Abstract B10-1217

Diagnostic of Li-ion commercial cells, case study

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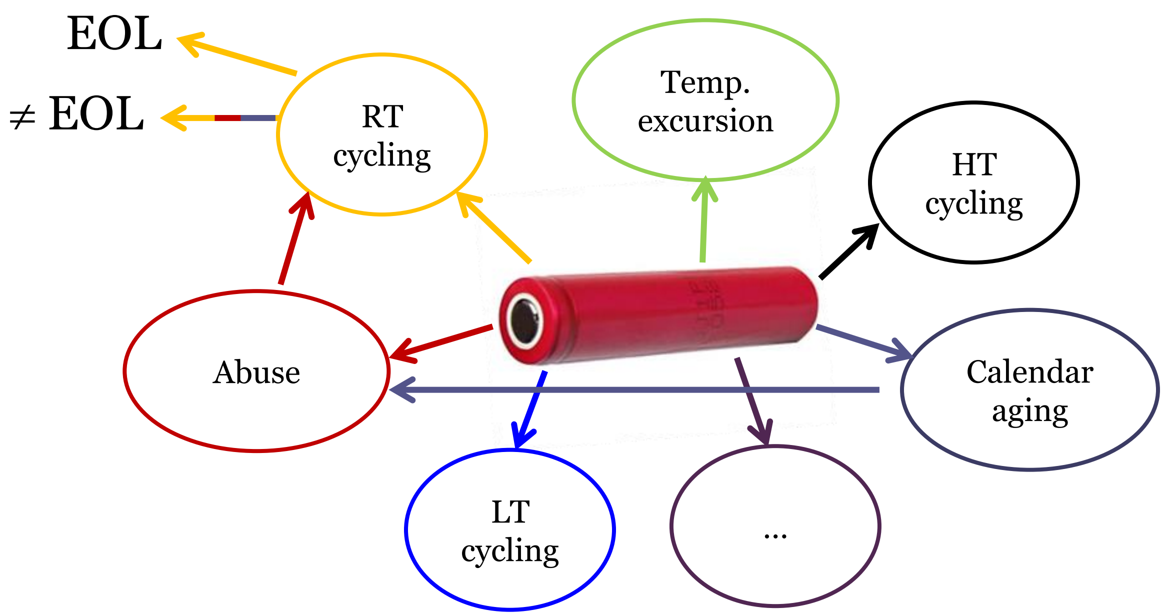
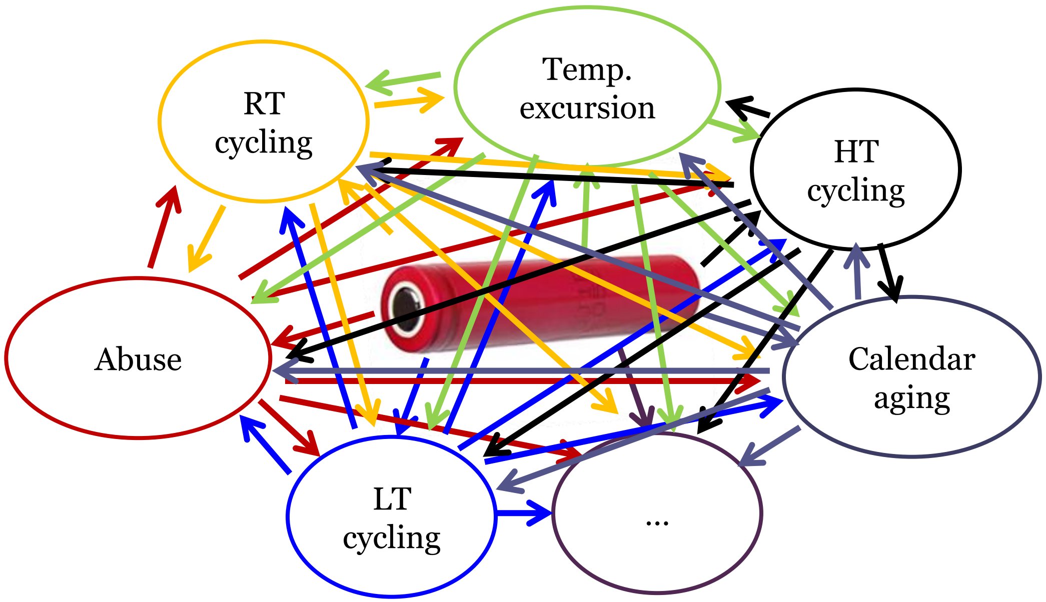
Objectives and motivations

To diagnose and predict battery behavior is challenging, mainly because degradation is path-dependent



Objectives and motivations

To diagnose and predict battery behavior is challenging, mainly because degradation is path-dependent



Laboratory testing cannot replicate the complexity of real usage.

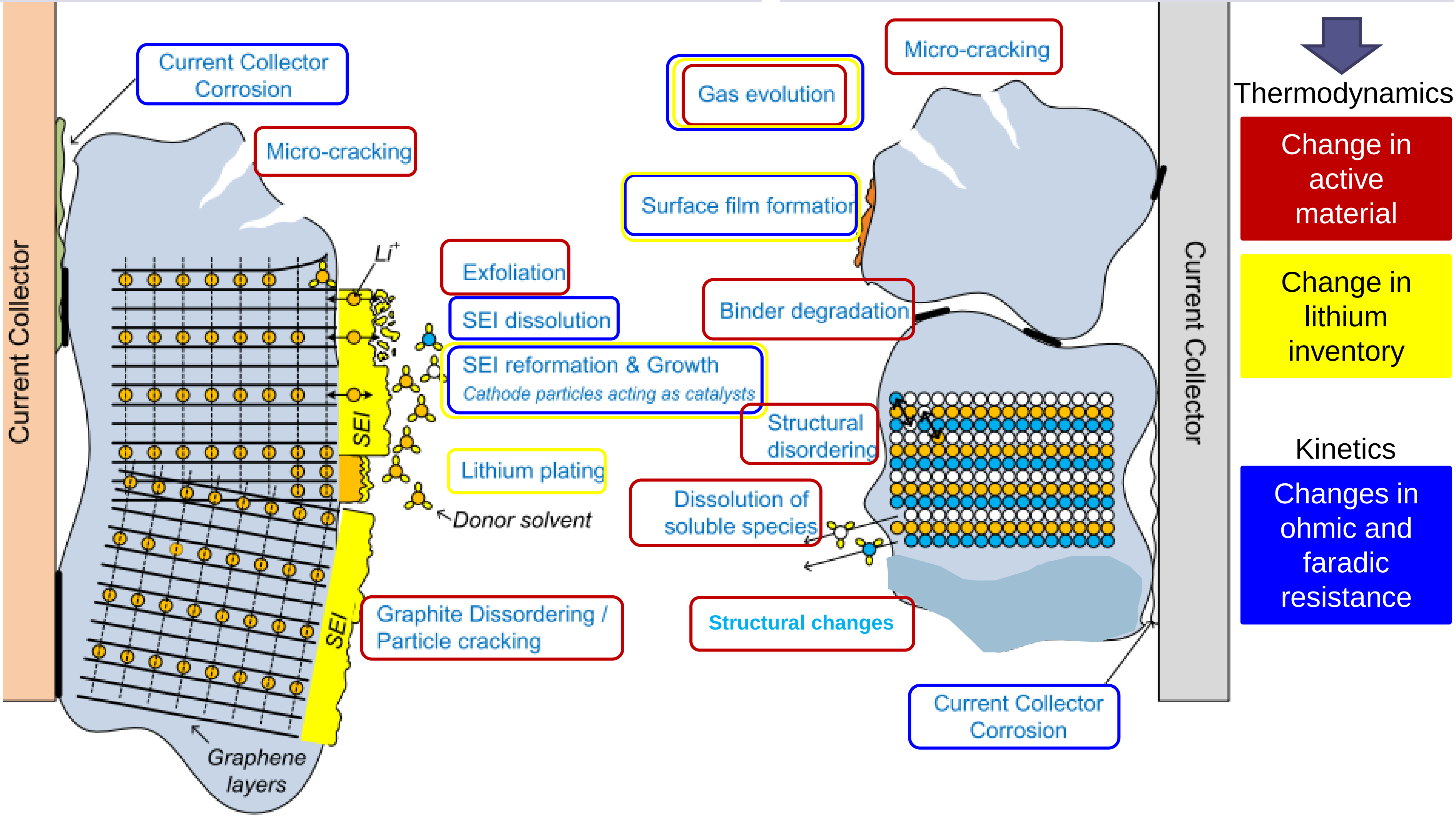
Need proper tools to understand, diagnose and predict cell behavior under conditions or variations in history (causality)

A prerequisite: Ability to synthesize battery degradation from different modes and sequences (A high fidelity mechanistic model)

Degradation Mechanisms:
Physical Characterization vs. EC Inference

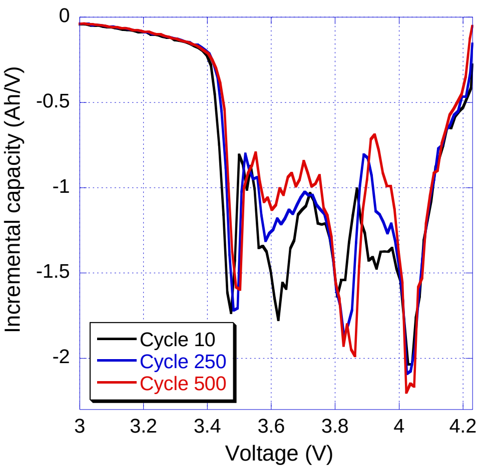
Physical characterizations: Identify fading modes but difficult to provide an overall quantification

Diagnostics: Tracking and quantifying the three fading modes through battery life



Adapted from: J. Groot, State of Health Estimation of Li-ion batteries cycle life test methods, 2011

Basis for diagnostics of cell degradation



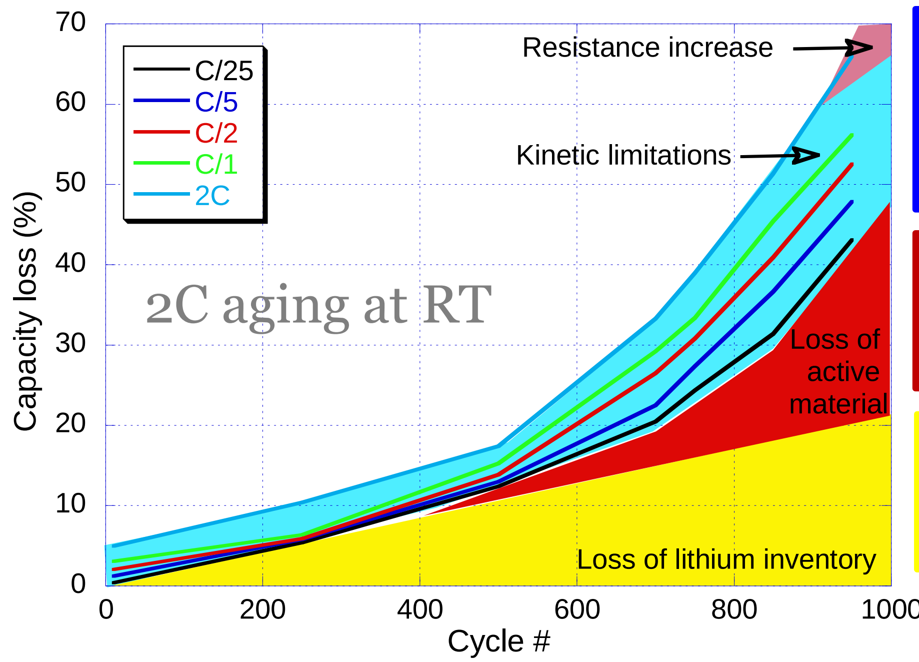
Incremental capacity curves evolution

Dubarry et al. *J. Power Sources* 196 (2011) 10336

Dubarry et al. J. Power Sources, 196(7), (2011) 3420

Dubarry et al. *J. Power Sources* 194 (2009) 551

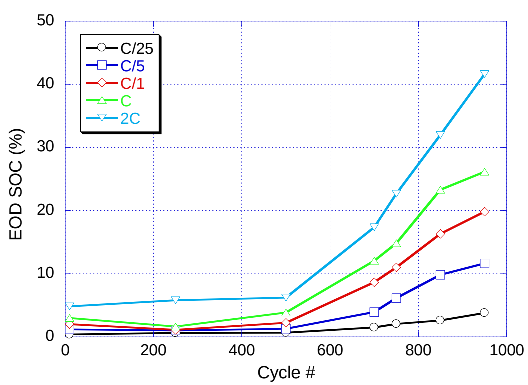
SOH tracking
+
SOC tracking



Change in ohmic and faradic resistances

Change in active material

Change in lithium inventory



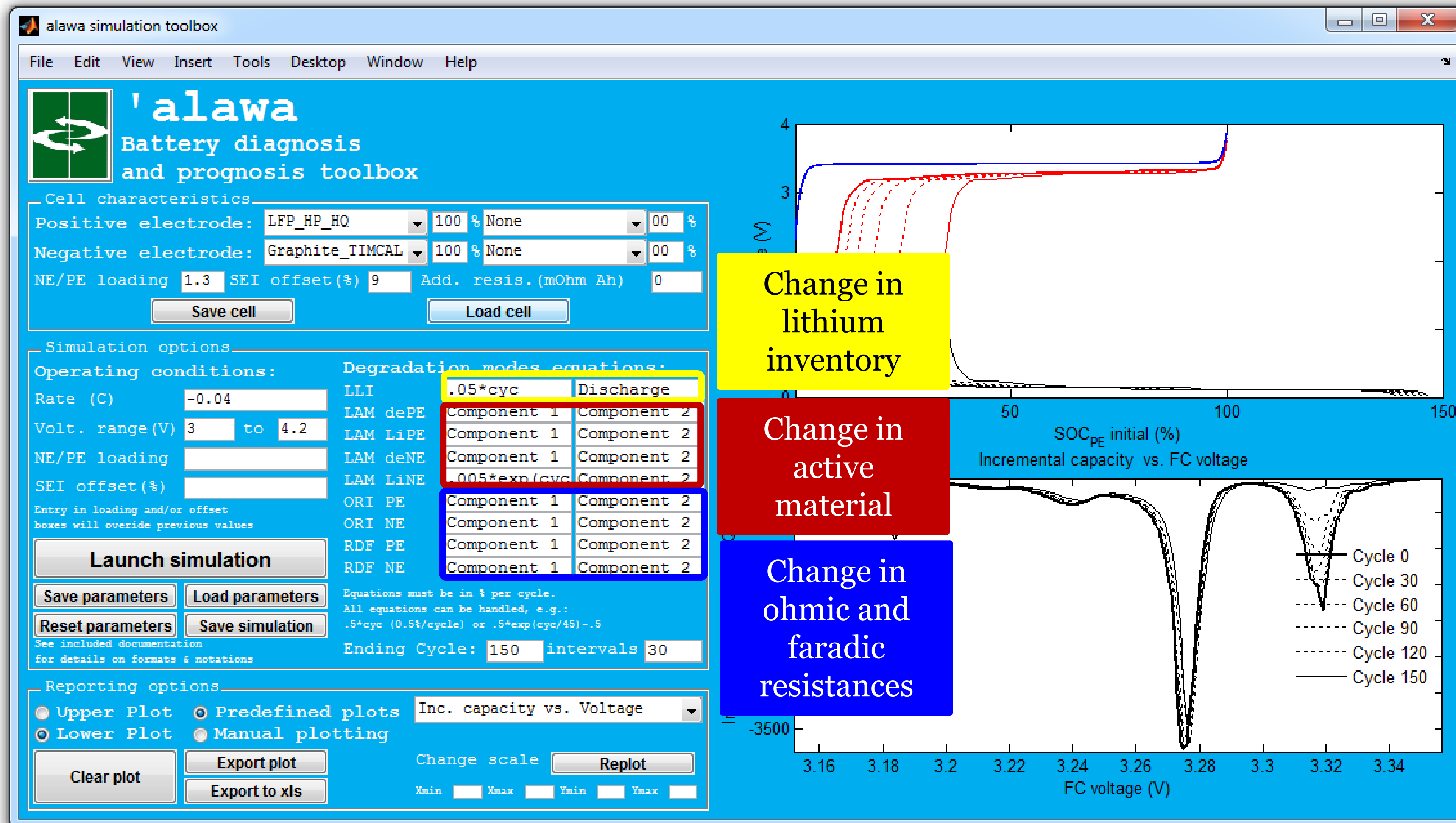
Rest cell voltages evolution

Variations might be complex and difficult to quantify
Need for a simple model to emulate them

Mechanistic Battery Diagnosis and Prognosis

Graphical User Interface: the ‘alawa toolbox

Simple, fast, powerful and accurate diagnosis and prognosis tool



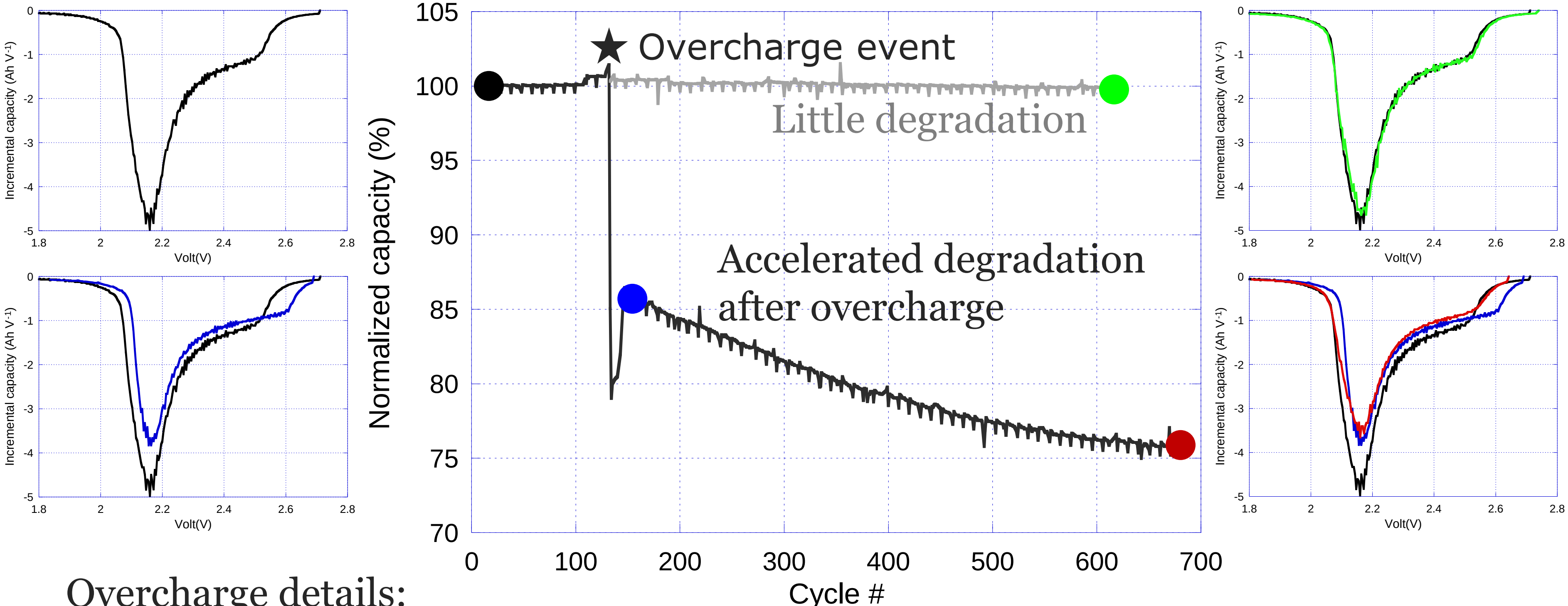
Stand alone GUI available for license or collaboration

Details in:
Dubarry, Truchot and Liaw, 219 (2012) 204-216

A case study

Commercial LTO//NMC cell

2 cells, regular C/3 cycling, 1 cell experienced 1 overcharge



Overcharge details:
On cycle 133 cell 1 overcharged 1 time to 3.6V instead of 2.8V.

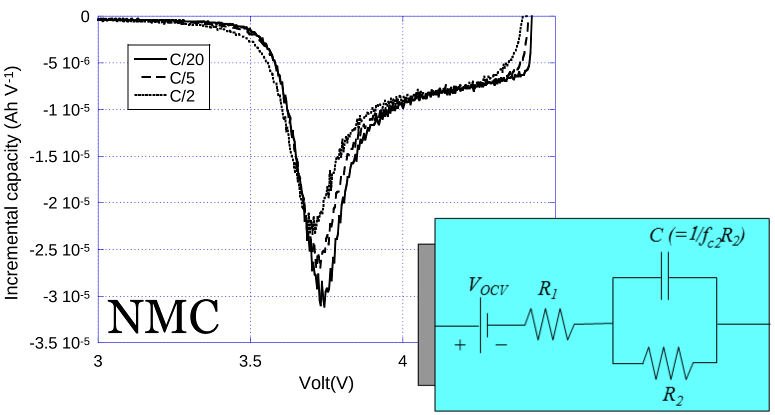
All IC (dQ/dV) curves are C/25 discharges

Effect of overcharge? Why faster degradation after?

IC curves evolution: use ‘alawa model to understand and quantify the fading modes

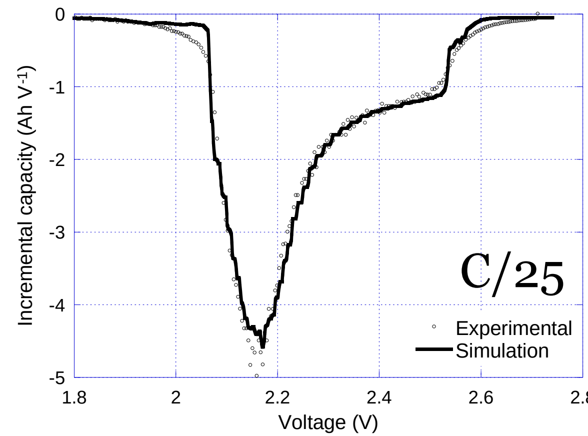
Mechanistic Model Construction

Half cell data obtained from commercial electrode sheets



V_{PE} (SOC_{PE})

Chemistry, rate, extent of rxn



Input from degradation mechanisms

Change in active material	Change in lithium inventory	Changes in ohmic and faradic resistance

Full cell module

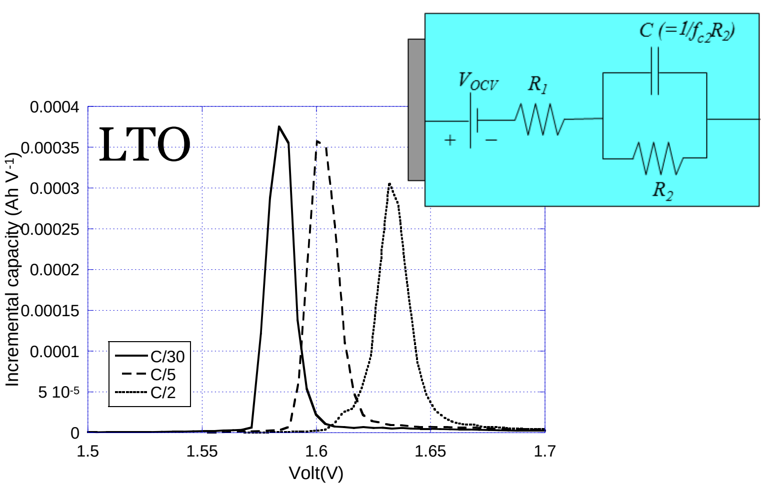
$$V_{FC} = V_{PE} - V_{NE}$$

$$V_{FC_{deg}} = V_{PE_{deg}} - V_{NE_{deg}}$$

Emulate every possible degradation mode and study effect on FC signature (capacity and voltage)

Chemistry, rate, extent of rxn

V_{NE} (SOC_{NE})

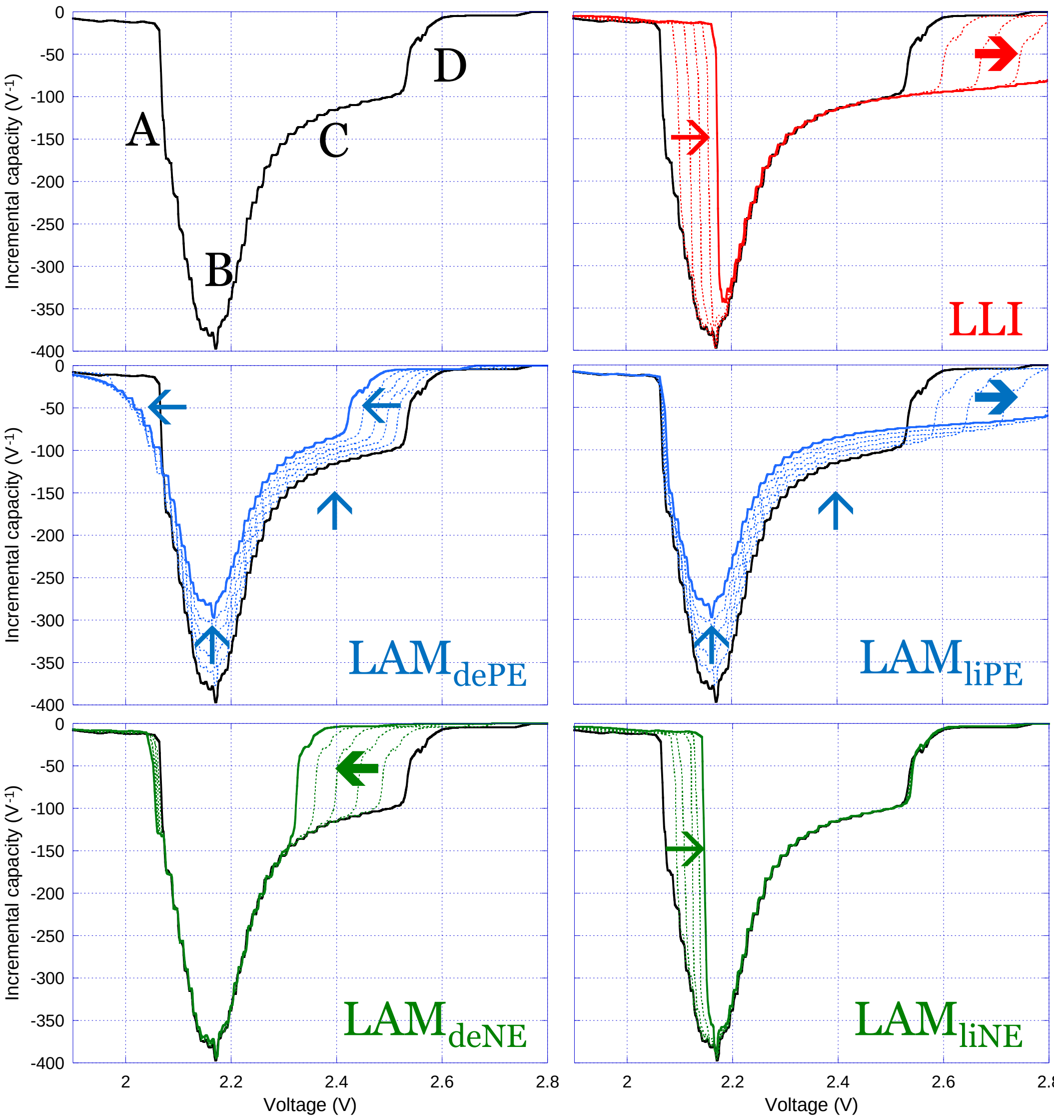


Details in: Dubarry, Truchot and Liaw, 219 (2012) 204-216

Diagnostics of a LTO//NMC commercial cell

Degradation Modes and Symptoms

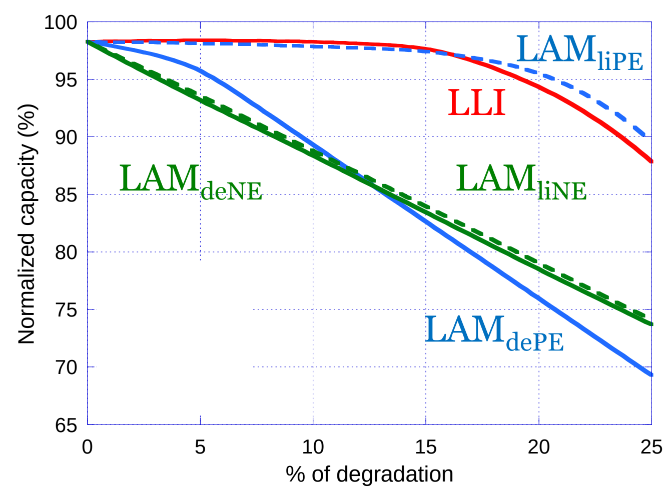
Symptoms: voltage & capacity evolution @ C/25



	A	B	C	D
LLI	→			→
LAM_{dePE}	←	↑	↑	←
LAM_{liPE}		↑	↑	→
LAM_{deNE}				←
LAM_{liNE}	→			

Symptoms from each mode can be unambiguously identified

Associated capacity evolutions:

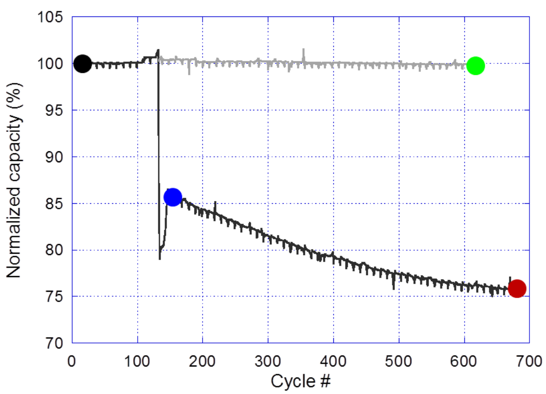


Diagnostics of a LTO//NMC commercial cell

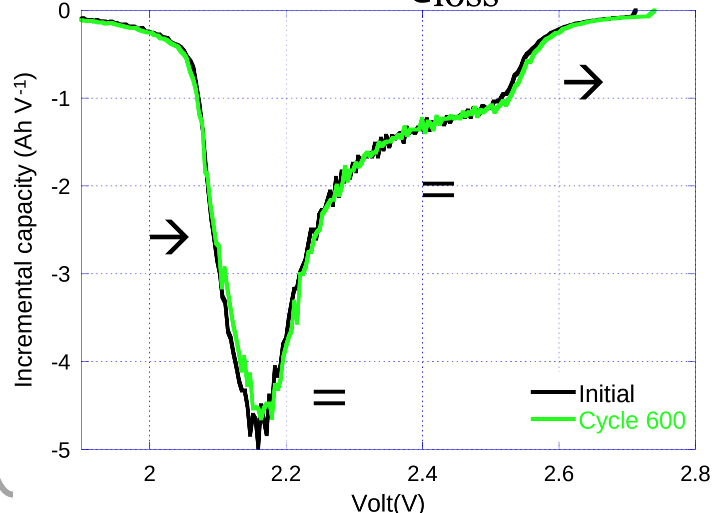
Experimental verifications

Regular cycling:
Slight loss of lithium inventory

Reference cell



Less than 1% Q_{loss} after 600 cycles



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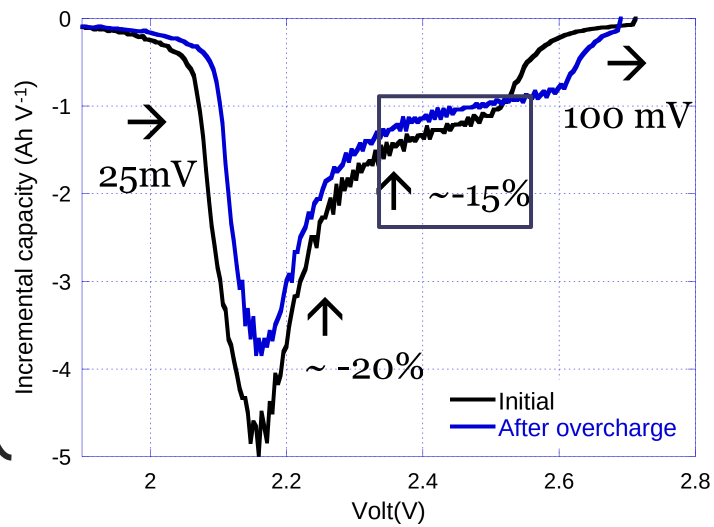
LAM_{dePE}	←	↑	↑	←
LAM_{liPE}		↑	↑	→
LAM_{deNE}				←
LAM_{liNE}	→			

Overcharged cell

15% Q_{loss} after overcharging event



	A	B	C	D
LLI	→			→
LAM_{dePE}	←	↑	↑	←
LAM_{liPE}		↑	↑	→
LAM_{deNE}				←
LAM_{liNE}	→			

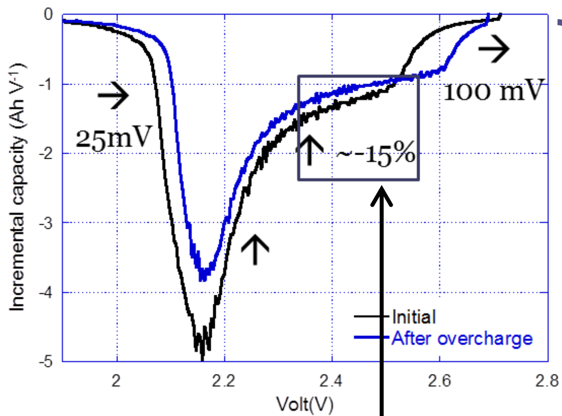
No single mode can explains all variations.

→ **15% LAM_{PE}**

→ **Multi-modes**

Diagnostics of a LTO//NMC commercial cell
Causality of Overcharge

Combination of multiple degradation mechanisms



	A	B	C	D
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LAM_{dePE}	←	↑	↑	←
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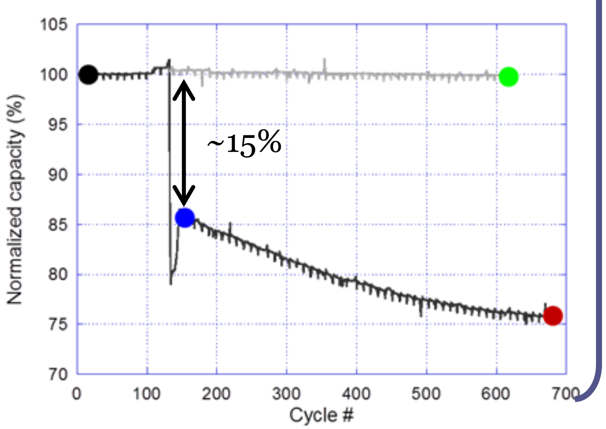
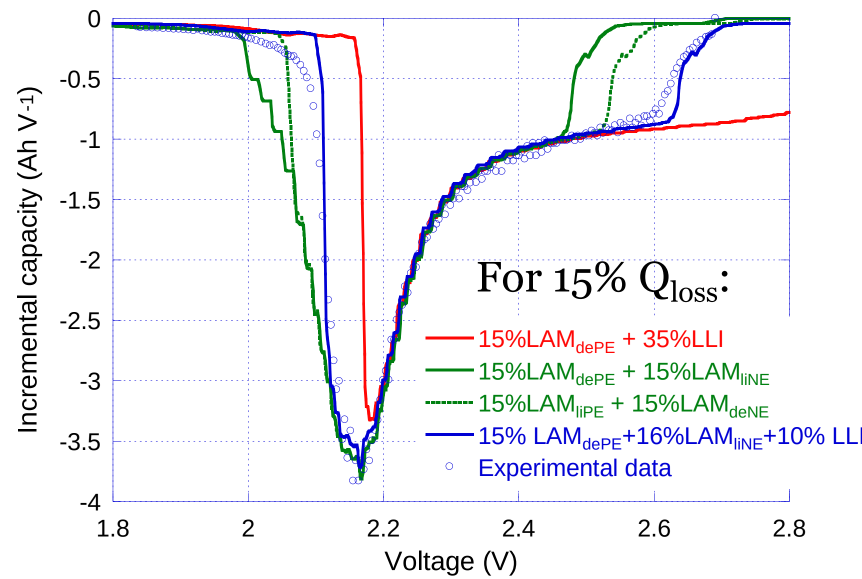


Multitude of combinations

Known:
15 % LAM_{PE} and 15% Q_{loss}

Unknown:
Quantify LLI
Quantify LAM_{NE}

To match Q_{loss} & shape



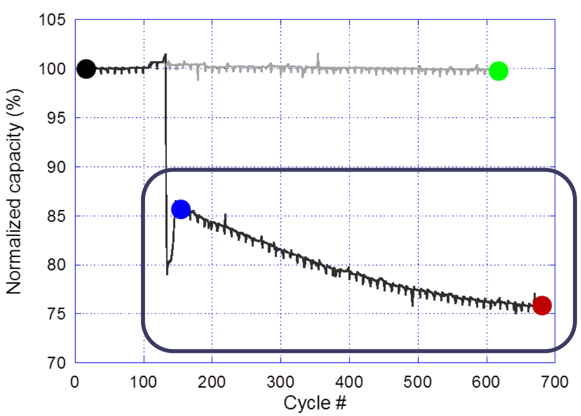
Only one combination gives the best fit

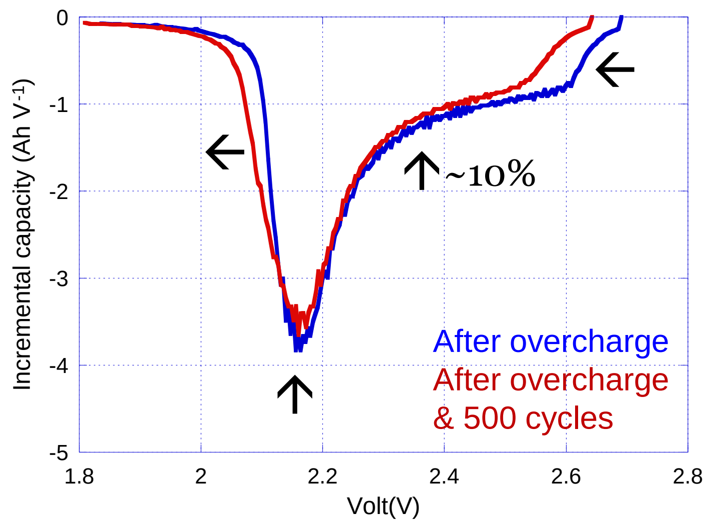
Overcharge induced **loss of active material** of same magnitude, ~15%, **on both electrodes** plus a 10% **loss of lithium inventory.**
Kinetics & resistance of the cell were not affected.

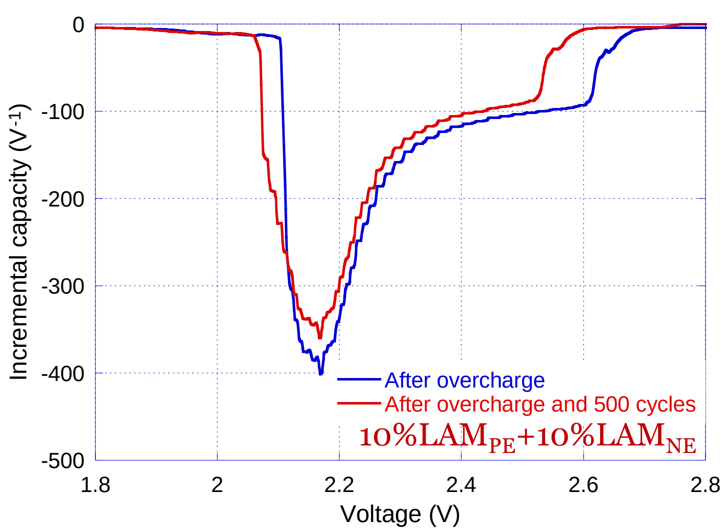
Diagnostics of a LTO//NMC commercial cell

Cycle Aging After the Overcharge

500 cycles, ~ 10% additional Q_{loss}







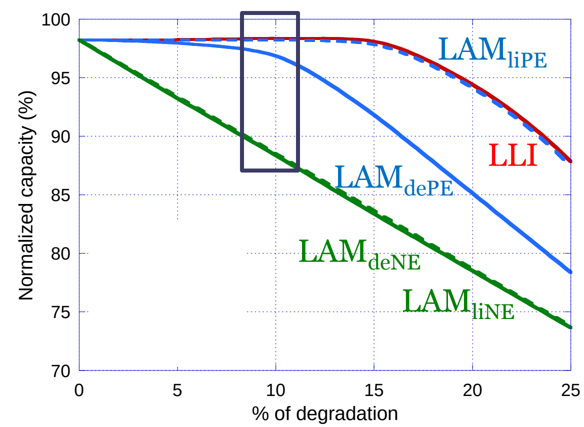
Overcharge permanently affects cell performance

Similar mode than of the overcharge event
10% Loss on each electrode

BUT Far less loss of lithium than of overcharge event:
~0.5%/1%AM vs.
~1.5%/1%AM
So probably no LLI at all

	A	B	C	D
LLI	→			→
LAM_{dePE}	←	↑	↑	←
LAM_{liPE}		↑	↑	→
LAM_{deNE}				←
LAM_{liNE}	→			

straight LAM_{dePE} ?



LAM_{PE} alone cannot explain Q_{loss}

Multi-mode degradation

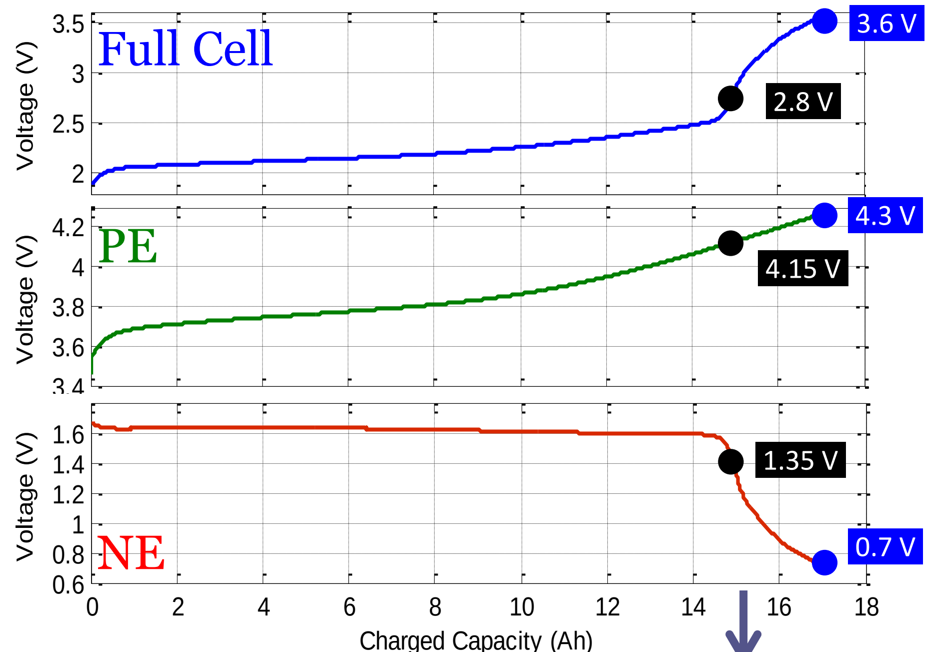
Only some LAM_{NE} can induce gradual Q_{loss}

Diagnostics of a LTO//NMC commercial cell

Observations of the Overcharge Phenomenon

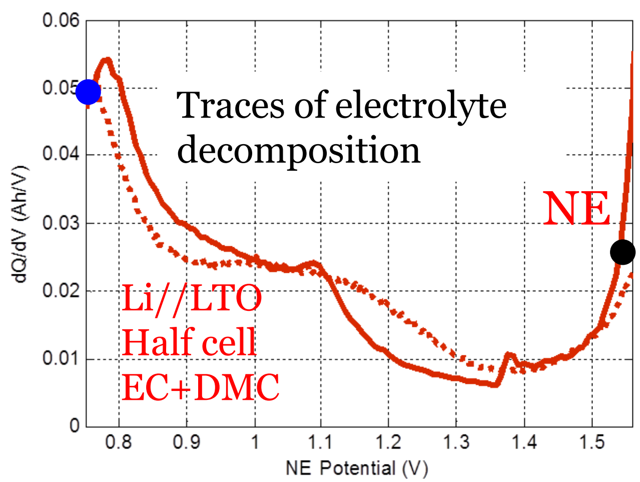
Overcharge Potential recorded

- NMC known at high voltage
  - Overcharged to extended composition range
    - NMC did not reach harmful potential
- LTO variation Calculated
  - LTO potential dropped to .7V vs. Li^+/Li^o
    - Unlikely for Li plating
    - Electrolyte decomposition?
  - Symptoms verified on half cell

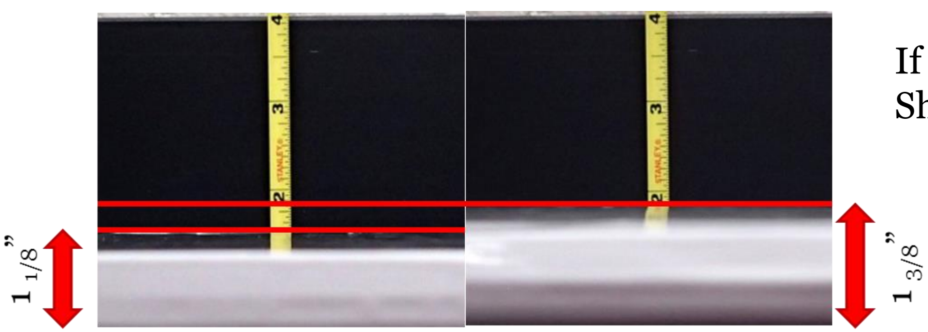


Overcharge resulted in significant **increase** of unconstrained pouch **cell thickness (+20%).**
Physical evidence of **gassing**
No evident of physical damage or Li plating

ICA on NE overdischarge



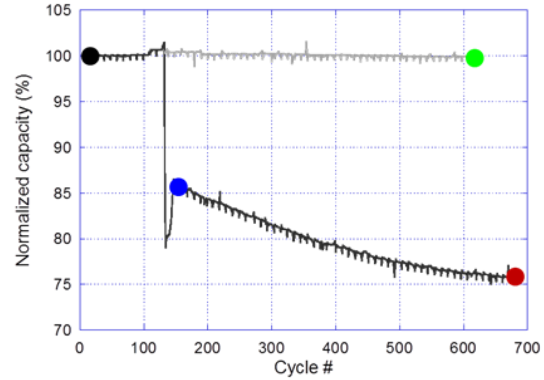
If decomposition Should be gassing



Conclusions

From overcharge IC analysis:
- 15% LAM on both electrodes
- 10% loss of lithium
- Electrolyte decomposition
- Gassing
- No electrodes damage or plating

From aftermath IC analysis:
- 10% LAM on both electrodes
- No evident loss of lithium
- Capacity fading slowing down



Possible scenario:

Electrolyte consumption → Cycling volume changes &/or pressure gradients → Moving towards a stable aged state?

Gassing

Altered contact between electrodes sheets
Similar LAM on both electrodes

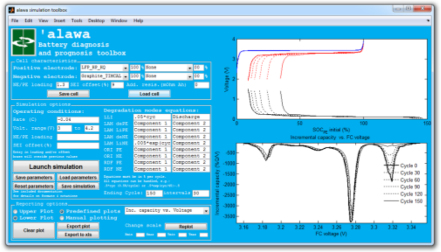
Solid residues
LLI by byproduct precipitation

Gas migration

Additional loss of contact
LAM on both electrodes

No additional decomposition
No more LLI

Less and less new contact loss
Less and less LAM
Slowing fading rate



Further validation in progress

Such analysis would not have been possible without the ‘alawa toolbox

With its degradation emulation:
- It allowed to exclude some degradation modes
- It allowed quantifying every present degradation mode

Acknowledgments

Mike Coleman (Altairnano) for half cell dat

Funding

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Mahalo for your attention! Questions ?

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Full publication list available on Google scholar

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