature for SV + TR is lower
- Shorter onset gas detection window



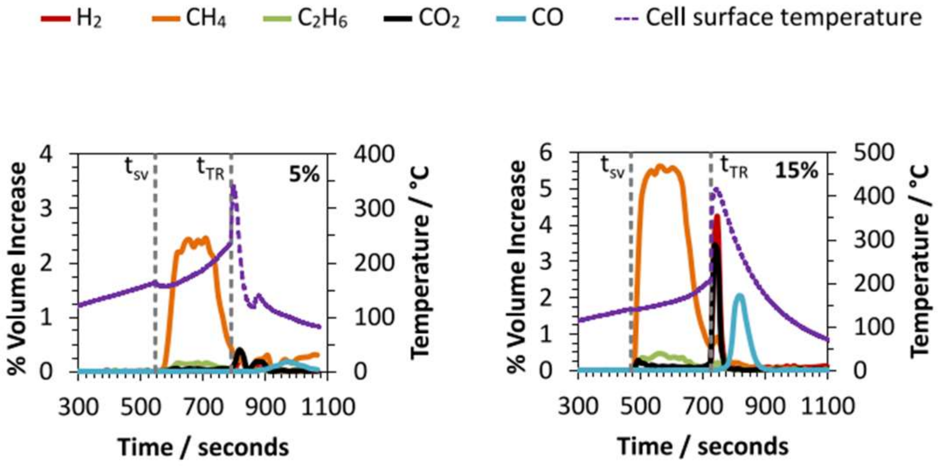
Source: [14]

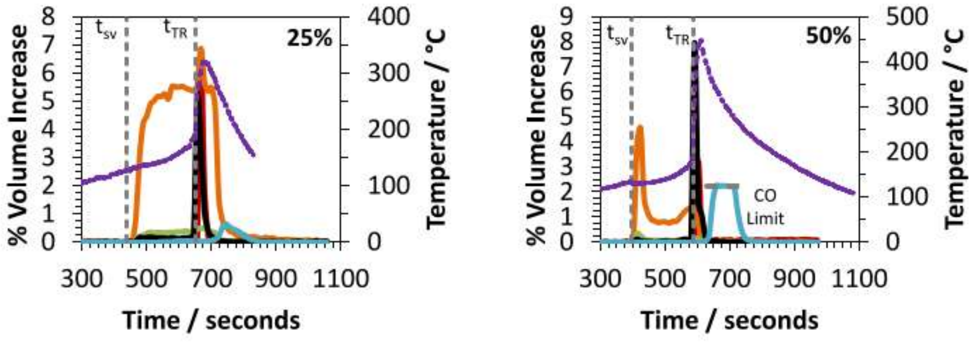


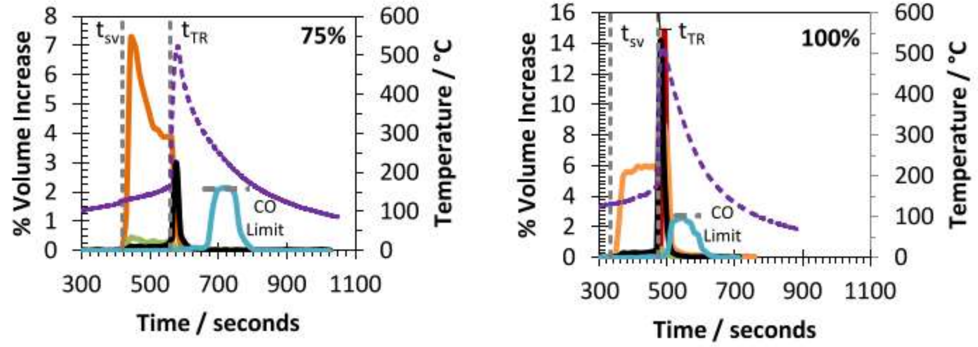
Onset gas detection window at each SoC. [14]

TR: State of Charge (SOC)

- Gas composition at different SOC [14]



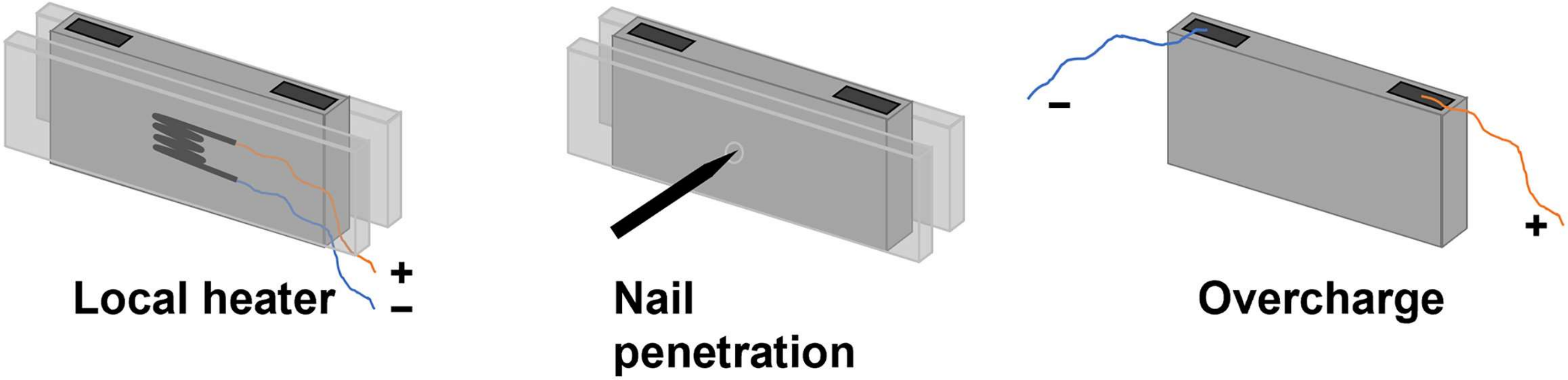




TR: Trigger methods

- Thermal – overheating
- Electrical – overcharging
- Mechanical – nail penetration

- One study: important for gas production, mass temp etc, but not composition [26]
- Other study: overcharging lead to more toxic and explosive gases [27]

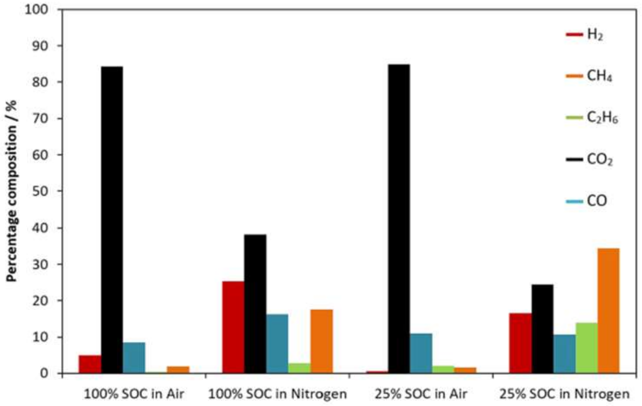


Sources: [25], [26], [27],

TR: Atmosphere

- Air – open, reactive
- Nitrogen gas – closed, inert

- More CO_2 in open atmosphere
- More CO in closed atmosphere



Gas composition in air vs nitrogen at 100% and 25% SOC [14]

Mass CO2 in closed/open atmosphere. Open atmosphere is divided into two catagories: no fire and fire (where gases are burned) [26]

Gas Monitoring System

- THE key for early detection of TR!
- Temperature, pressure, current, etc is not quick enough
- Combination is suggested
- With early detection, the consequences of TR can be mitigated.
- Avoid false positives
- What sensors? Which gases? Sensor principle?

Sources: [15]

Target gas

- **Which gas(es) should we measure for early detection?**
  - Found in chosen battery chemistry
  - Easy to measure

- **Suggested from literature:**
  - CO_2
  - CO
  - VOC
  - DEC, DMC
  - H_2

Sources: [18], [19], [20]

How to measure?

- Background sensors
- Actual value?
- Rate of rise (acceleration of concentration change)? (Li-ion tamer)

Sources: [18], [19], [20]

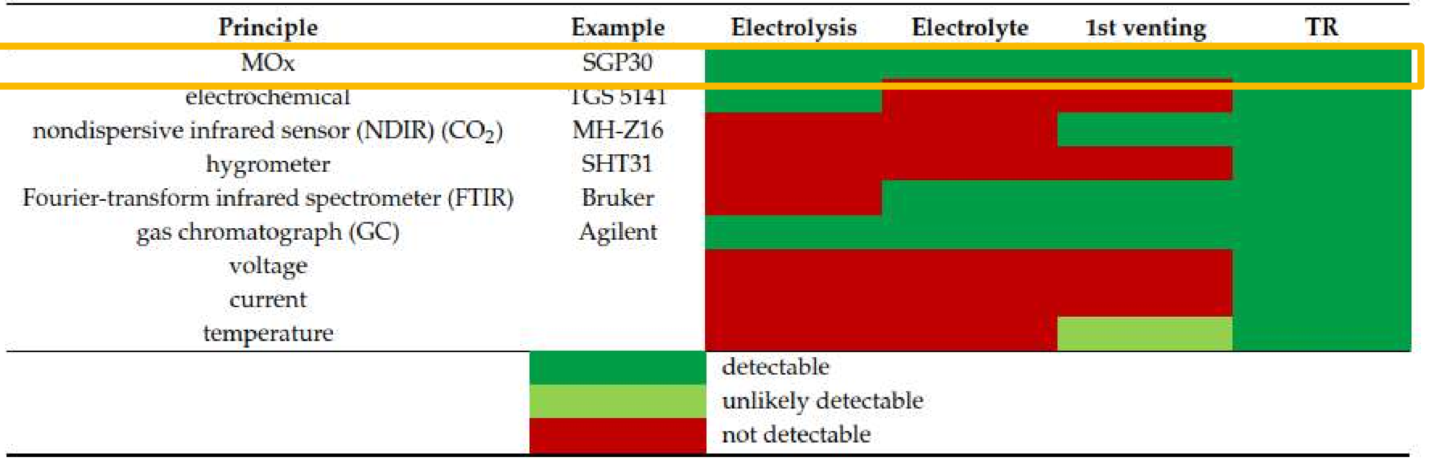
Sensor principles

Suggested from scientific papers:

- Chemical
- Electrochemical
- NDIR (Non dispersive infrared)
- MOx (Metal Oxide Sensor), SMOx
- FTIR (Fourier infra red spectrometer)
- GC (Gas chromatography)

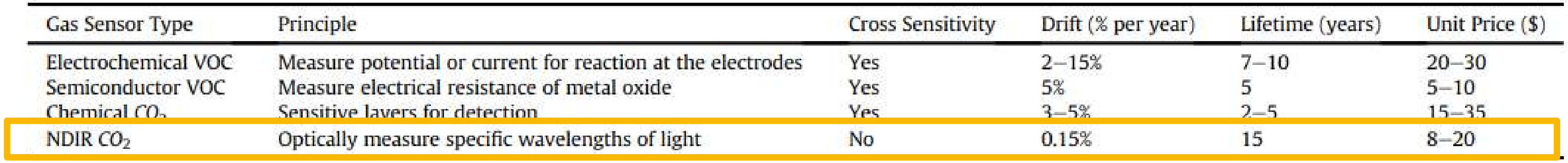
Sources: [14], [15], [25]

Sensor principles



Principle	Example	Electrolysis	Electrolyte	1st venting	TR
MOx	SGP30	🟩	🟩	🟩	🟩
electrochemical	TGS 5141	🟩	🟥	🟥	🟩
nondispersive infrared sensor (NDIR) (CO_2)	MH-Z16	🟥	🟥	🟩	🟩
hygrometer	SHT31	🟥	🟥	🟥	🟩
Fourier-transform infrared spectrometer (FTIR)	Bruker	🟥	🟩	🟩	🟩
gas chromatograph (GC)	Agilent	🟩	🟩	🟩	🟩
voltage		🟥	🟥	🟥	🟩
current		🟥	🟥	🟥	🟩
temperature		🟥	🟥	▨	🟩
	🟩	detectable			
	▨	unlikely detectable			
	🟥	not detectable			

[15]

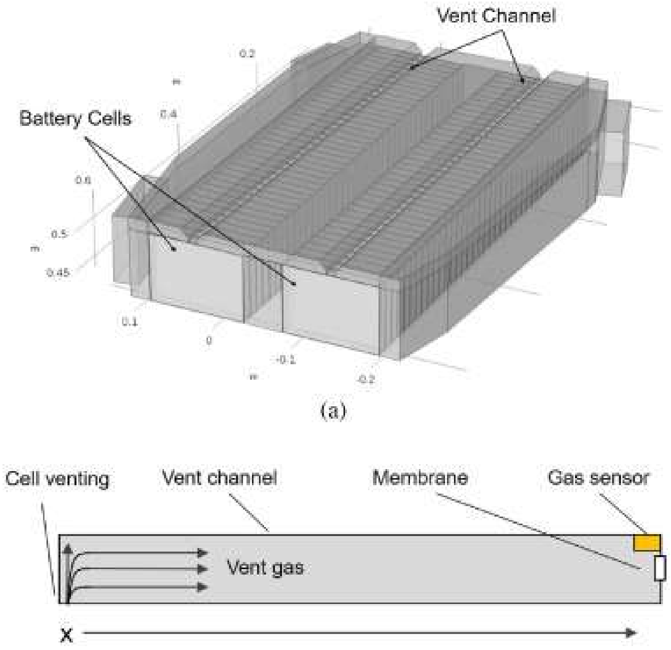


Gas Sensor Type	Principle	Cross Sensitivity	Drift (% per year)	Lifetime (years)	Unit Price ($)
Electrochemical VOC	Measure potential or current for reaction at the electrodes	Yes	2–15%	7–10	20–30
Semiconductor VOC	Measure electrical resistance of metal oxide	Yes	5%	5	5–10
Chemical CO_2	Sensitive layers for detection	Yes	3–5%	2–5	15–35
NDIR CO_2	Optically measure specific wavelengths of light	No	0.15%	15	8–20

[25]

Gas handling/venting

- Evs: network of ventilation channels
- Shouldn't be released into submarine atmosphere
- Evacuate through ventilation ducts to exit submarine?
- Collect?



[25]

Conclusions

- Rapid innovations & studies
- Li-ion batteries in future submarines?
- Gas monitoring essential for early warning of thermal runaway
- Gas handling
- More research on gas monitoring for Li-ion batteries.
- Submarine specific research

- How can we monitor to prevent TR on submarines?
- What gases should we monitor?
- How should we handle gases produced in TR?

Thank you!

SAMAP 2024

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