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Path Dependence in Lithium-Ion Batteries Degradation: A Comparison of Cycle and Calendar Aging

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Objectives & Motivations

HNEI is leading research efforts to understand the degradation of lithium-ion batteries under two distinct projects.

Electric vehicles (EVs) and their synergy with the grid. (Poster A01-0077)

Grid-scale battery energy storage systems (BESS) (Poster A01-0078)

Both applications require a combination of long cycle-life to meet the expectations of the customers.

To determine whether these durability goals are realistic or not, we performed laboratory testing with cycle and calendar aging experiments.

Ultimately, we would like to accelerate the aging.

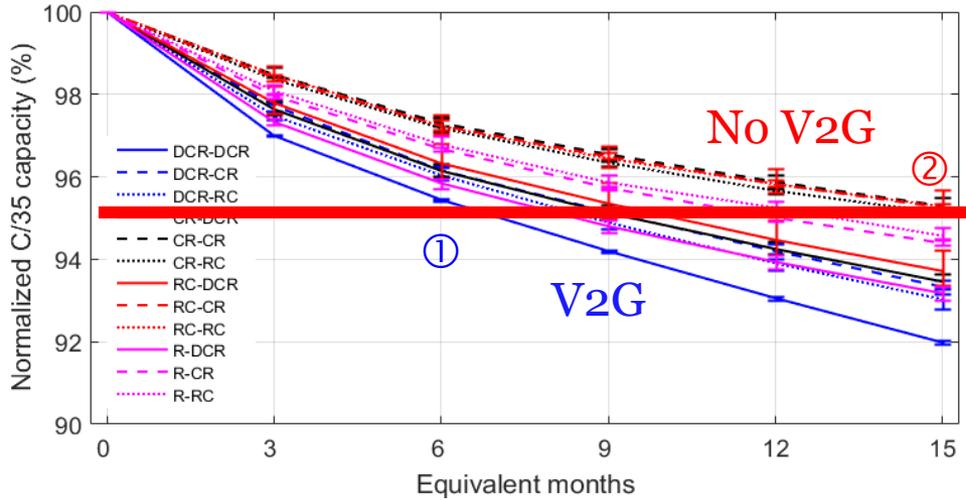
The concept of accelerated aging is only valid if the degradation the cell underwent is the same than of the one it experienced in real life.

Can identical capacity losses come from different degradation pathways?

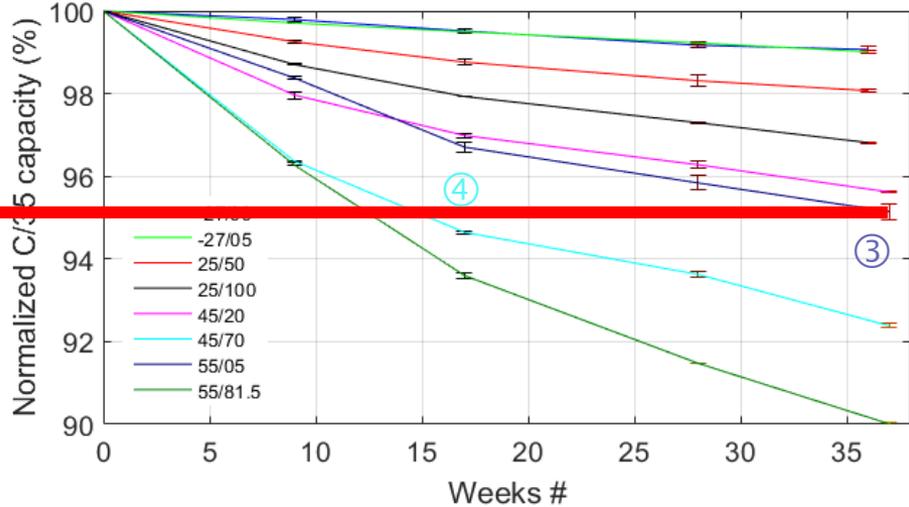
Capacity loss vs. duty cycle

20 different experiments
4 different paths to 5% capacity loss

Cycle aging experiment



Calendar aging experiment



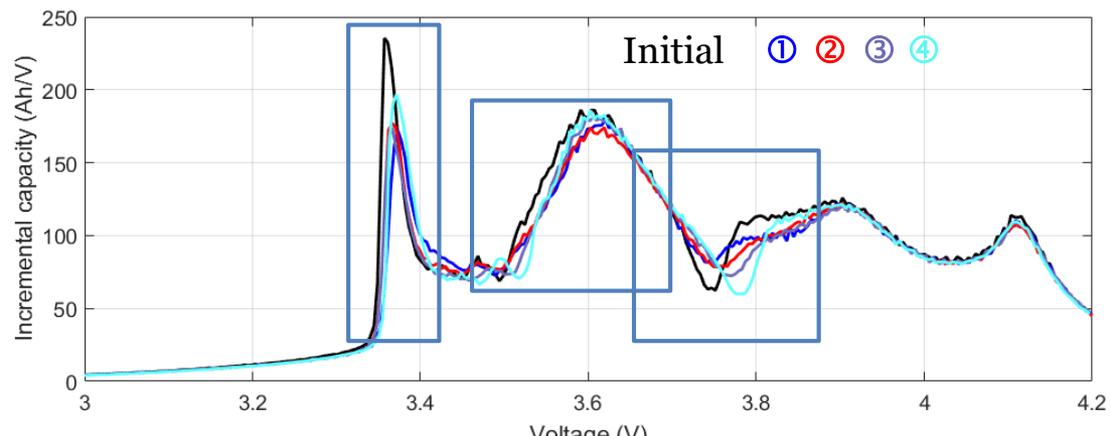
Study voltage response

Traditional V vs. Q:

Hard to visualize

Incremental capacity:

Differences visible

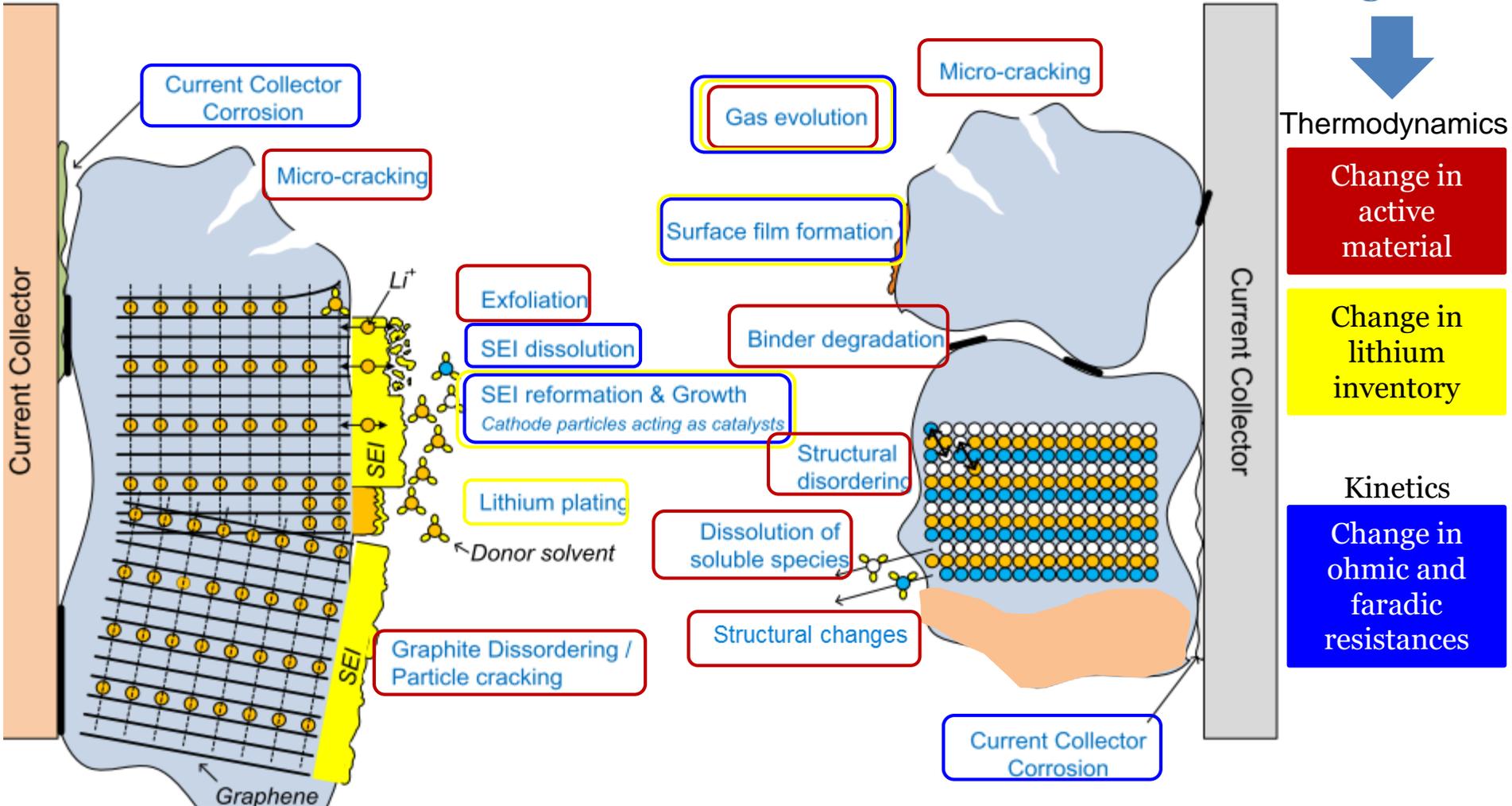


More details: Poster A01-0077

Path Dependence in Lithium-Ion Batteries Degradation Li-ion battery degradation mechanisms

Multiple of possible degradation mechanisms

Useful categorization for diagnostics

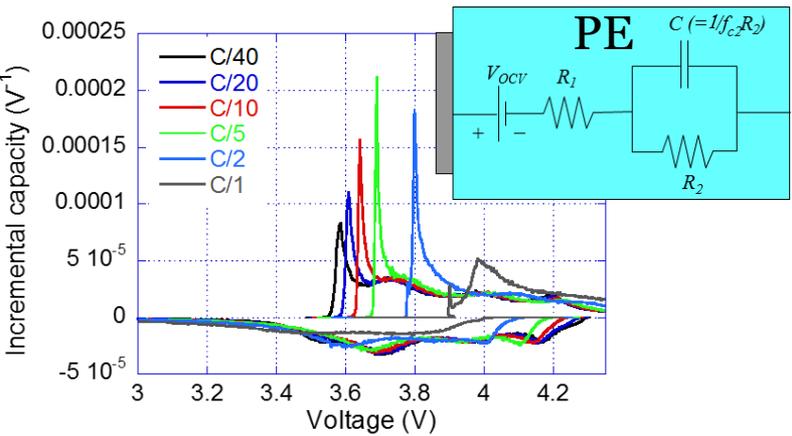


Differences can come from different ratio of LAMs, LLI and kinetic degradations

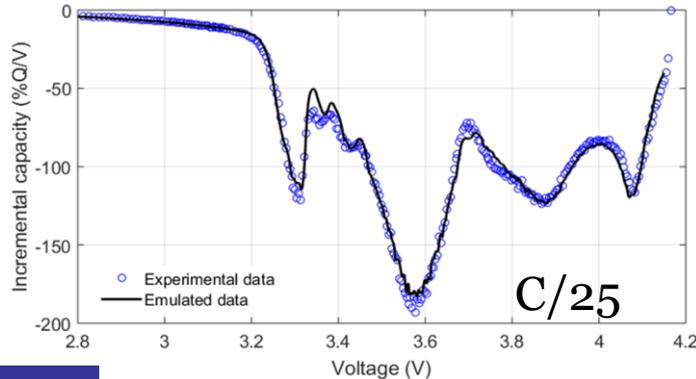
J. Groot, State of Health Estimation of Li-ion batteries cycle life test methods

Path Dependence in Lithium-Ion Batteries Degradation Degradation emulation

Use half cell data harvested from cell

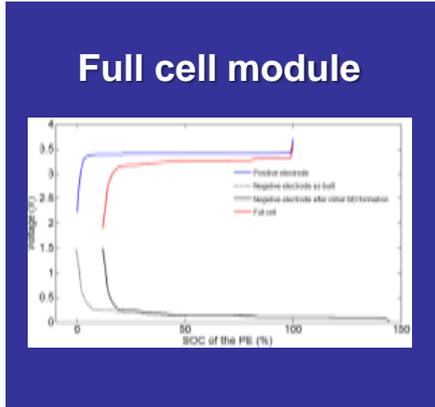


$V_{PE} (SOC_{PE})$



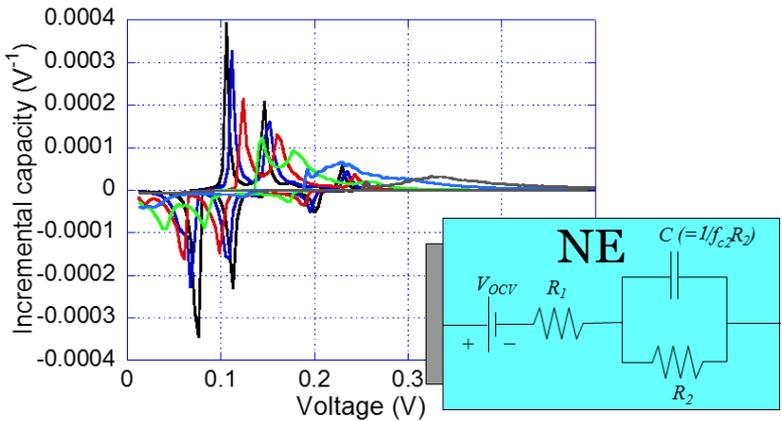
Input from degradation mechanisms

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



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

$$V_{FCdeg} = V_{PEdeg} - V_{NEdeg}$$



$V_{NE} (SOC_{NE})$

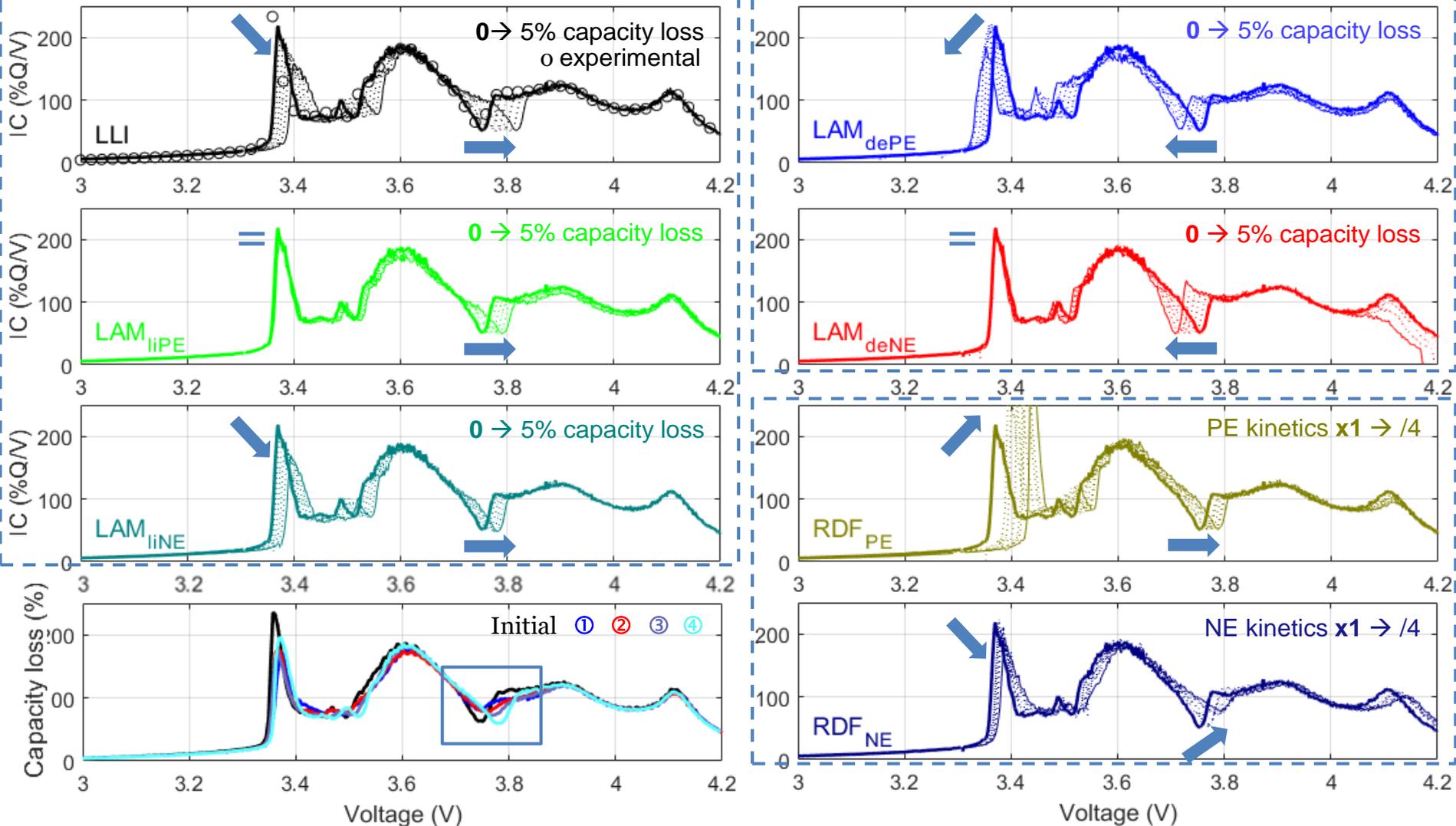


Emulate every possible degradation mode and study effect on full cell (capacity and voltage)

Path Dependence in Lithium-Ion Batteries Degradation

Degradation emulation

Emulate impact of degradation modes



Degradation mechanisms

NE kinetic degradation

Compare arch intensity change with model

Kinetic degraded for cells ①, ② and ③

Compare arch position change with model

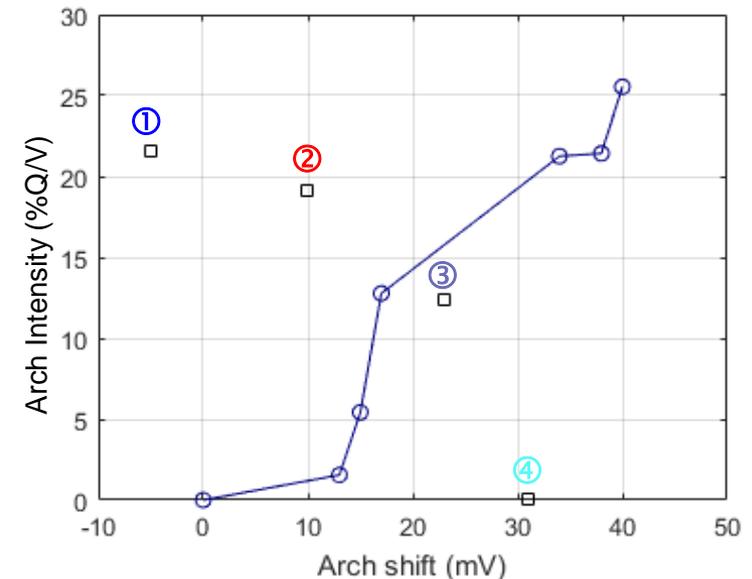
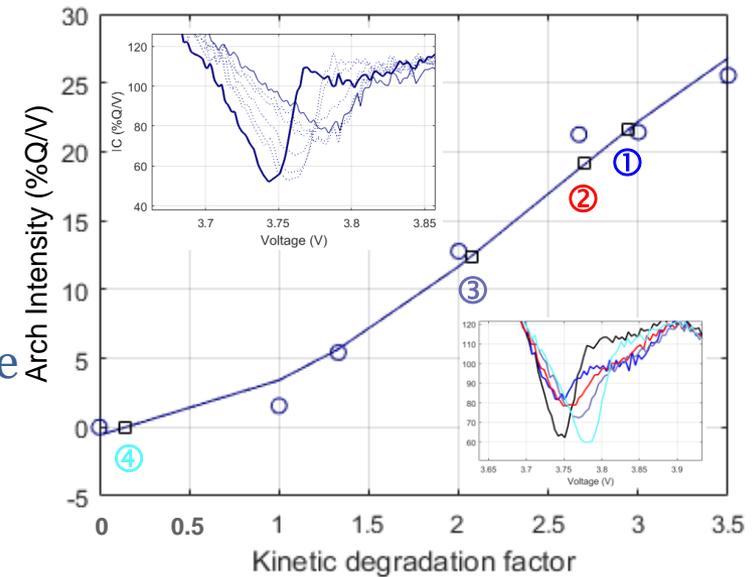
Changes not compatible with kinetic change alone

Origin of NE kinetic degradation

Passivation layer?

Higher local current density?

Cells are showing different level of kinetic degradation (from 0 to 3 time slower kinetics)
But cannot explain arch position changes and capacity loss → Something else is occurring



Degradation emulation – Cell ①

Simulate 5% capacity loss with a kinetic 3 times slower

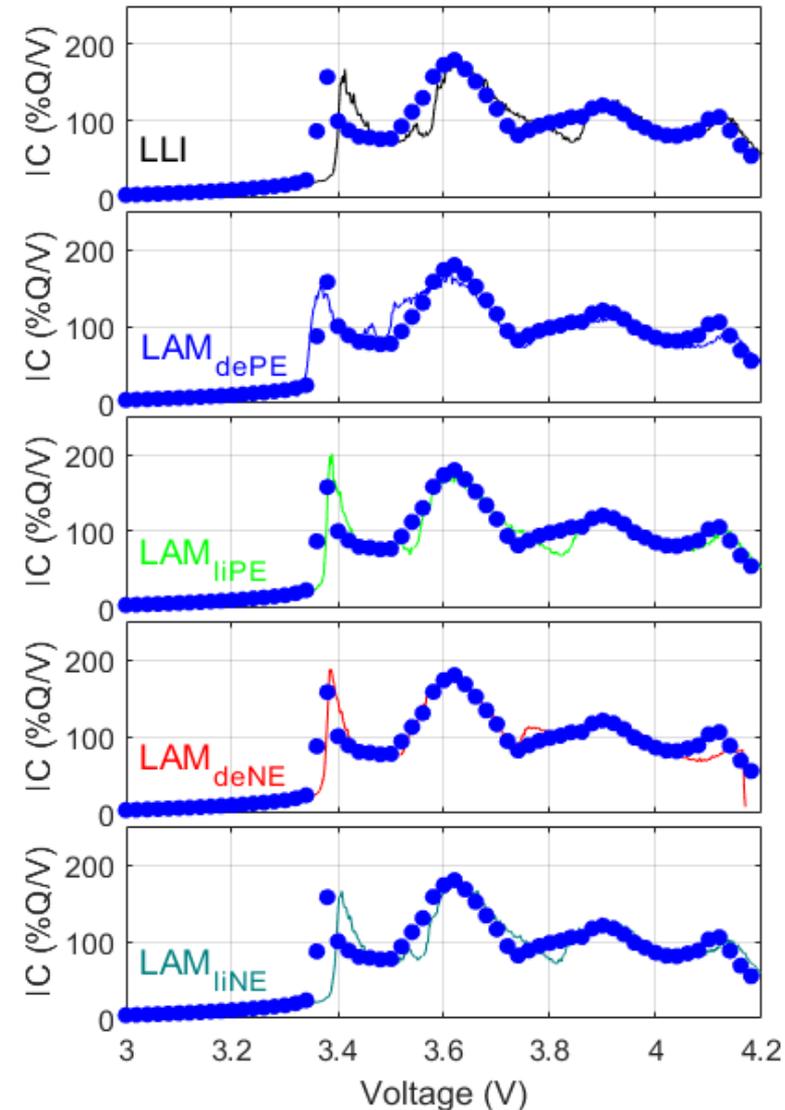
No single mode can explain the observed changes

LAM_{deNE} matched pretty well except last peak
Both moved arch towards lower voltages too much

True degradation is a mix with LLI
in ratio $> 1:1$ (LAM_{liNE})

Best fit found for mix of LAM_{deNE} and LLI
10% LAM_{deNE} , and 3% LLI

Cell ①: Kinetics degraded by a factor 3
~ 10% LAM_{deNE}
~ 3% LLI



Degradation emulation – Cell ②

Simulate 5% capacity loss with a kinetic 2.8 times slower

No single mode can explain the observed changes

LAM_{deNE} matched pretty well except last peak

Both moved arch towards lower voltages too much

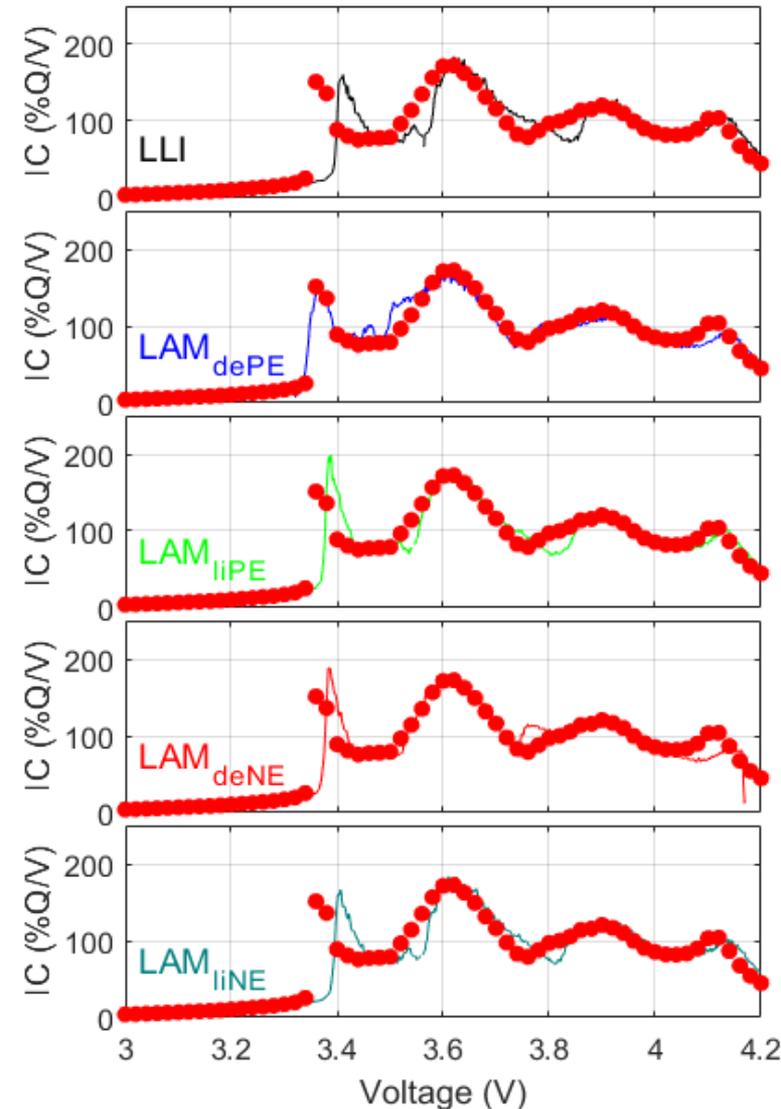
True degradation is a mix with LLI

$V_{Arch②} > V_{Arch①}$: Higher LLI/ LAM_{deNE} ratio

Best fit found for mix of LAM_{deNE} and LLI

8% LAM_{deNE} and 4% LLI

Cell ② : Kinetics degraded by a factor 2.8
 ~ 8% LAM_{deNE}
 ~ 4% LLI



Degradation emulation – Cell ③

Simulate 5% capacity loss with a kinetic 2 times slower

No single mode can explain the observed changes

LAM_{LiNE} matched pretty well overall shape

LAM_{dePE} matched pretty well 1st peak

Arch voltage too high

→ Too much lithium

→ % LLI < (% LAM_{dePE} + LAM_{deNE})

Best fit found for mix of LAMs and LLI

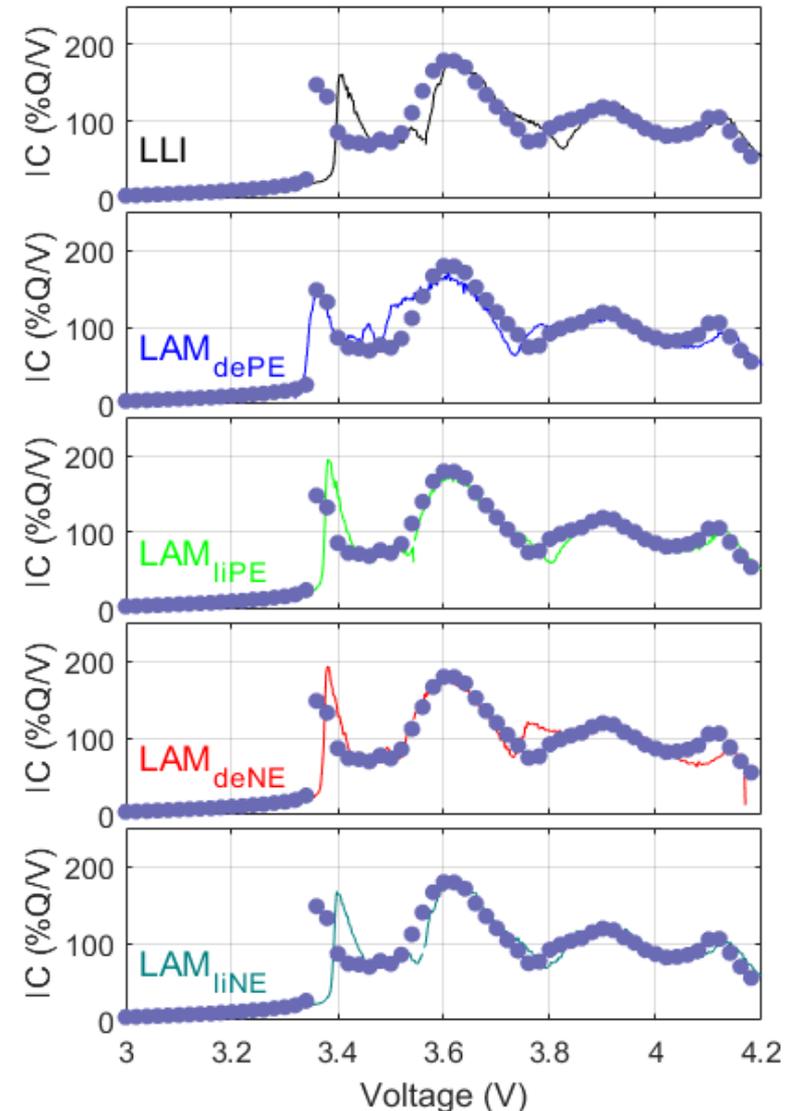
5% LAM_{deNE} , 4.5% LLI and 2.5% LAM_{dePE}

Cell ③ : Kinetics degraded by a factor 3

~ 5% LAM_{deNE}

~ 4.5% LLI

~ 2.5% LAM_{dePE}



Degradation emulation – Cell ④

Simulate 5% capacity loss no change of kinetics

No single mode can explain the observed changes

LAM_{liPE} and LAM_{liNE} matched pretty well

Arch voltage is well simulated

→ $\% LLI = (\% LAM_{dePE} + LAM_{deNE})$

Best fit found for 5.5% LLI

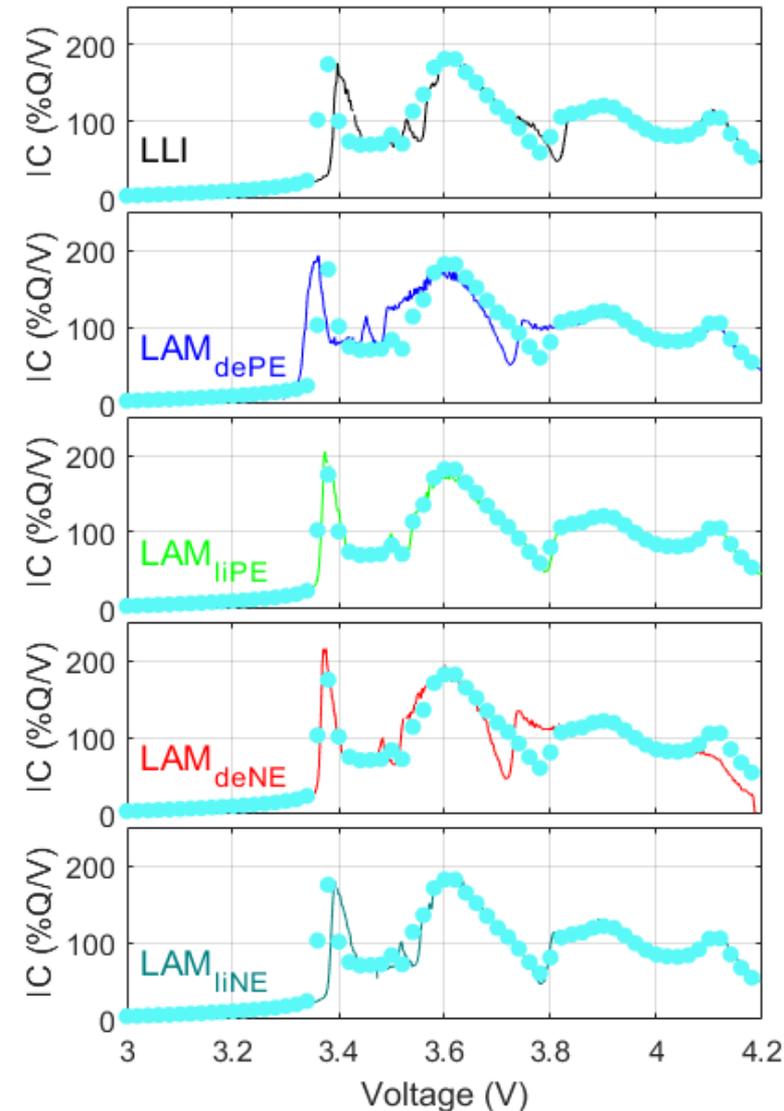
With a mix of 5.5% LAM_{dePE}

Hard to quantify exactly, might be a little LAM_{deNE}

Cell ④: No kinetic degradation

~ 5.5% LLI

~ 5.5% LAM_{dePE}



Conclusions

For 5% capacity loss:

- | | |
|---------------------------|---|
| ① 6 months V2G usage | 10% LAM_{deNE} , and 3% LLI |
| ② 15 months no V2G | 8% LAM_{deNE} and 4% LLI |
| ③ 9 months @55°C/05%SOC | 5% LAM_{deNE} , 4.5% LLI, 2.5% LAM_{dePE} |
| ④ 4.5 months @45°C/70%SOC | 5.5% LAM_{dePE} and 5.5% LLI |

V2G strategy none only induces x2 capacity loss but also impact more the negative electrode

High temperatures seems to induce LAM_{PE}

SOC might have an impact on calendar aging

Clear path dependence of the battery degradation

Might influence durability

Next step is repeat analysis at a later stage to forecast remaining life

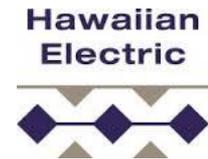
Acknowledgments

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<http://evtc.fsec.ucf.edu/research/>

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Thank you for your attention! Questions ?



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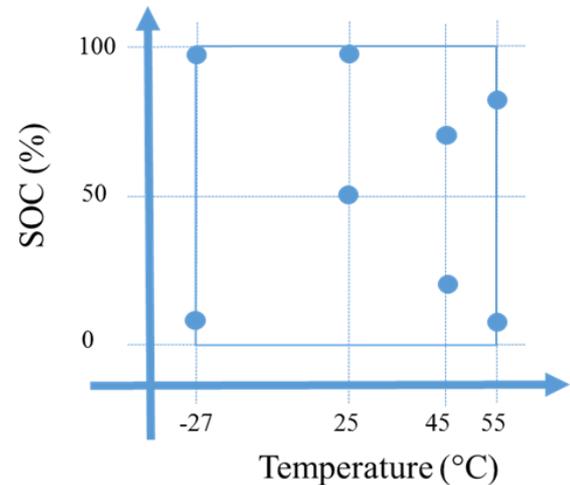
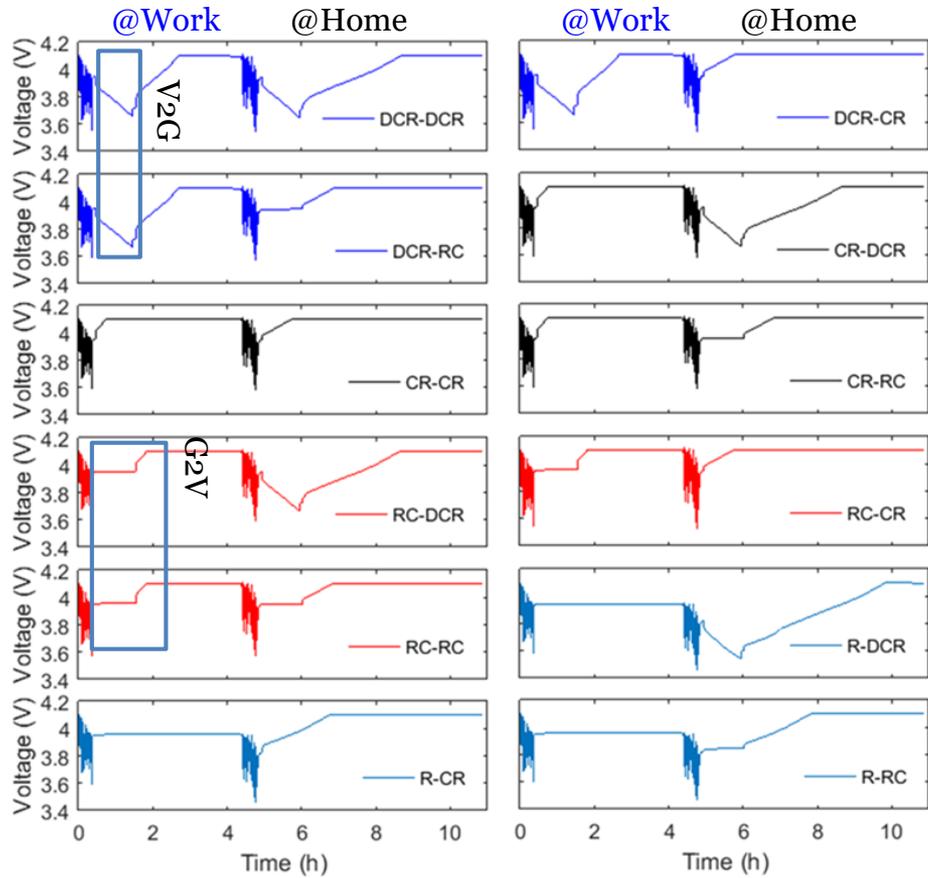


Capacity loss vs. duty cycle

20 different experiments

Cycling

Calendar aging



Calendar aging experiment designed for maximum accuracy @ high temperature & high SOC

Unique set of protocols
 Shall yield unique insight in real effect of V2G/G2V strategies on battery degradation