Detection of liquid electrolyte leakage by signalling the presence of Li ions

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April 2021

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Motivation

Experimental results - 8-Hydroxyquinoline

Future Work

Motivation

EVS GTR:
"…visual inspection without disassembling any part of the Tested-Device" is adopted in Phase 1 as a method for verification of the occurrence of electrolyte leakage and venting.

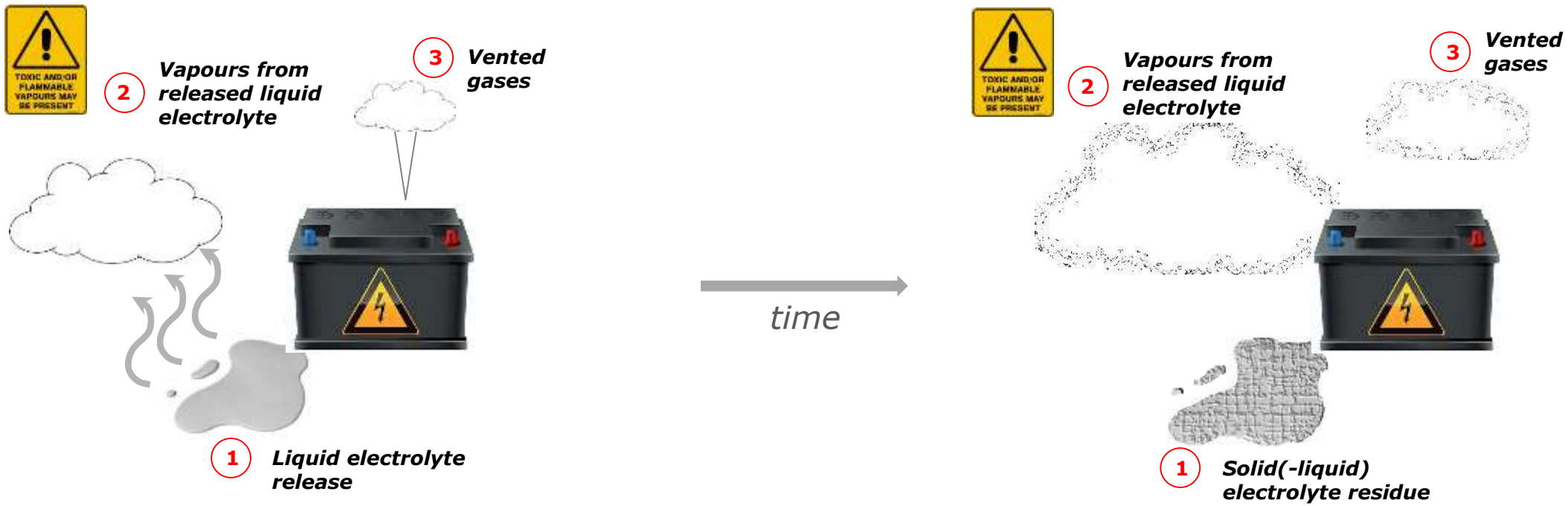
JRC concerns:

- Due to high volatility of some electrolyte components and limited release volume, electrolyte leakage and venting may not always be easily detectable, while potentially creating hazardous environment.
- Special measures may be required to ensure safety of inspecting personnel.
- Release of other substances, e.g. coolant, is currently treated equally to release of electrolyte.

6.1.6.2.6. Electrolyte leakage.

An appropriate coating, if necessary, may be applied to the physical protection (casing) in order to confirm if there is any electrolyte leakage from the REESS resulting from the test. Unless the manufacturer provides a means to differentiate between the leakage of different liquids, all liquid leakage shall be considered as the electrolyte.

Introduction



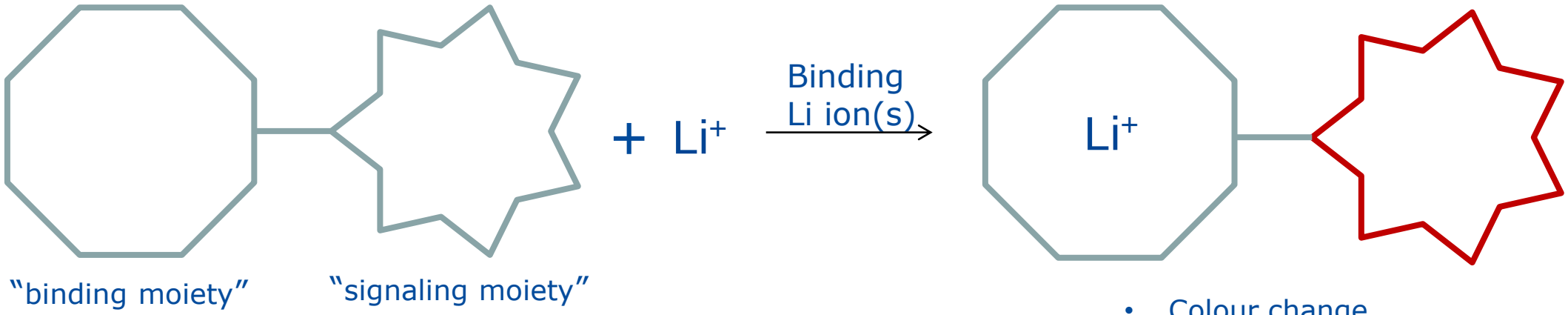
Possible approaches for detection of electrolyte release

1 Detection of Li-ion presence

2 + 3 Gas detection

8-Hydroxyquinoline (8-HQ)

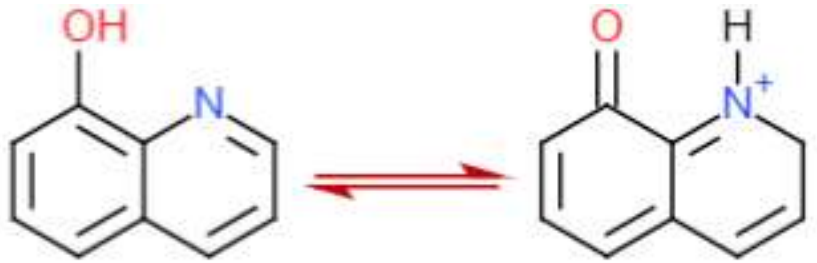
Chemosensor – molecule able to simultaneously bind and signal the presence of other species[a].



- Colour change
- Fluorescence change

[a] *F. Pina et al, J. Photochem. Photobiol. A, 126 (1999), 65-69*

8-Hydroxyquinoline (8-HQ)



Second most important chelating agent, after EDTA.[b]

Bifunctional H-donor (-OH) and H-acceptor (N).

Bidentate ligand capable of complexing various metal ions forming a five-membered inner complex ring, by H replacement.

Fluoresces with **greenish** light upon UV excitation…

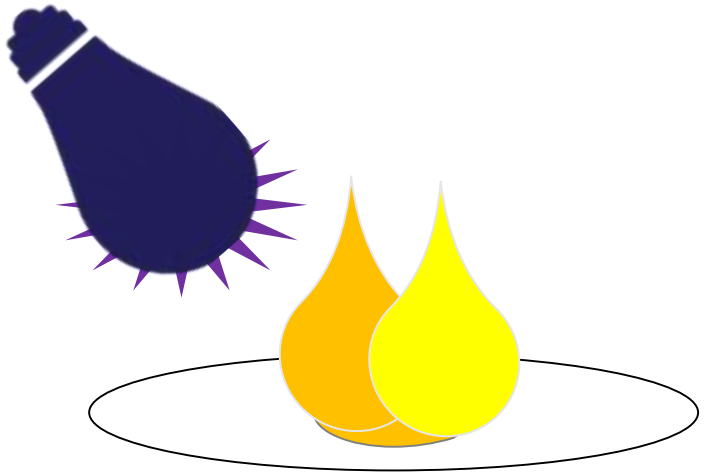
…but not with sodium (Na^+) or potassium (K^+)!!![c]

[b] *B. Valeur, I Leray, Coord. Chem. Rev., 205 (2000) 3–40*

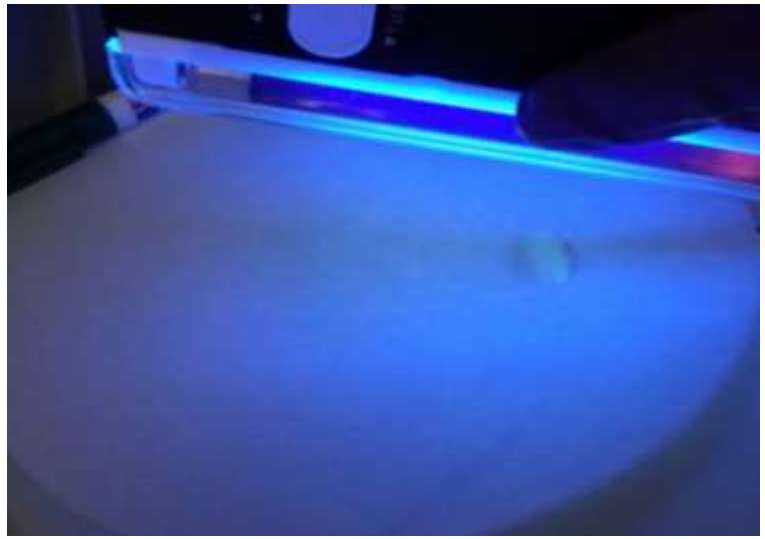
[c] *N.B. Hansen, Mikrochim Acta, 80 (1983) 277–285*

Experimental Results: 8-Hydroxyquinoline (8-HQ)

Does it work with electrolyte?



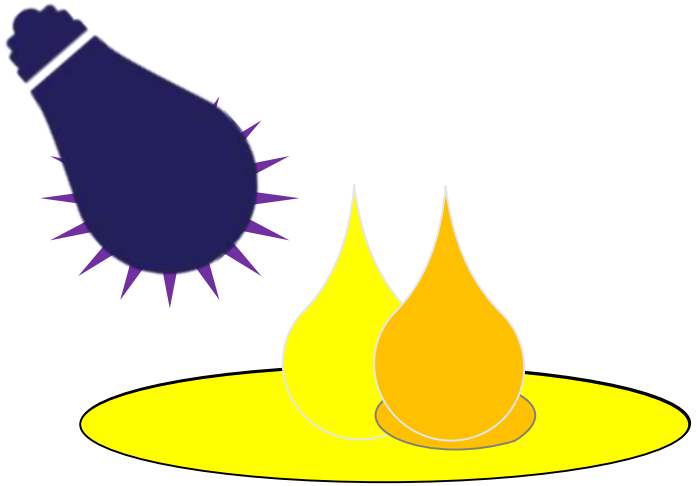
Droplet of electrolyte was placed on filter paper, then droplet of 8-HQ added to the same spot

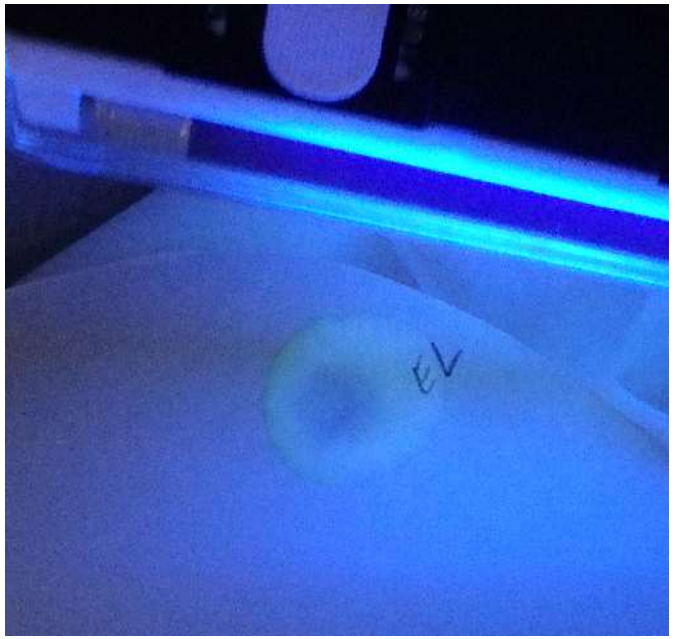


After ca. 5 min green fluorescence was visible upon exposure of the spot to UV light

Electrolyte
8-HQ solution in Ethanol
UV-Light

Experimental Results: 8-Hydroxyquinoline





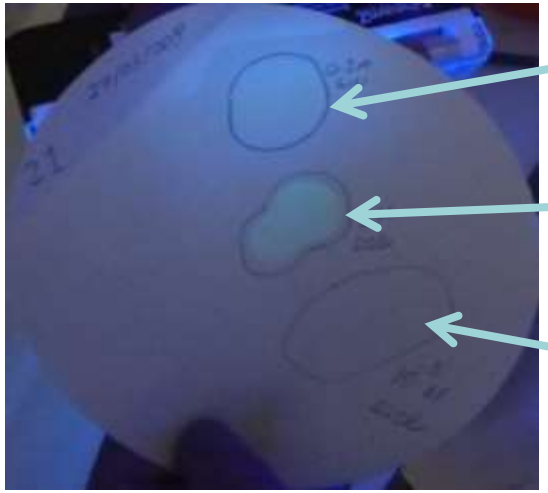
Filter paper was pre-treated with 8-HQ and allowed to dry at RT overnight, then droplet of electrolyte was added to the 8-HQ pre-treated paper

After ca. 5 min green fluorescence was visible upon exposure of the spot to UV light

Electrolyte
8-HQ solution in Ethanol
UV-Light

Experimental Results: 8-HQ - sensitivity

Fluorescence is Li-ion concentration dependent.



10^{-1} M (LiCl in EtOH)

1 M (LiCl in EtOH)

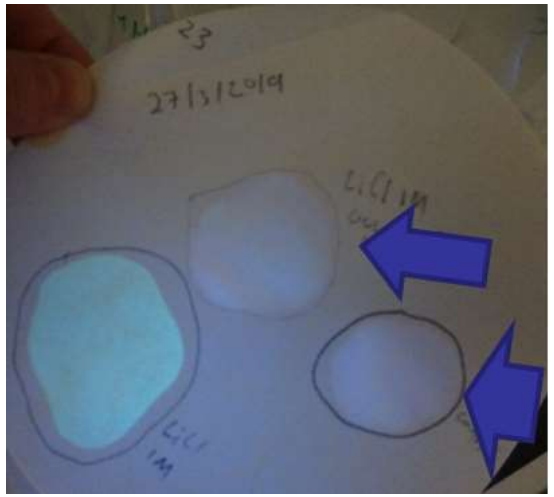
10^{-3} M (LiCl in EtOH)

10^{-3} M not visible!

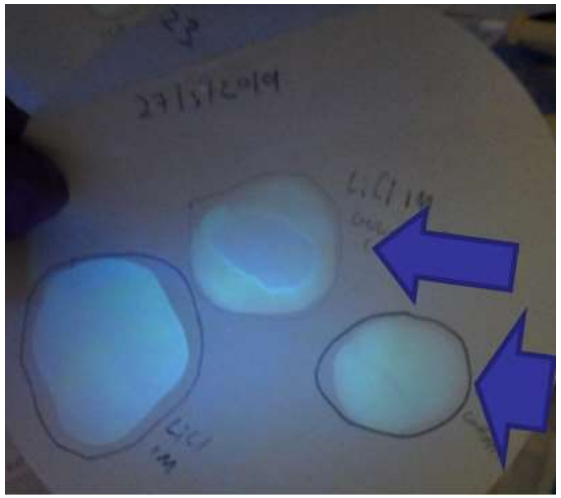
In case of failure, the mixing of electrolyte (few ml, typically 1M) and coolant (up to 10 l), can lead to Li-ion concentrations in the 10^{-4} M to 10^{-3} M range.

Experimental Results: 8-HQ - interferences

From EVS GTR 6.1.6.2.6.
"Unless the manufacturer provides a means to differentiate between the leakage of different liquids, all liquid leakage shall be considered as the electrolyte."

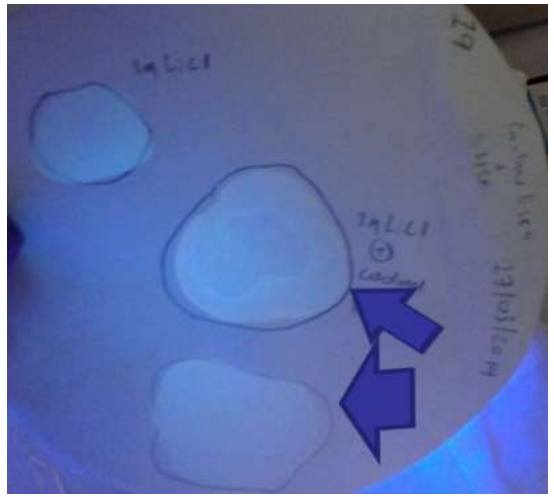


1 M LiCl (left); Coolant A(right); Coolant A +1M LiCl (middle)



1 M LiCl (left); Coolant A (right); Coolant A + 1M LiCl, after 2 months

1 M LiCl (left); Coolant B (right); Coolant B + 1M LiCl



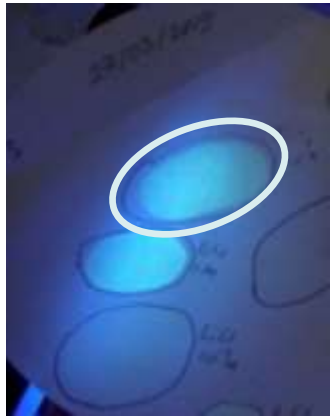
1 M LiCl (left); Coolant B (right); Coolant B + 1M LiCl, after 2 months

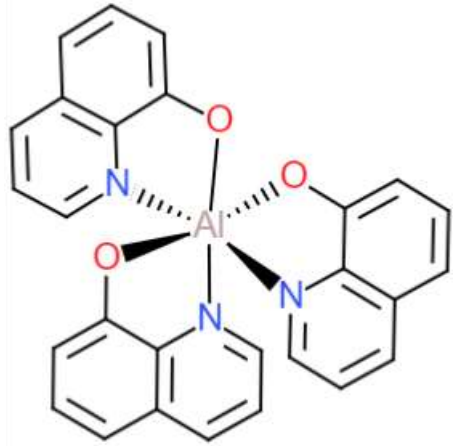
Coolants are fluorescent!

Experimental Results: 8-HQ - specificity

Experimental result: 0,1M $MgCl_2$ in EtOH vs 1M LiCl in EtOH.

Not Li specific!





Experimental result: 0,1M AlCl3 in EtOH vs 1M LiCl in EtOH.

BUT from our ICP-MS results we know coolants do not contain a significant amount of interfering cations

Experimental Results: 8-HQ – Coolant Composition

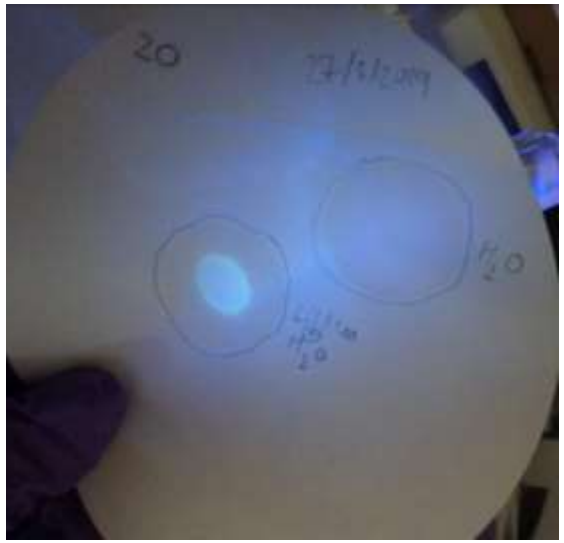
Element	Concentration in ppm	
	Coolant A	Coolant B
Al	1.3	1.3
Ba	0.039	0.028
Ca	20	31
Fe	0.24	0.094
K	310	360
Li	0.26	< 0.08
Mg	18	22
Mn	0.059	0.0099
Mo	0.14	0.077
Na	3800	4400
Ti	0.026	< 0.02
Zn	0.073	0.068

1M $[Li^+]$ = 6941 ppm

Experimental Results: 8-HQ - interferences

Fluorescence of a 8-HQ-treated filter paper after addition of water (right spot) and water followed by addition of 1 M LiCl to a 8-HQ-treated filter paper (left spot) upon illumination with UV light.

Quenched by water

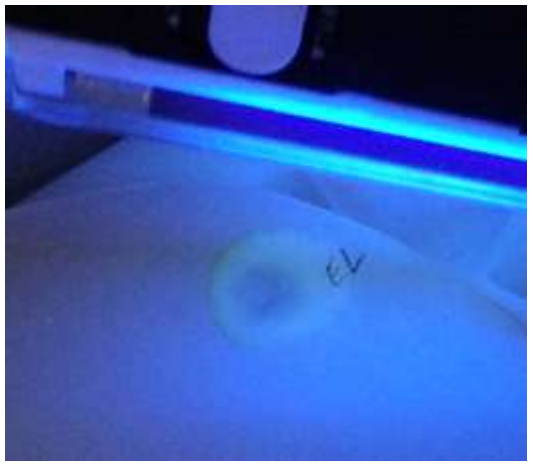


Same filter paper 2 months after the test. Drying of the paper increases the fluorescence of the LiCl spot.

Experimental Results: 8-HQ - Summary

Proof of concept:

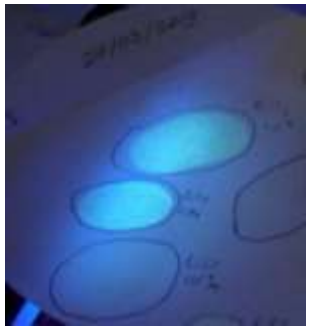
- use of 8-HQ can help detecting Li-ion battery electrolyte release
- a coating based on 8-HQ treated filter paper was demonstrated



Low sensitivity

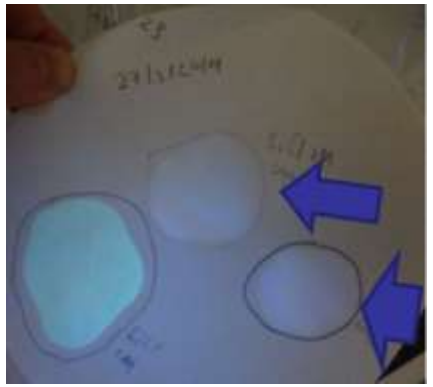
EXPERIMENTAL CONDITIONS
Detector: human eye.
UV Source: handheld dispersive lamp.
Sample holder: coating around the pack.

Quenched by water



Not Li specific

Coolants are fluorescent



Future Work - Selective Li(-i)on Hunters

Future Work

8-Hydroxyquinoline	Ideal Chemosensor
Not Li-ion selective	Li-ion selective
Fluorescence indistiguishable from coolants	Ideally change of visible colour
Low sensitivity under experimental conditions	High sensitivity under experimental conditions
Quenched by water	Not solvent or pH sensitive
Commercially available	Commercially available

Thank you

European Commission