225th ECS Meeting

A2: Material and Electrode Designs for Energy Storage and Conversion
Battery Design and Application #A2-0209

Experimental diagnostic of Li-ion commercial cells, case studies : High power and High energy commercial GIC//LFP cells

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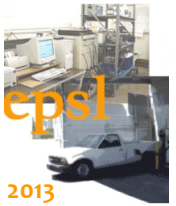
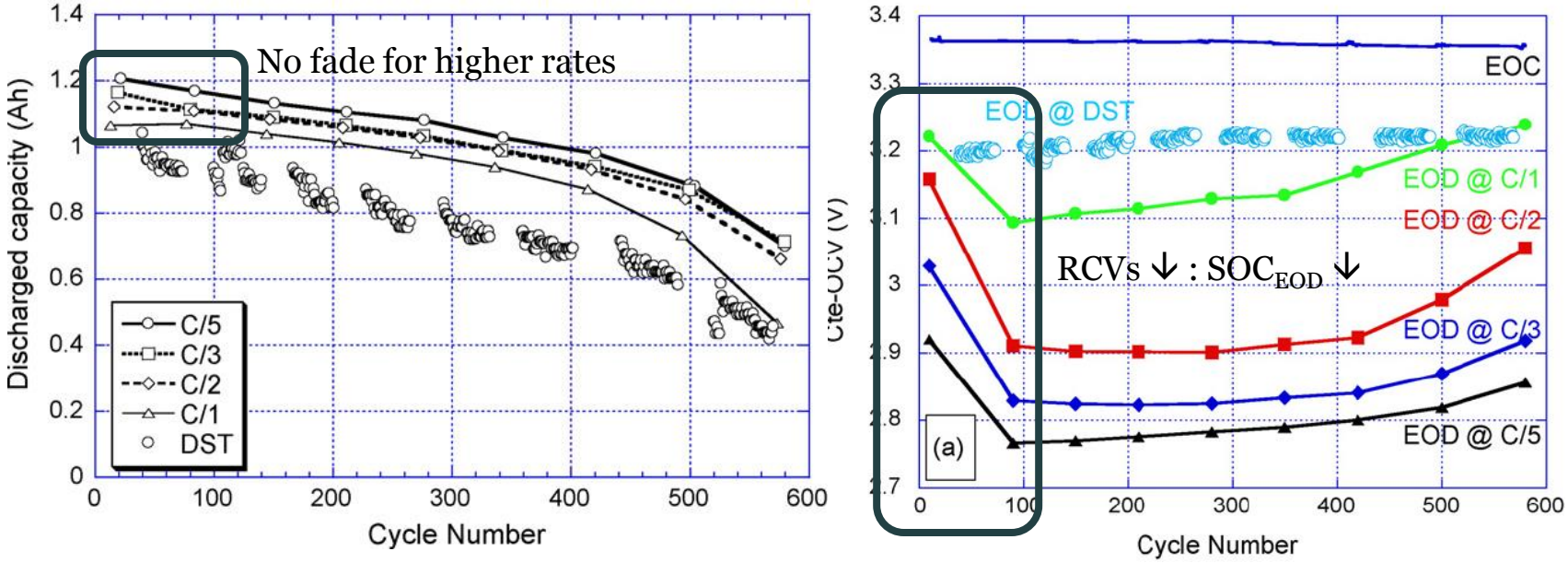


Objectives & Motivation

From a previous study, Journal of Power Sources 194 (2009) 541–549

A peculiar behavior was observed while cycling a HE GIC//LFP cell:

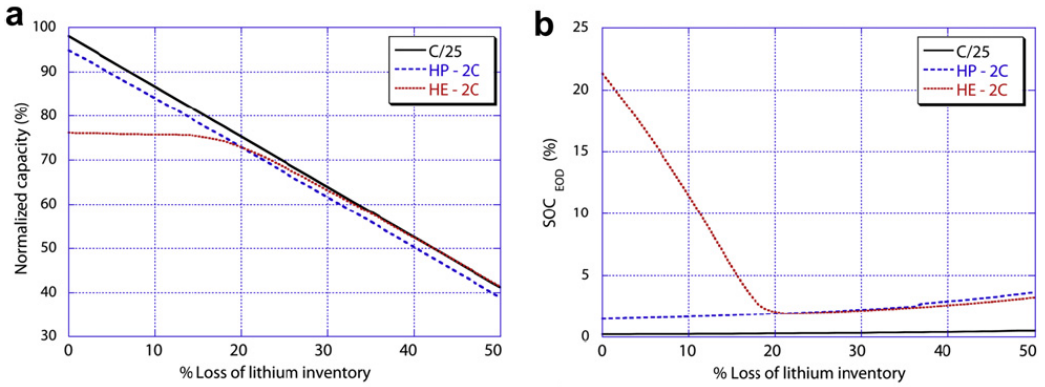


We speculated it was the result of a combination of LLI and a "reservoir effect" arisen from the loading matching between the PE and the NE.

As the discharge rate increases, a portion of the PE would not be fully utilized, freeing Li ions from the NE to compensate the LLI.

Objectives & Motivation

Mechanistic degradation simulation agrees and suggests that will only occur for HE type cells, not HP.

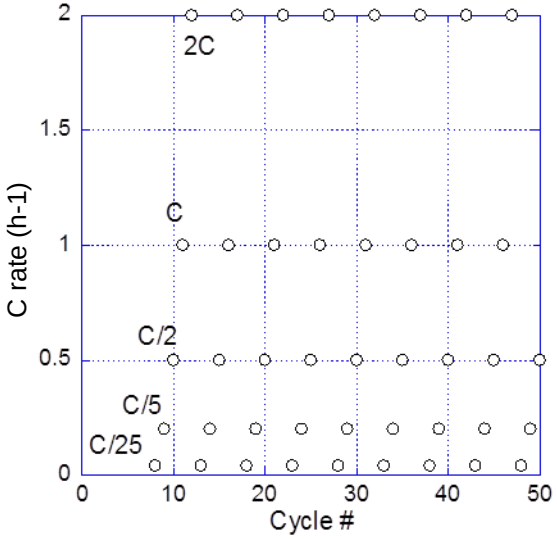


Journal of Power Sources 219 (2012) 204-216

This study aims to provide experimental validation

- HE and HP cells cycled with specially designed protocol
  - Step protocol to access evolution of capacity loss for rates from C/25 to 2C

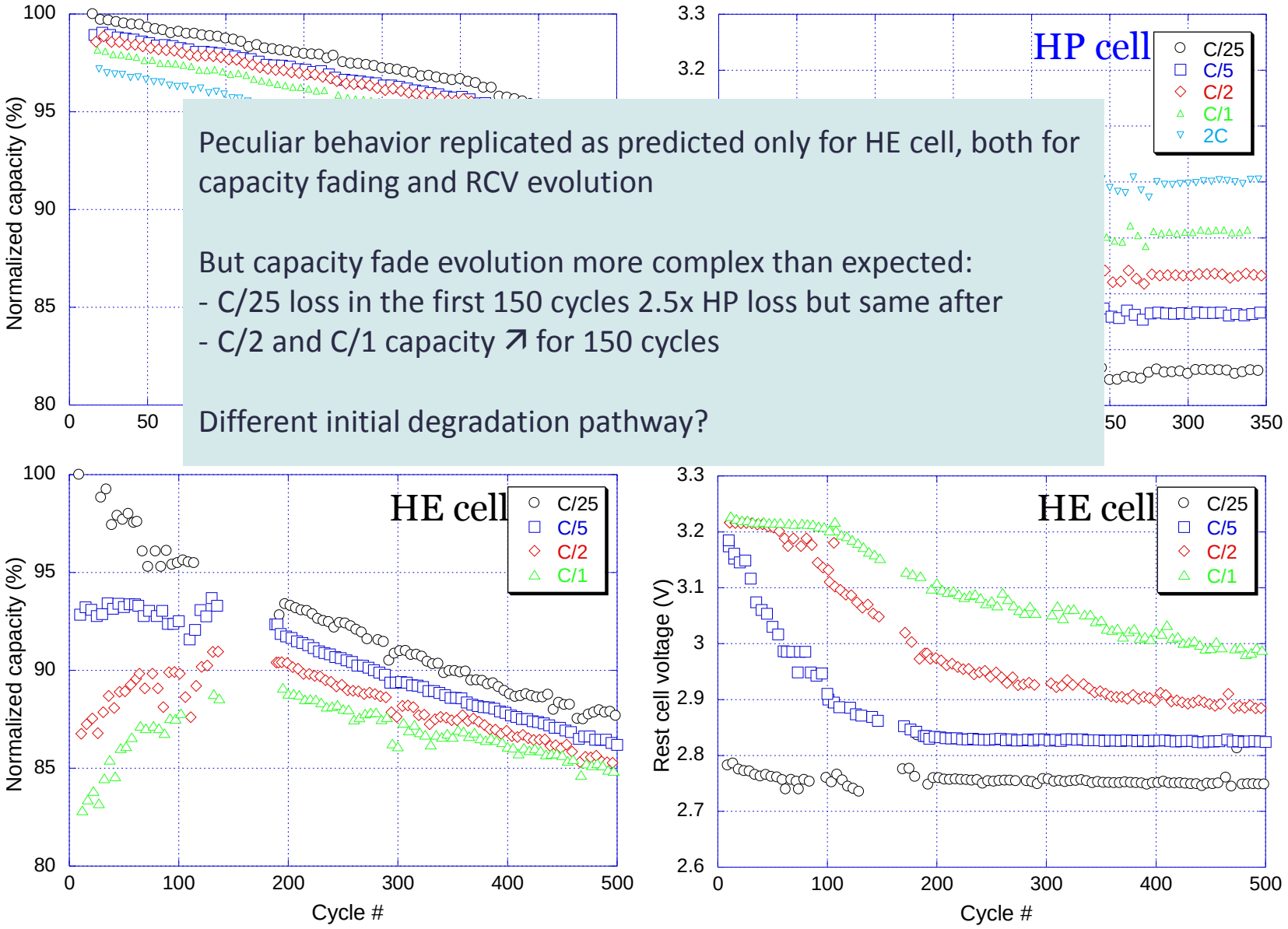
- Degradation mechanisms assessed from IC analysis and mechanistic emulation



Journal of Power Sources 258 (2014) 408-419

Aging of the cells

Capacity fading and rest cell voltages evolution



Peculiar behavior replicated as predicted only for HE cell, both for capacity fading and RCV evolution

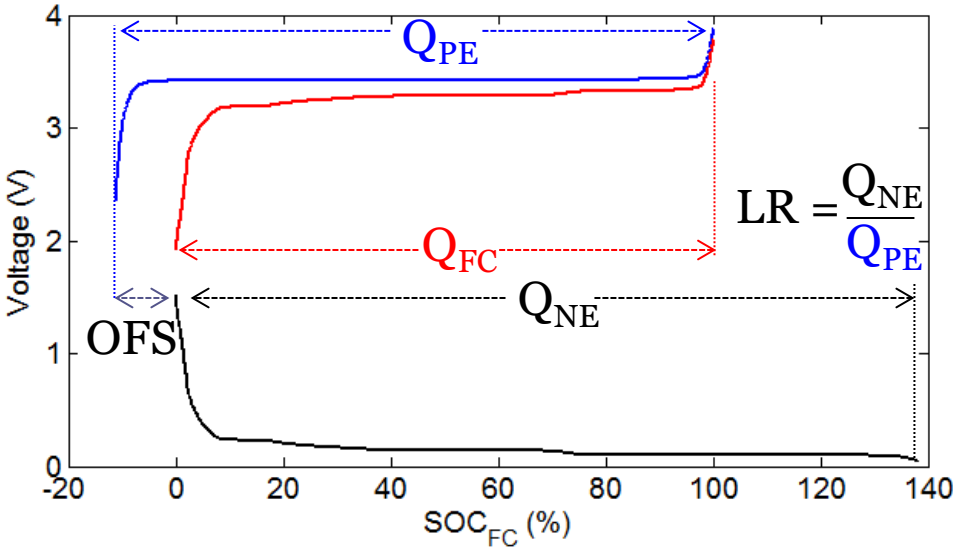
But capacity fade evolution more complex than expected:
- C/25 loss in the first 150 cycles 2.5x HP loss but same after
- C/2 and C/1 capacity ↗ for 150 cycles

Different initial degradation pathway?

Mechanistic emulation
The ‘alawa toolbox

Principles:

- OCV: 5 main degradation modes
  - Loss of active materials
    - On lithiated PE (LAM_{liPE})
    - On delithiated PE (LAM_{dePE})
    - On lithiated NE (LAM_{liNE})
    - On delithiated NE (LAM_{deNE})
  - Loss of lithium inventory (LLI)



Degradation modes affect thermodynamic properties differently:

Electrodes balance

$$LR = LR_{ini}\left(\frac{100\% - \%LAM_{deNE} - \%LAM_{liNE}}{100\% - \%LAM_{dePE} - \%LAM_{liPE}}\right)$$

Lithium ions balance

$$OFS = OFS_{ini} + LR \times \%LAM_{liNE} - \frac{LR}{LR_{ini}} \times \%LAM_{dePE} + \%LLI$$

Unique approach Allows simulations of voltage response (IC,DV,RCVs), capacity and power fading

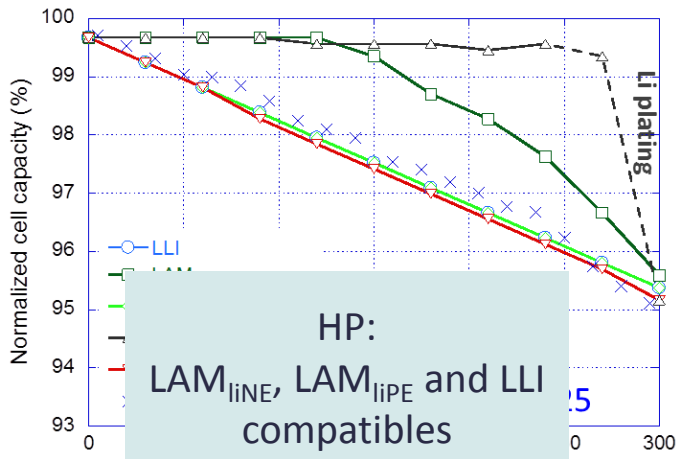
Details in Journal of Power Sources 219 (2012) 204-216

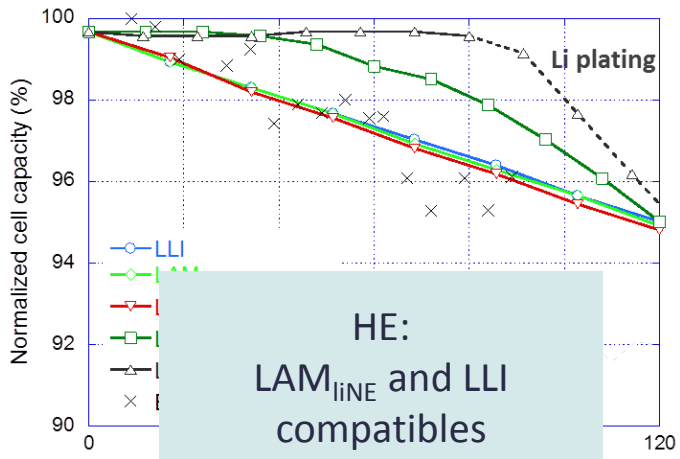
Focus on the first 5% capacity loss for both cells

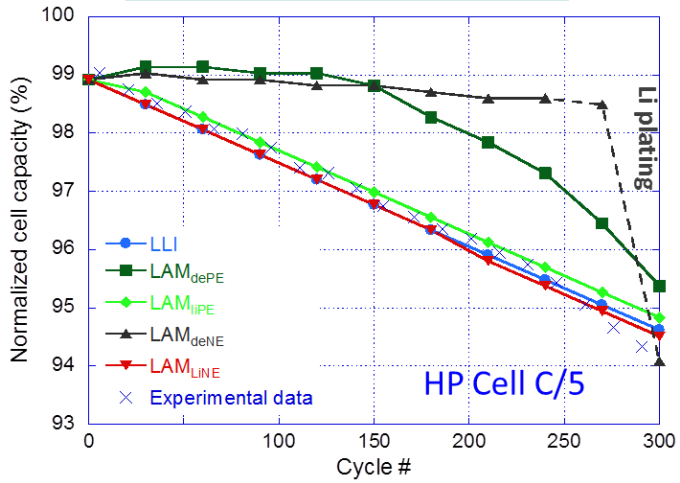
HP cell: 350 cycles, HE cell: 150 cycles

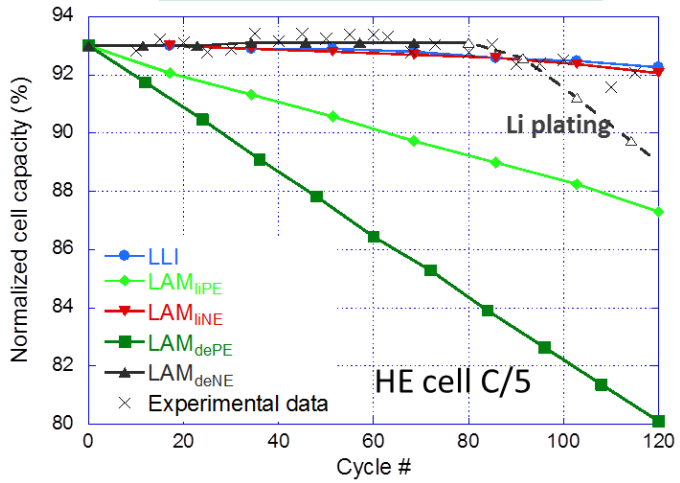
Use of mechanistic emulation: the ‘alawa toolbox

Capacity loss (assuming linear degradation for each mode):









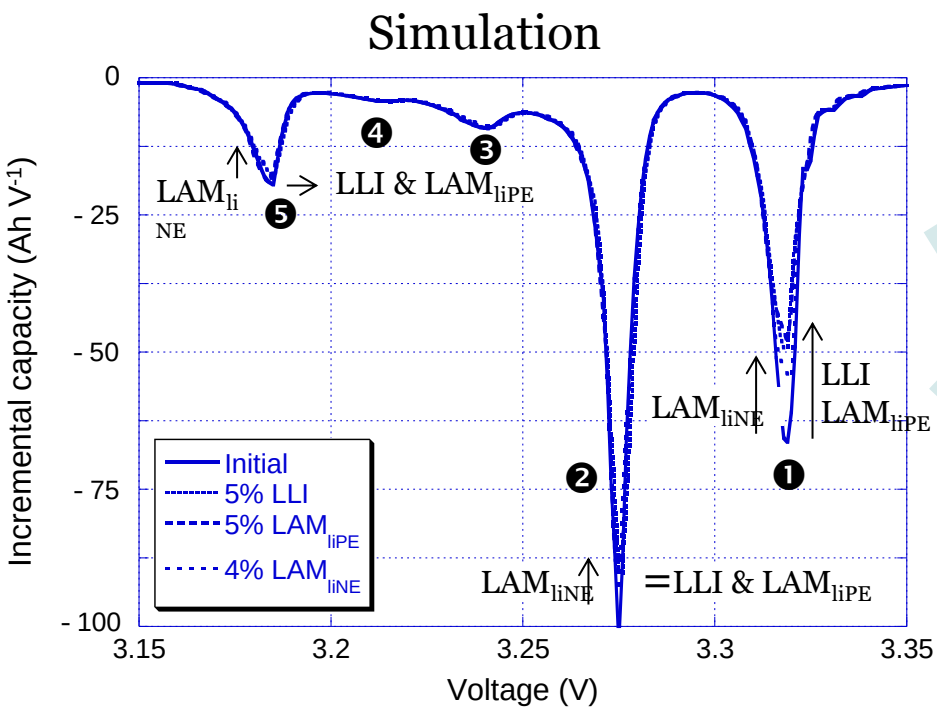
Simulations details in Journal of Power Sources 258 (2014) 408-419

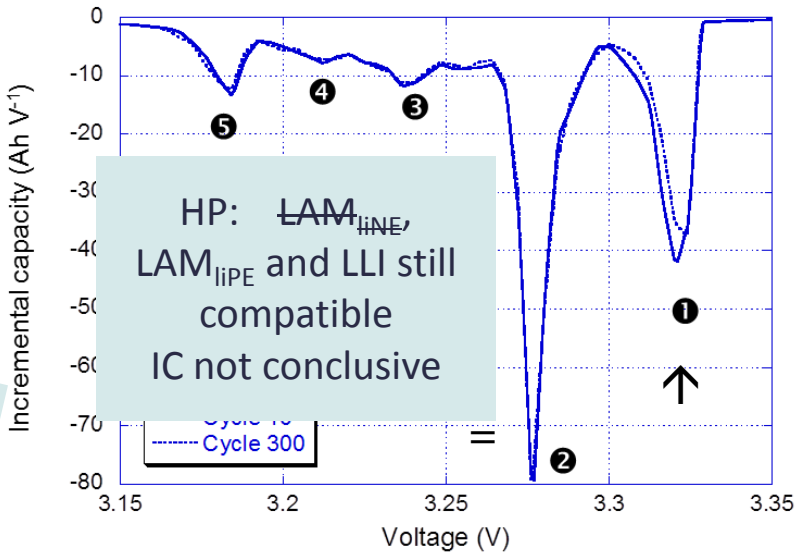
Focus on the first 5% capacity loss for both cells

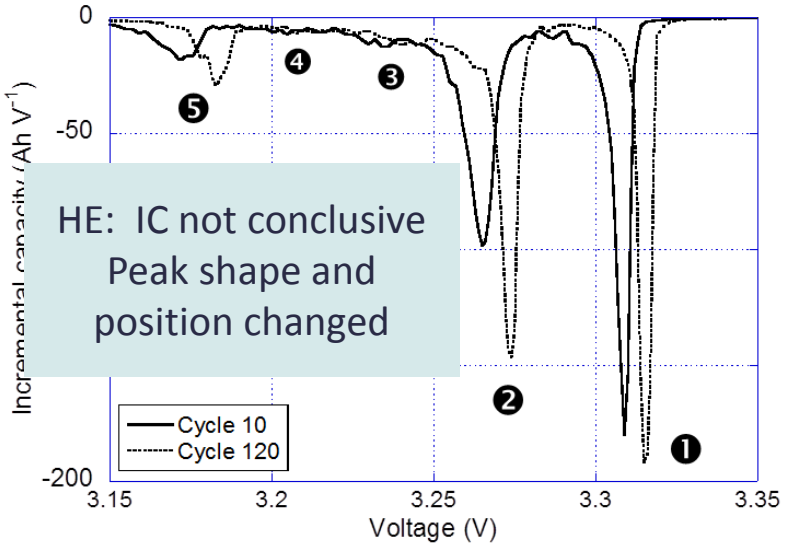
HP cell: 350 cycles, HE cell: 150 cycles

Use of mechanistic emulation : the ‘alawa toolbox

Incremental capacity signature







Focus on the first 5% capacity loss for both cells

HP cell: 350 cycles, HE cell: 150 cycles

Use of mechanistic emulation : the ‘alawa toolbox

Look for other “*in-situ* sensors”

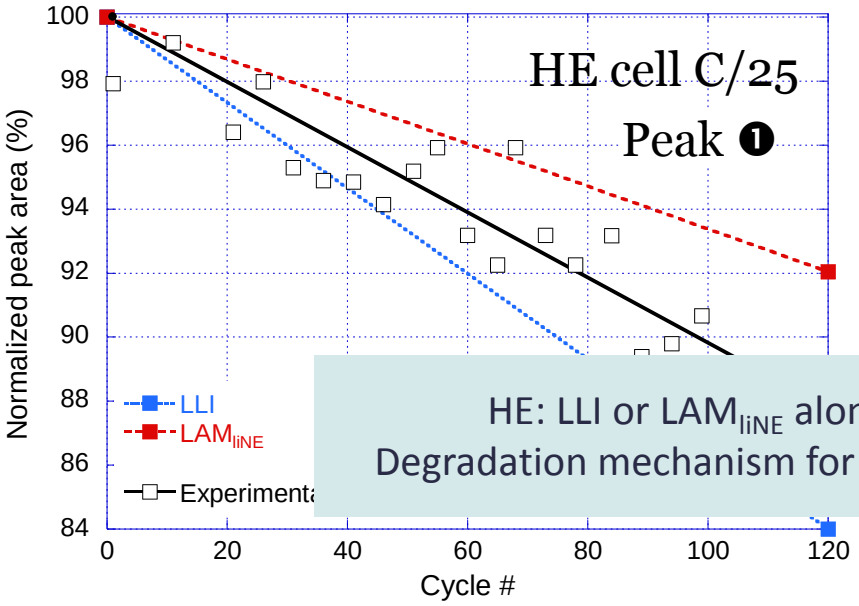
For HP cell, use resistance evolution

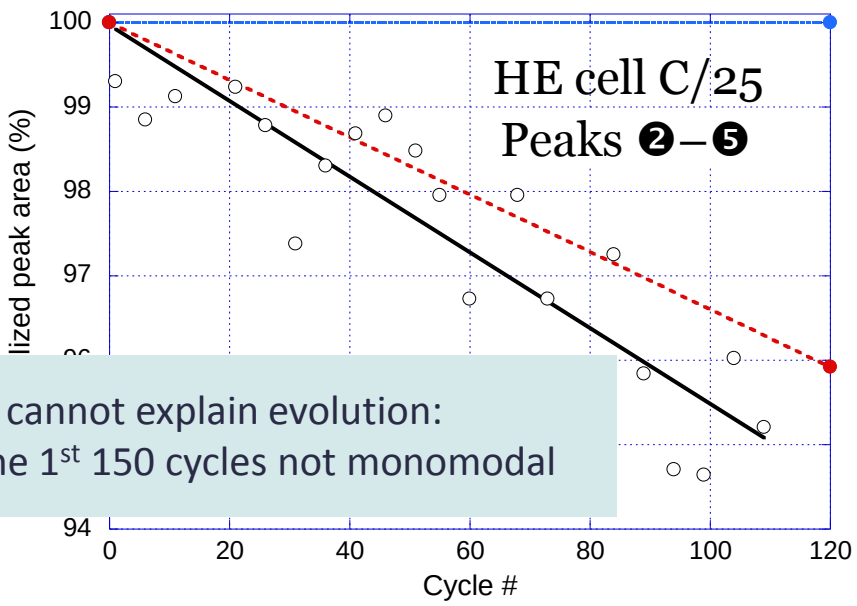
if 5% LAM_{liPE}, resistance should increase (same current on smaller surface area)

Resistance constant → Capacity loss is due to loss of lithium inventory

For HE cell, use IC peak area evolution

SHAPE changed but peak area (i.e. the capacity of each reaction) is still relevant





HE: LLI or LAM_{liNE} alone cannot explain evolution:
Degradation mechanism for the 1st 150 cycles not monomodal

Focus on the first 5% capacity loss for both cells

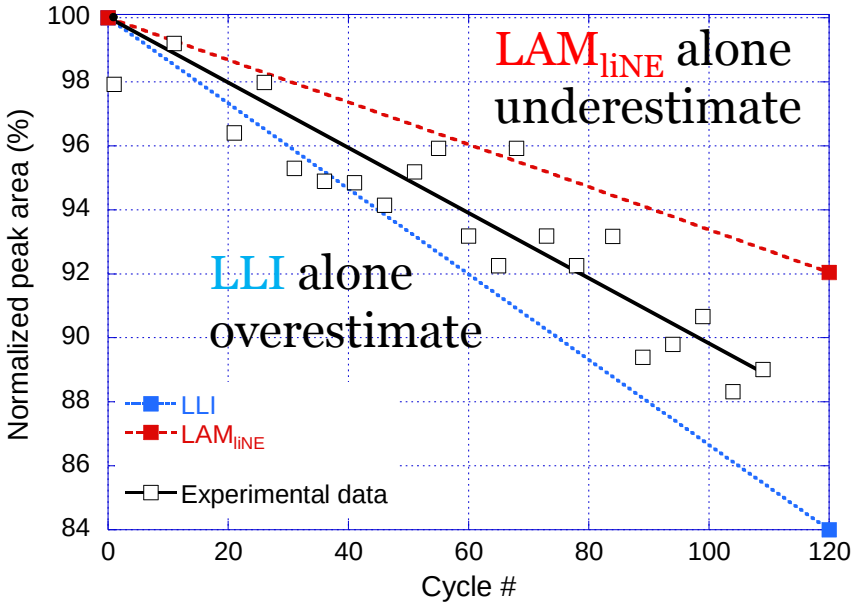
HE cell: 150 cycles – IC peak area evolution

Combine modes to match capacity fade & area variations

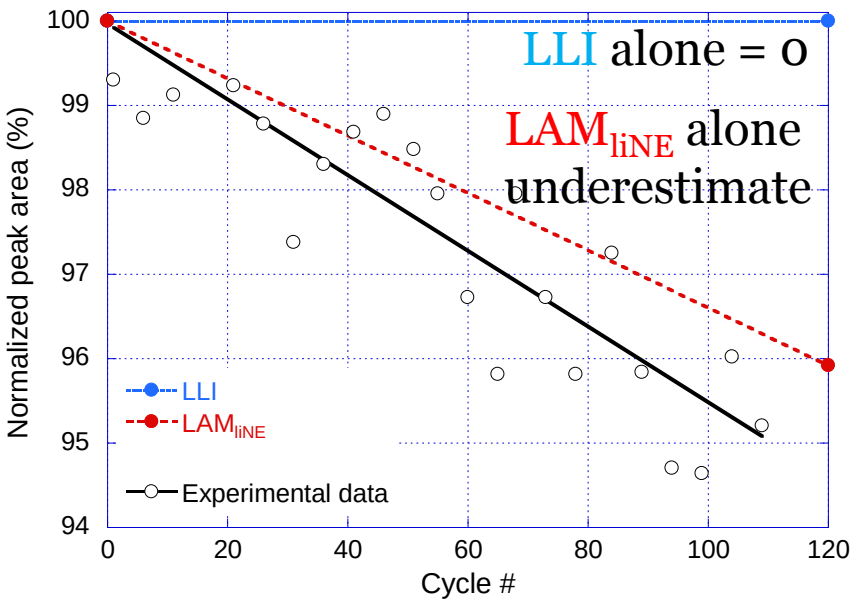
- LAM_{dePE} and LAM_{liNE} can occur without capacity loss
  - BUT they'll alter voltage response
    - If main LAM_{liNE}: need to ↑∫❶ & ↑∫❷-❺
      - No match
    - If main LLI: need to ↓∫❶ & ↑∫❷-❺
      - LAM_{deNE} is matching

	❶	❷	❸	❹	❺
LLI	↑	= ↑	=	=	= →
LAM_{deNE}	↓	↑	↑	↑	↑
LAM_{liNE}	↑	↑	↑	↑	↑
LAM_{dePE}	=	=	↑	↑	↑
LAM_{liPE}	↑	= ↑	=	=	=

Peak ❶



Peaks ❷–❺



Focus on the first 5% capacity loss for both cells

HE cell: 150 cycles – IC peak area evolution

Combine modes to match capacity fade & area variations

LAM_{dePE} and LAM_{liNE} can occur without capacity loss

BUT they'll alter voltage response

If main LAM_{liNE}: need to ↑∫❶ & ↑∫❷-❺

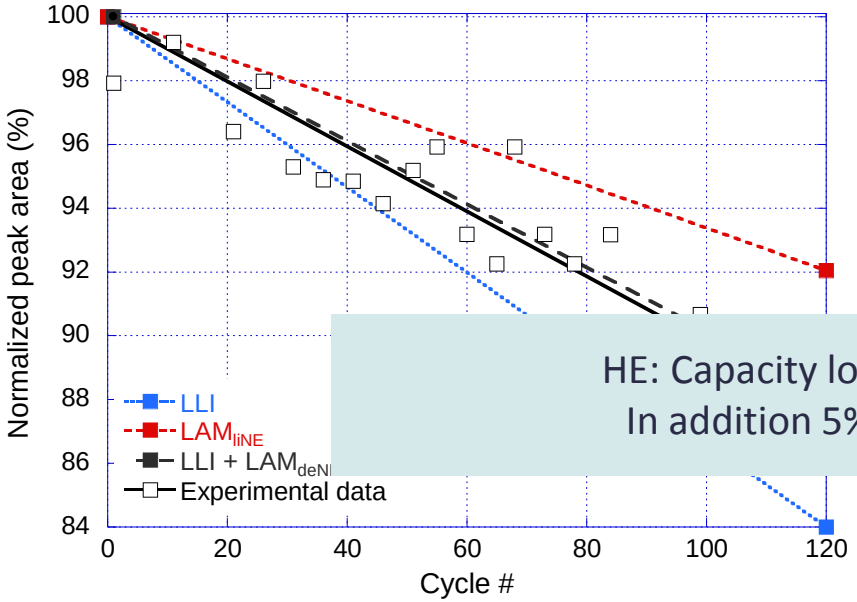
No match

If main LLI: need to ↓∫❶ & ↑∫❷-❺

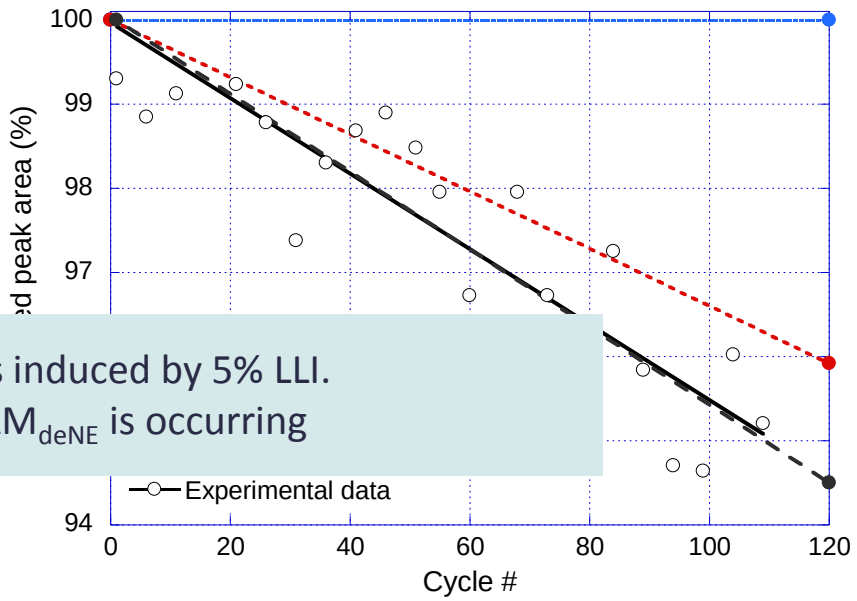
LAM_{deNE} is matching

	❶	❷	❸	❹	❺
LLI	↑	= ↑	=	=	= →
LAM_{deNE}	↓	↑	↑	↑	↑
LAM_{liNE}	↑	↑	↑	↑	↑
LAM_{dePE}	=	=	↑	↑	↑
LAM_{liPE}	↑	= ↑	=	=	=

Peak ❶



Peaks ❷–❺



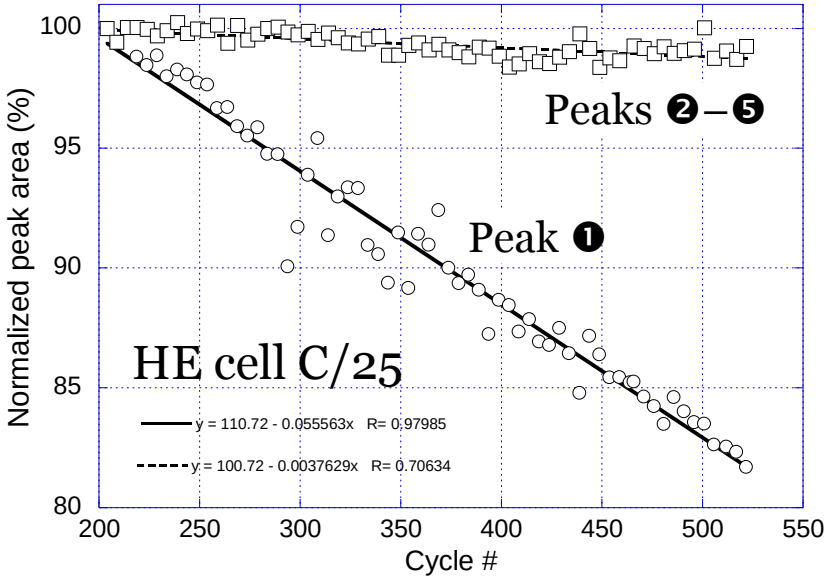
HE: Capacity loss is induced by 5% LLI.
In addition 5% LAM_{deNE} is occurring

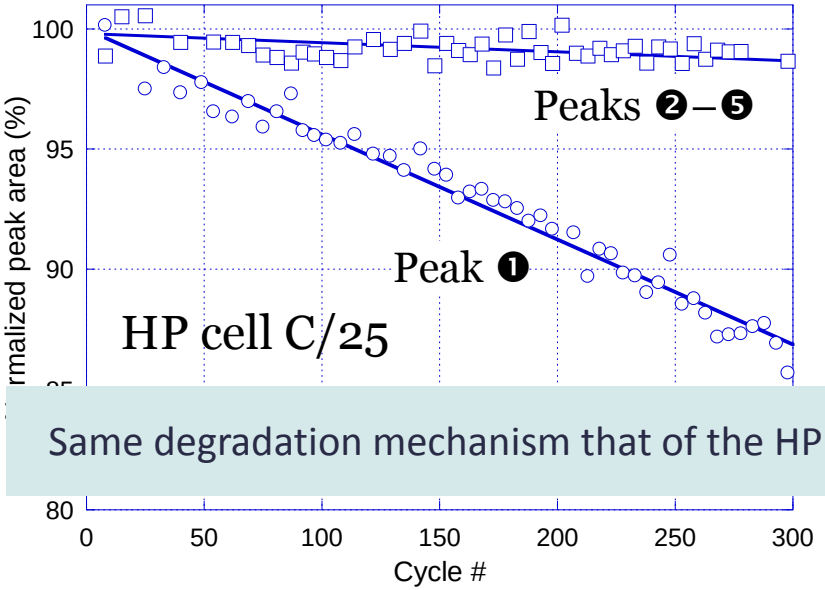
Focus on the HE cell – cycle 200 to 550

IC peak area evolution

Same area analysis for the HE later cycles:

Additional LLI + trace of LAM_{deNE}





Same degradation mechanism that of the HP cell

Mechanistic analysis proved that the capacity loss for both cells is solely induced by LLI and that it seems to be always accompanied by some LAM_{deNE}

BUT it also raised more questions on the HE cell first 150 cycles:

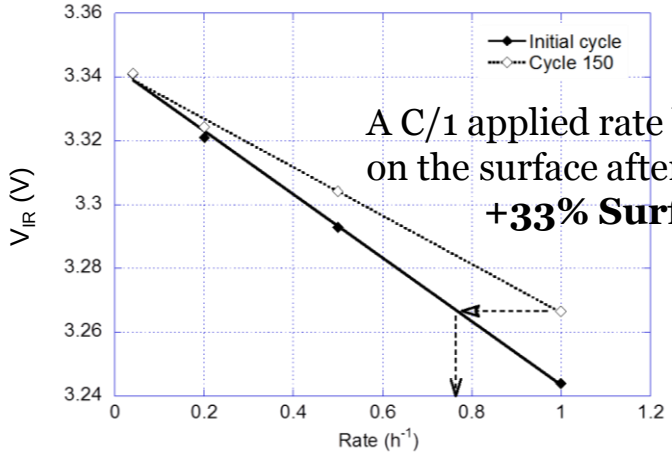
Why at a 2.5x higher LLI pace? Why higher LAM_{deNE} rate?
Why did the kinetics improved (IC peak shape changed, $Q_{C/2}$ and $Q_{C/1}$ ↗)?

Focus on the HE cell

Origin of the higher LLI, LAM_{deNE} and kinetics

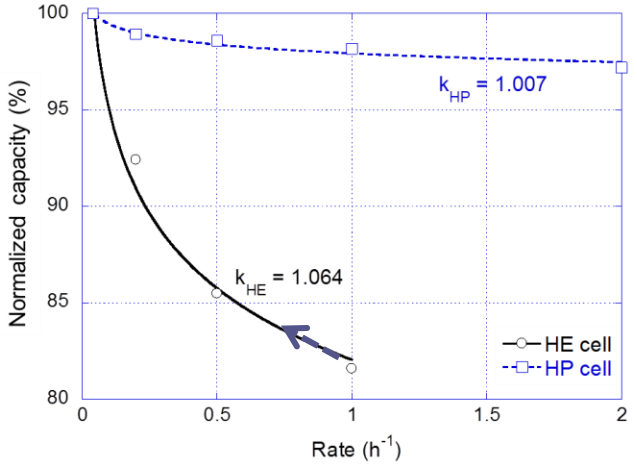
Electrochemical milling of the PE?

- Increases electrode surface area
  - Explain apparent resistance decrease



A C/1 applied rate becomes C/.75 on the surface after milling

+33% Surface area



  - Explain increased capacity at high rates (because of high Peukert constant)
  - Explain changes in peak shapes since PE kinetics improved

- Grain cracking releases Fe ions that could have migrated to the NE
  - Surface poisoning → Higher LLI and LAM

Electrochemical milling explains the additional features of the fist HE 150 cycles

Conclusions

Two commercial GIC//LFP cells were cycled and analyzed by electrochemical inference techniques and mechanistic emulations

The HP cell showed a linear loss of lithium inventory at about 0.016% per cycle associated with a 0.003% loss of active material on the NE.

The HE cell showed the same degradation but with some electrochemical milling in the first 150 cycles that induced better kinetics but additional 5% LLI and 5 % LAM_{deNE}.

The use of mechanistic emulation and of the 'Alawa toolbox created unprecedented benefits to derive fading mechanism with quantitative comparisons for validation.

Full study : Journal of Power Sources 258 (2014) 408-419

Acknowledgments

Karim Zaghib of IREQ (Hydro-Quebec) for the LFP
and Michael Spahr of TIMCAL for the GIC half-cell data.

Funding

US Dept. of Energy, Office of EERE
Hawai'i Energy Sustainability Program
PI: R. Rocheleau
Award No. DE-EE0003507.

Mahalo for your attention! Questions ?

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