Influence of aging on the failing behavior of automotive lithium-ion batteries

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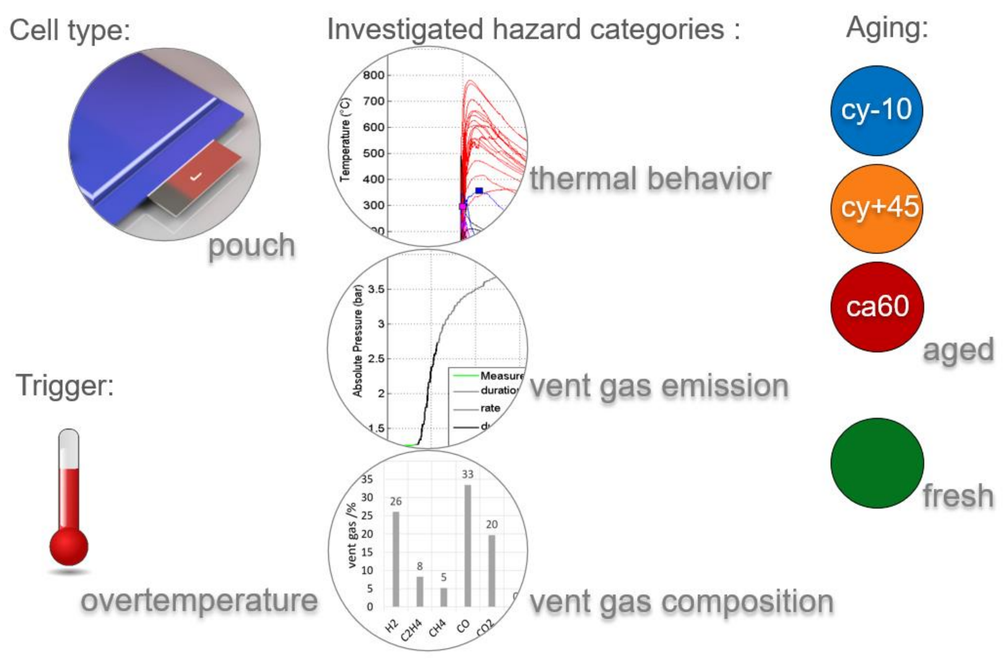
Motivation:

Lithium-ion batteries suffer from aging effects and battery failures are possible, which can lead to exothermic chemical reactions inside the cell, ending up in thermal runaway (TR). Since statistically most battery incidents happen with aged cells, in particular, the failing behavior of aged cells needed to be investigated.



Aging paths:

Cells after three different aging paths

- Cyclic aged at -10°C
- Cyclic aged at 45°C
- Calendric aged at 60°C

were compared to fresh cells

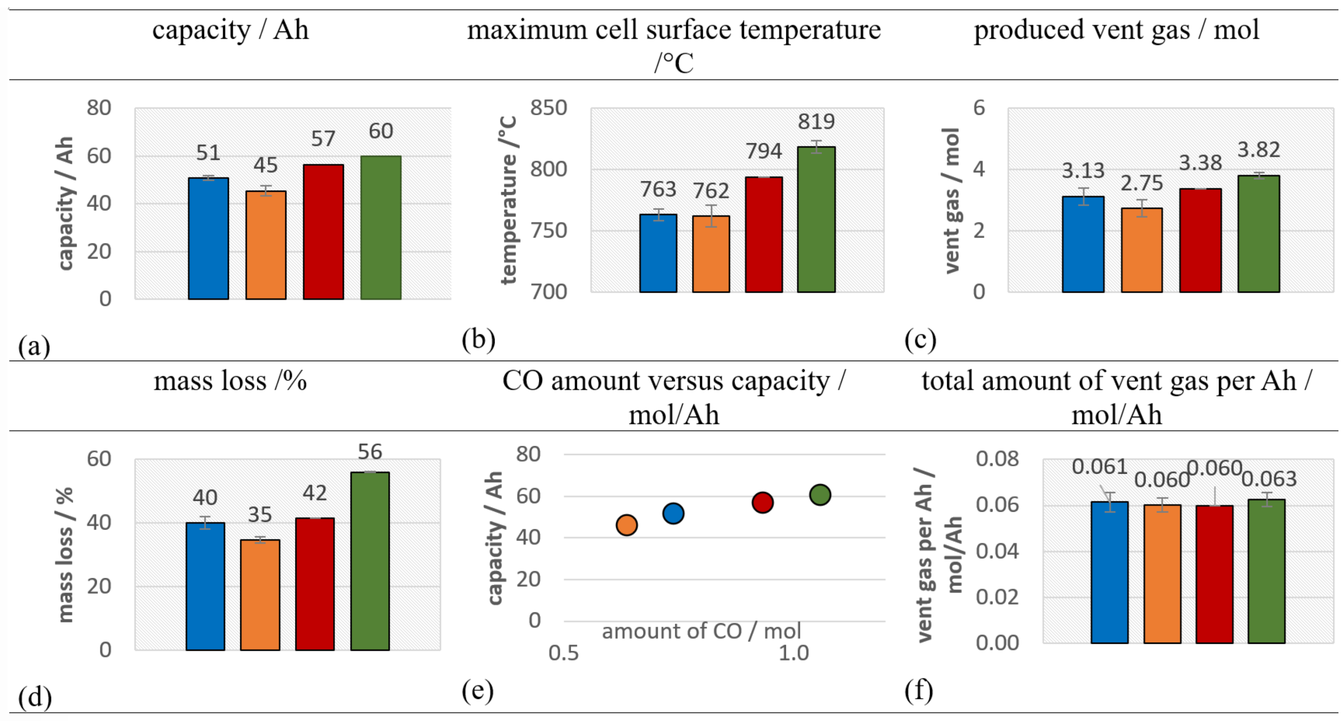
Investigated cell

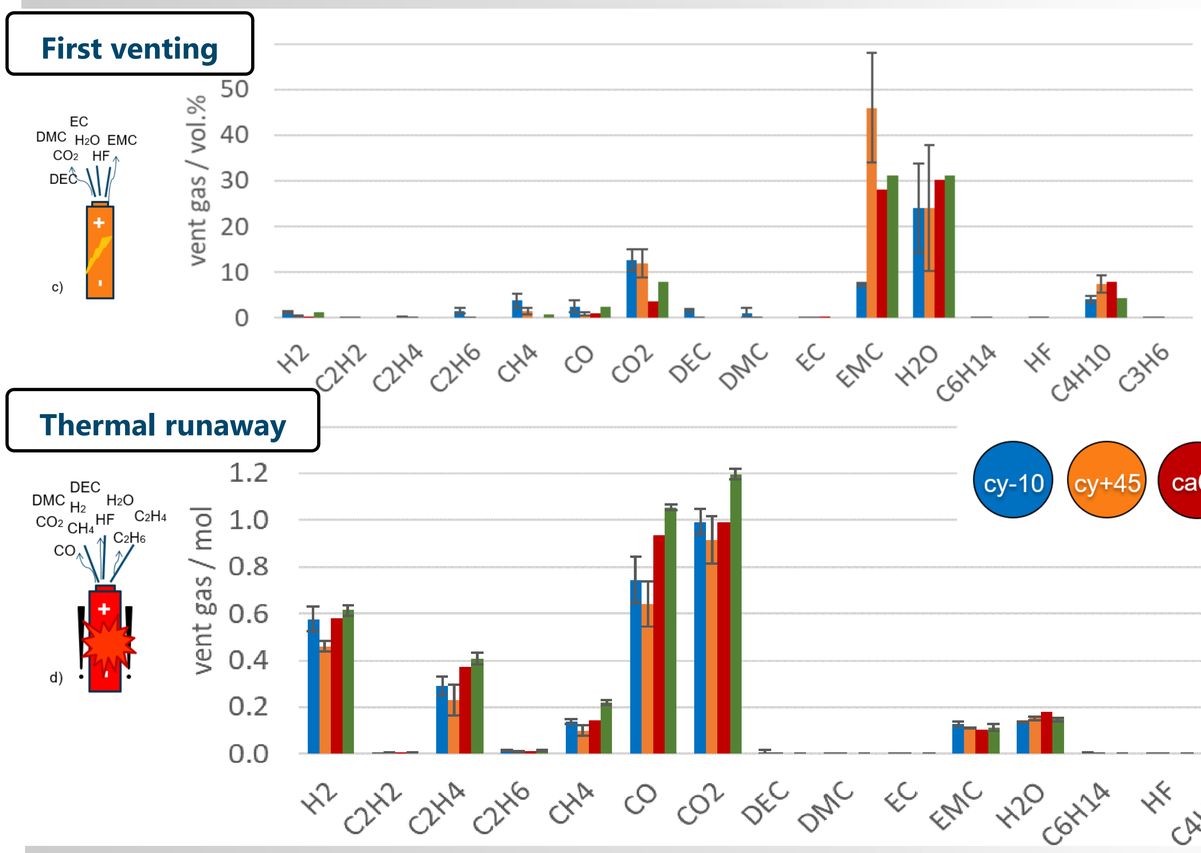
Cathode: *NMC 622*
Anode: graphite
Electrolyte: EC:EMC (1:1)
Spec. energy: 250 Wh/kg
Start SOC: 100%

aging description	abbr.	T / °C	SOC /%	charge current / A	discharge current / A	ΔSOC / %	duration / days	nr. of cycles	SOH / %
calendric 60°C	ca60	60	100	-	-	-	150 days	-	94
cycling -10°C	cy-10	-10	-	12	20	0-100	-	800	85
cycling 45°C	cy+45	45	-	20	20	0-100	-	1000	76

Main results:

- Significant effect of aging on the failing behavior
- No fresh metallic Li plating for cy-10°C
- Increased thermal stability for cy+45 and ca60, but not for cy-10 –> lower TR onset
- Reduced TR reaction for aged cells: less gas, reduced CO amount, lower maximal temperatures, lower mass loss
- Remaining capacity is decisive for the reaction and safety relevant parameters! Linear correlations to produced amount of gas, mass loss and CO amount





- No influence on first venting temperature
- Main gas compounds after first venting and TR comparable, but exact vent gas composition depends on different aging paths (e.g. trans–esterification EMC)
- 0.06 mol/Ah vent gas produced during overtemperature TR for NMC 622 – graphite cells with liquid electrolyte (EC, EMC, DMC, DEC)

Take-home messages

+ Increased thermal stability and safety for aged cells (fresh Li-plating excluded)
+ Recommendation for safety testing: test fully charged fresh cells - they represent the worst case

Conclusion:

Aged cells in overtemperature TR experiments ended up in reduced maximum temperatures, lower amount of produced gas, significantly lower amount of CO in the vent gas and lower mass loss than in the same experiments using fresh cells. During the rest time after Li plating, the plated Li might have intercalated or chemically reacted, which had positive effects on the safety behavior.

These experiments have been done at VIRTUAL VEHICLE in Graz.

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