European Commission

Evaluation of volume of free electrolyte in various cell types - Method and preliminary results

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JRC-Institute for Energy and Transport

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18650 cell

Sample

18650 commercial cell

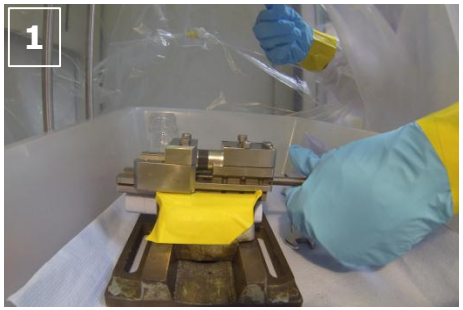
Lithium ion battery (Lithium iron phosphate chemistry) - 1.1 Ah

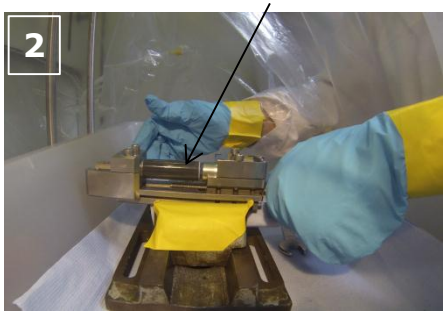
Methodology

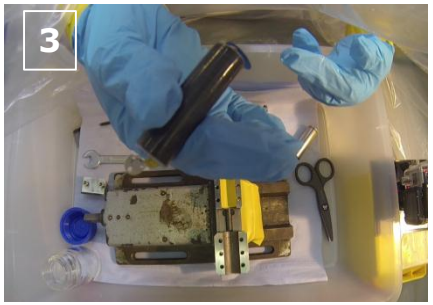
Sample was discharged as recommended by the manufacturer to lower cut off voltage. Then casing was scored using a custom made cell opening tool inside an Argon purged Glove bag. The amount of leaked electrolyte was checked and the mass loss was monitored in an analytical balance (1 mg accuracy) over time .

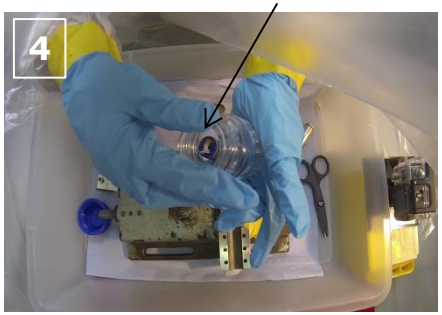
Exposed Jelly roll

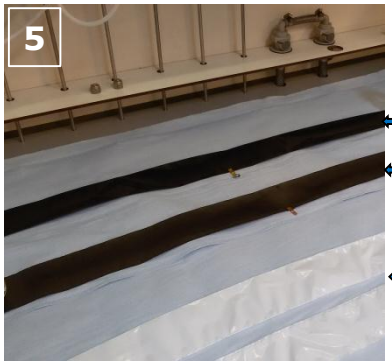
Jelly roll in Pyrex bottle for evaporation measurements







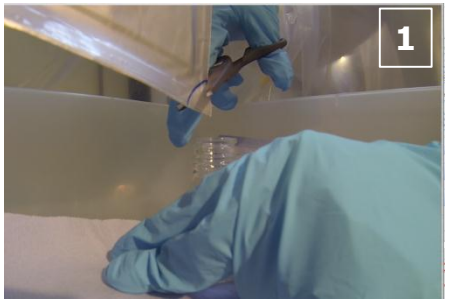


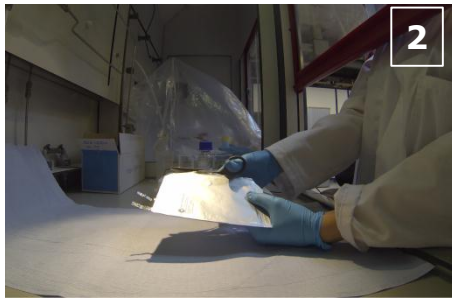


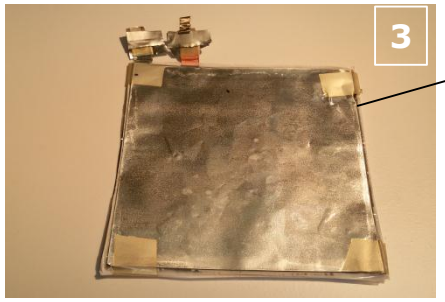
- No free electrolyte observed
- Electrolyte fully soaked in electrodes
- Evaporation of 50 mg of solvent after 30 minutes (0.8 % of total battery solvent)
- Evaporation of 66 mg of solvent after 60 minutes (1.1 % of total battery solvent)
- Total battery solvent 15wt.% of total battery weight

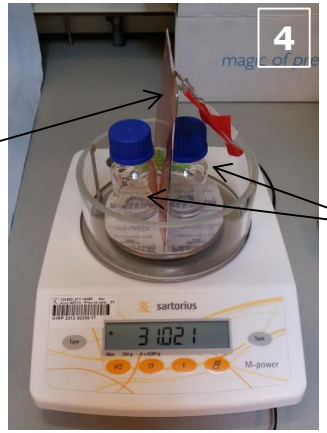
Pouch cell

Sample
Soft pouch commercial cell
Lithium ion battery (NCA chemistry) - 1Ah
Around 8 mL of electrolyte according to manufacturer
Methodology
Sample was discharged as recommended by the manufacturer to lower cut off voltage. Then casing was cut with a pair of ceramic scissors inside an Argon purged Glove bag. The amount of leaked electrolyte was checked and the mass loss was monitored in an analytical balance (1 mg accuracy) over time .









holders

anode

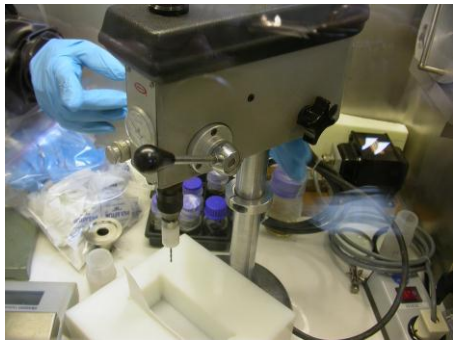
separator

cathode

- No free electrolyte observed
- Electrolyte fully soaked in electrodes
- Evaporation of 75 mg of solvent after 30 minutes (0.75 % of total battery solvent)
- Evaporation of 139 mg of solvent after 60 minutes (1.39 % of total battery solvent)
- Total battery solvent estimation = 23 wt.% of total battery weight

Prismatic cell – type I

Sample
Prismatic commercial cell; 2 identical cells, #4 and #11
Lithium ion battery (Lithium iron yttrium phosphate chemistry) – 40 Ah
Methodology
Sample was discharged as recommended by the manufacturer to lower cut off voltage and cooled to -20° C.
Then casing was open by drilling holes of ca. ø 2 mm in an argon-purged glove box.
The amount of leaked electrolyte was checked and the weight loss was monitored using a balance (0.1 g accuracy) over time.



electrolyte collected from cell#4

electrolyte collected from cell#11

- Cell #4 – 25.6 g (ca. 25 ml) free electrolyte collected
- Cell #11 – 72.6 g (>> 50 ml) free electrolyte collected

- Evaporation of up to 0.1 g of electrolyte from an opened battery in 30 min
- Evaporation of up to 0.4 g of electrolyte from an opened battery in 60 min

Prismatic cell – type II

Sample

Prismatic commercial cell; 2 identical cells, #12 and #13

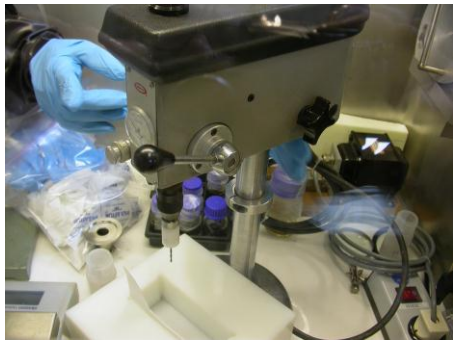
Lithium ion battery (Lithium iron phosphate chemistry) – 40 Ah

Methodology

Sample was discharged as recommended by the manufacturer to lower cut off voltage and cooled to -20° C.

Then casing was open by drilling holes of ca. Ø 3 mm in an argon-purged glove box.

The amount of leaked electrolyte was checked and the weight loss was monitored using a balance (0.1 g accuracy) over time.



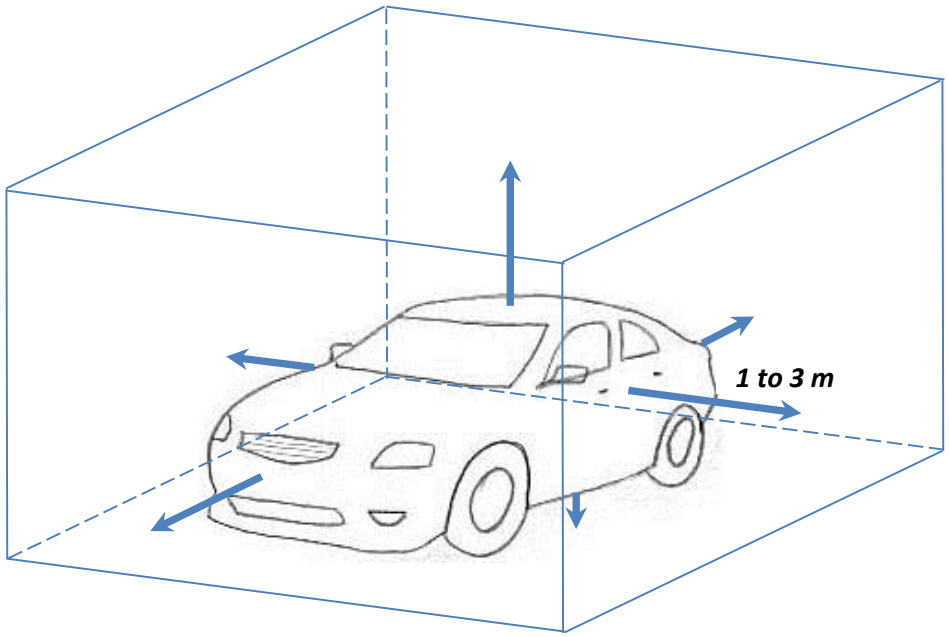
electrolyte collected from cell#12

electrolyte collected from cell#13

- Cell #12 – 30.4 g (ca. 30 ml) free electrolyte collected
- Cell #13 – 19.5 g (ca. 20 ml) free electrolyte collected

- Evaporation of up to 0.4 g of electrolyte from an opened battery in 30 min
- Evaporation of up to 0.6 g of electrolyte from an opened battery in 60 min

Acute exposure to chemical substances



Acute exposure to chemical substances - Protective Action Criteria (PAC)

PAC-1: Mild, transient health effect
PAC-2: Irreversible or other serious health effects that could impair the ability to take protective action
PAC-3: Life-threatening health effects

http://www.atlintl.com/DOE/teels/teel.html

Chemical substances considered:

- 24 solvents used in the contemporary Li-ion battery cells
- Hydrogen fluoride (HF) as product of $LiPF_6$ decomposition

Acute exposure to chemical substances

Substance	Volume of evaporated solvent, cm^3	
	PAC-2 level	PAC-3 level
γ-Butyrolactone (γ-BL), CAS # 96-48-0	0.22	17
Diethyl carbonate (DEC) CAS # 105-58-8	1.4	21.5
Propylene carbonate (PC) CAS # 108-32-7	1.9	Not achievable at RT
2-Methyl-Tetrahydrofuran (2-Me-THF) CAS#96-47-9	11.5	67
Dimethyl carbonate (DMC), CAS # 616-38-6	25	149

Substance	Volume of electrolyte release*, cm^3	
	PAC-2 level	PAC-3 level
Hydrogen fluoride (HF), CAS #7664-39-3	20.5	36.9

Volume, solvent evaporates into, is defined as vehicle + 1-m clearance around it; 61.5 m3 in this study
** Assuming 1:3 stoichiometry of the salt decomposition*
** Assuming 1M concentration of $LiPF_6$ salt in electrolyte*

Summary

- Commercial 18650 and pouch cells investigated did not contain any free liquid electrolyte
- Commercial prismatic cells investigated contained ≥ 20 ml free liquid electrolyte
- Electrolyte release from prismatic cells through evaporation is measured to occur at the rate of 0.08-0.11 g/min·cm^2 for the first hour in the experimental set-up used in this study.
- Our calculations have shown that a release of 20 ml of Li-ion battery electrolyte in a 61.5m^3 room is sufficient to reach a PAC-2 level concentration for various common electrolyte components, e.g. diethyl carbonate (DEC), propylene carbonate (PC), etc., and/or products of electrolyte decomposition, e.g. hydrogen fluoride (HF).
- Taking this into account hazards and risks associated with a release of electrolyte from REESS need to be addressed in the GTR draft:
  - requirements for electrolyte release need to be specified
  - method(s) for direct measurement(s) to verify the compliance need to be proposed

X-ray imaging of cells

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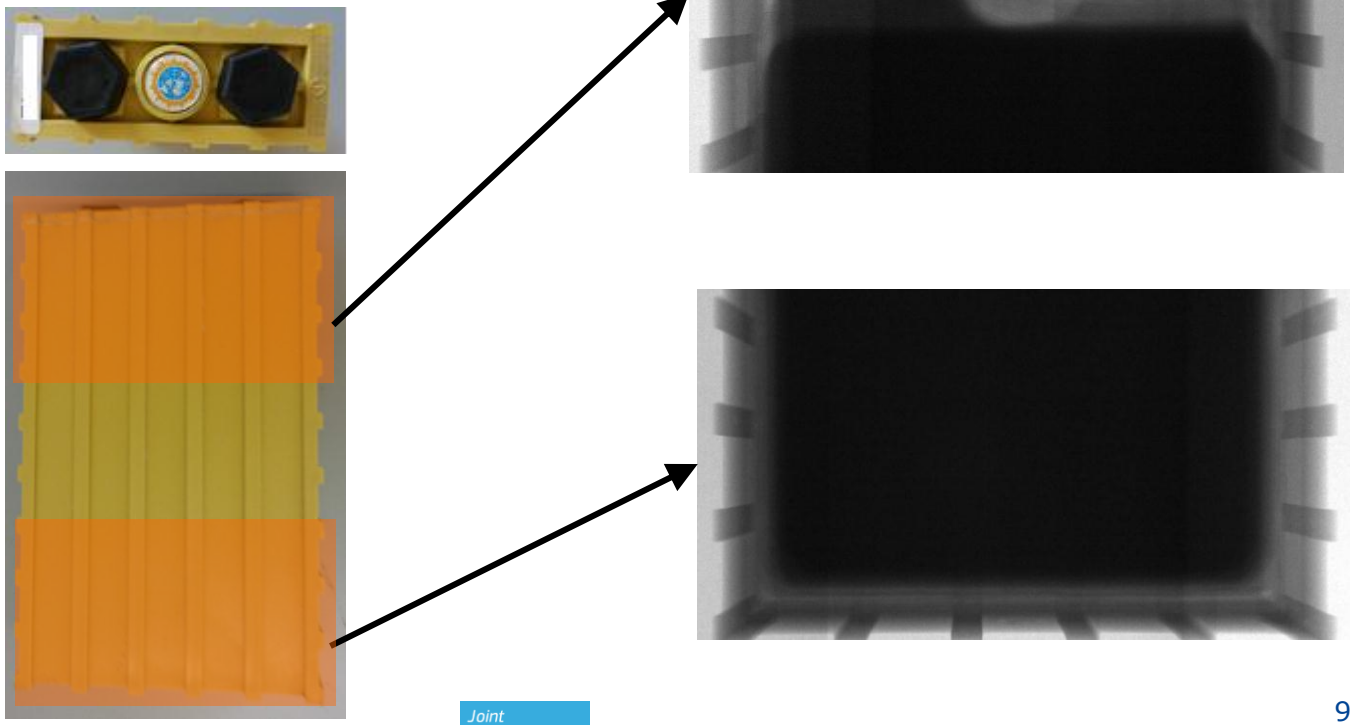
Type I cells (2 cells)
imaged in GE nanotom, 180 kW, 60 µA



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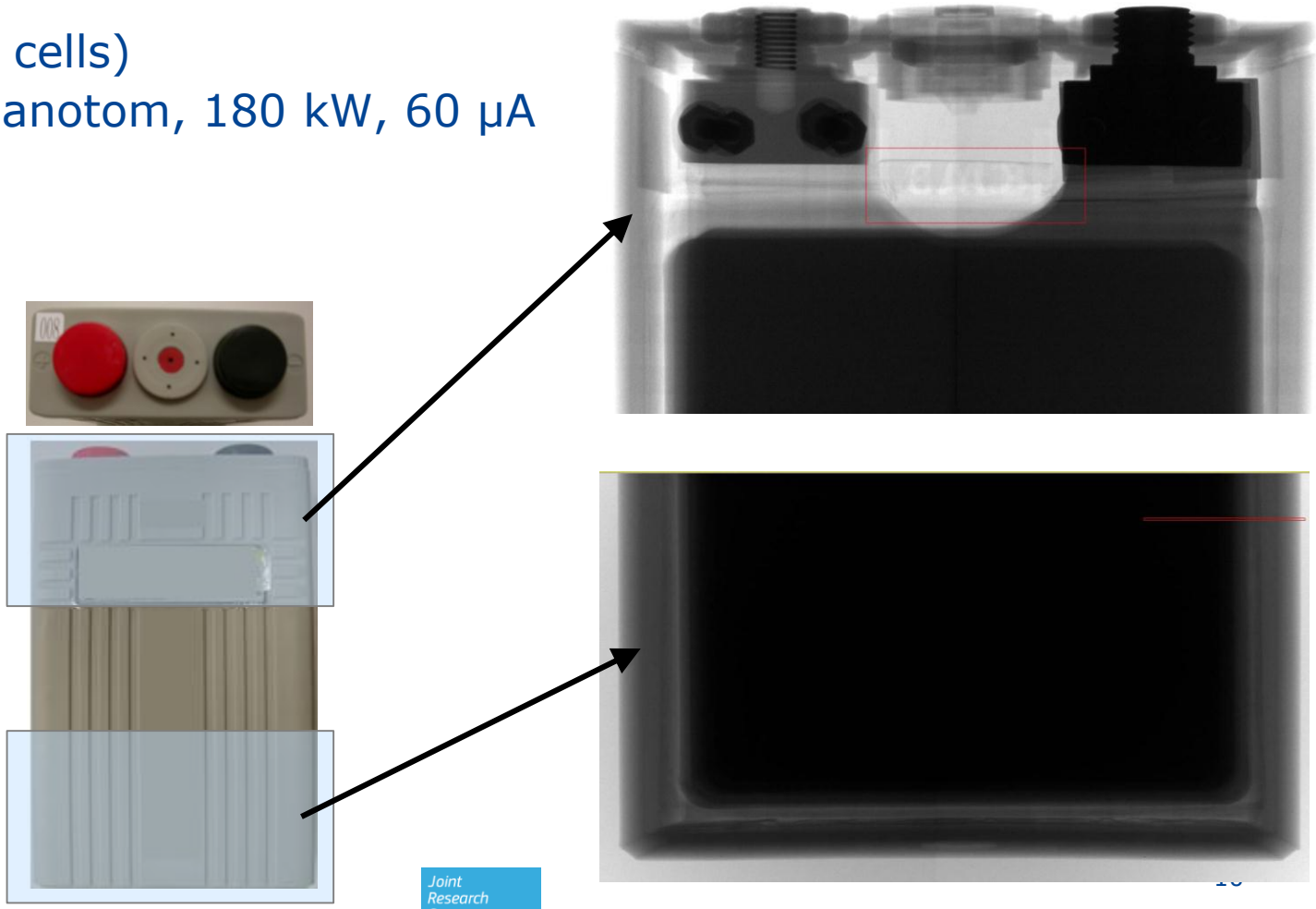

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