

# Intrinsic degradation variability in commercial lithium-ion batteries

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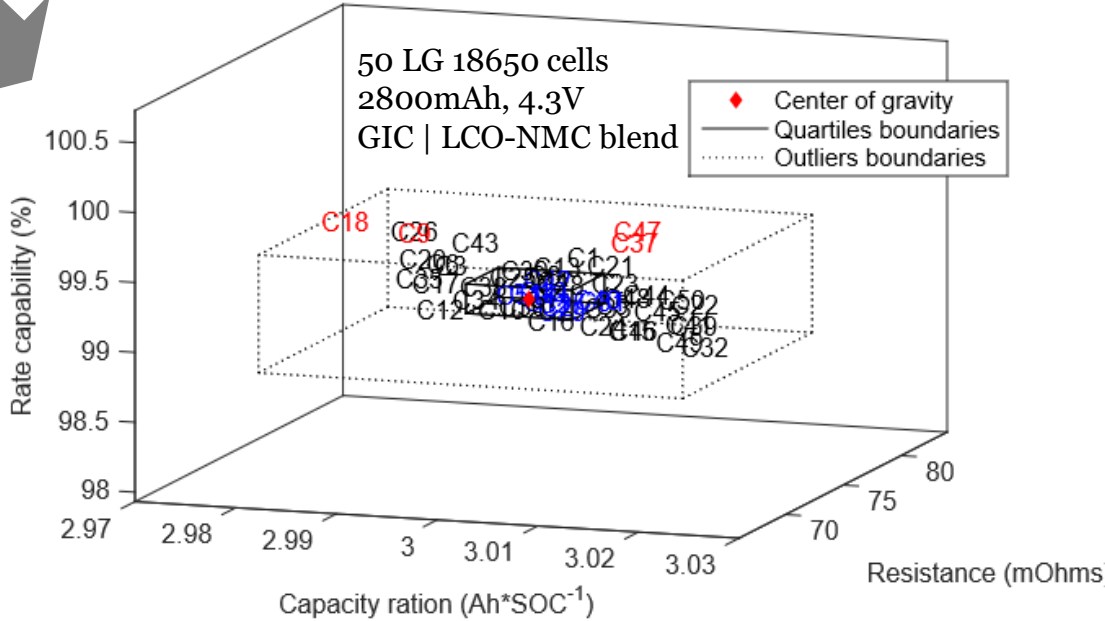
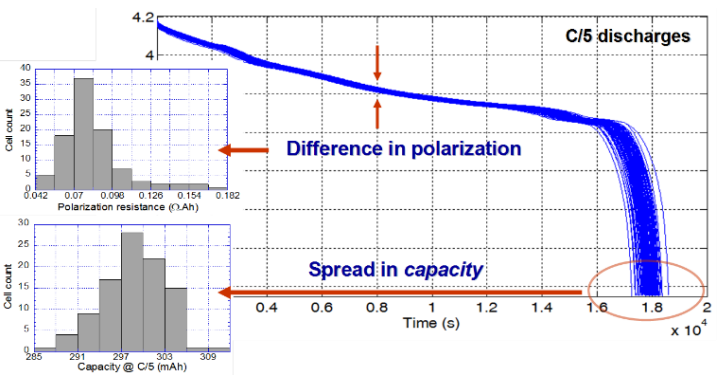
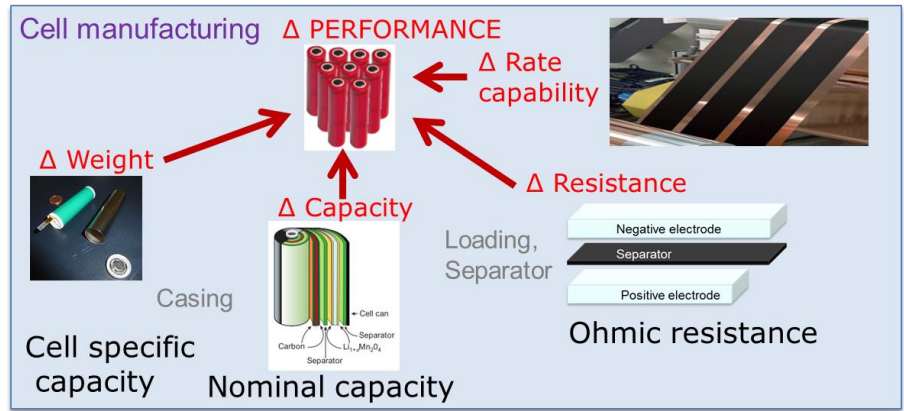


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# Assessing Cell-to-cell Variations

- HNEI's know-how



Dubarry et al., International Journal of Energy Research, **34**, p216 (2010)  
 M. Dubarry, C. Truchot, M. Cugnet, B.Y. Liaw, K. Gering, S. Sazhin, D. Jamison, , J. Power Sources, **196**, p.10328 (2011)

# Sources Of Variability In Battery Manufacturing



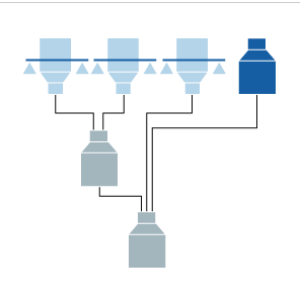
**HNEI**

Hawai'i Natural Energy Institute

University of Hawai'i at Mānoa

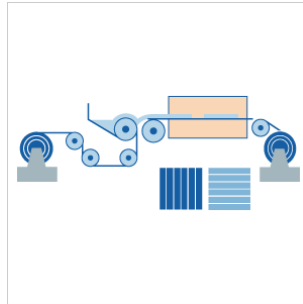
3

## Mixing



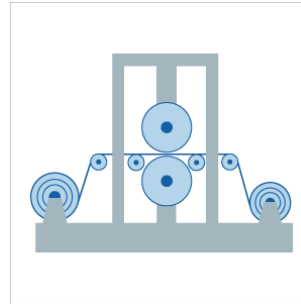
- Composition
- Morphology
- Impurities

## Coating



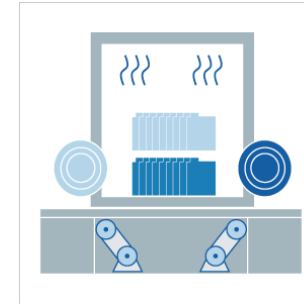
- Loading ( $\text{g}/\text{m}^2$ )
- Homogeneity
- Edges

## Calendering



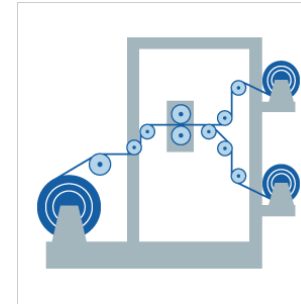
- Thickness
- Porosity

## Drying



- Residual Moisture

## Slittering



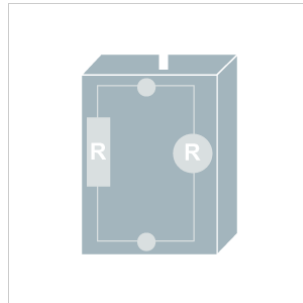
- Length

## Shipping



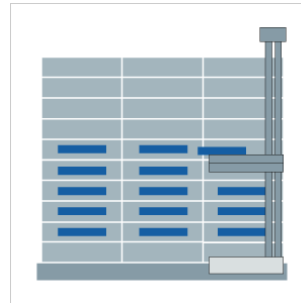
- Duration
- Environment

## Grading



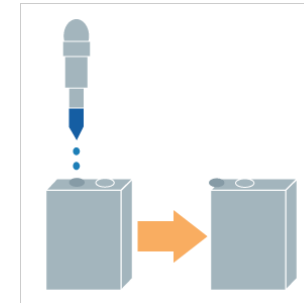
- Tolerances

## Formation



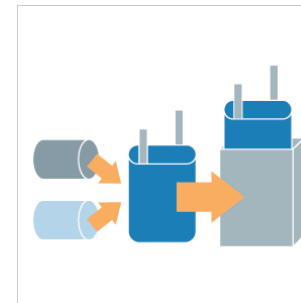
- Device Calibration
- Contact Resistance

## Filling



- Volume
- Composition
- $\text{H}_2\text{O}$  ppm

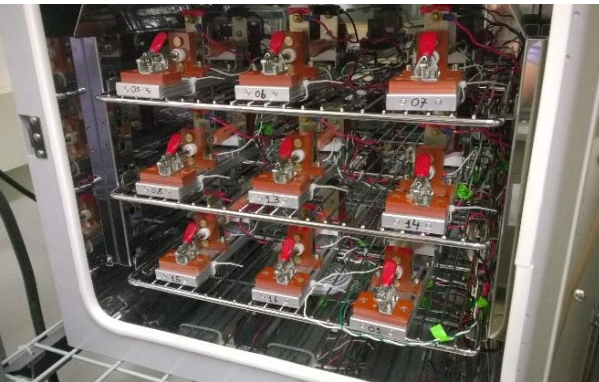
## Assembly



- Ratio
- Overlay
- Weld Quality

# This Experiment

Minimization of initial differences



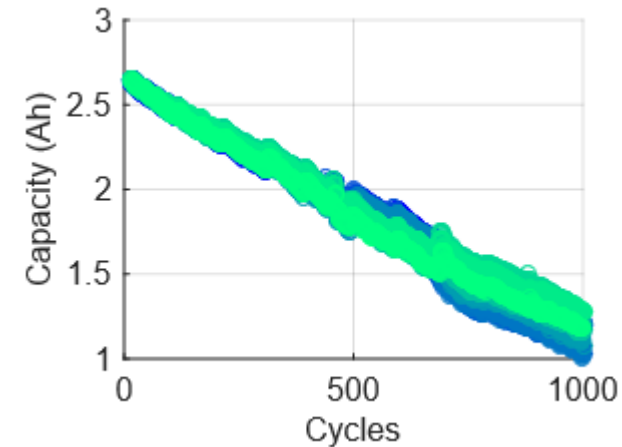
Matched cells

Neutralization of extrinsic factors



Controlled environment

Long-term continuous cycle aging



6 months  
1000 cycles  
[3.0 4.3]V  
-1.5C DIS | C/2 CH



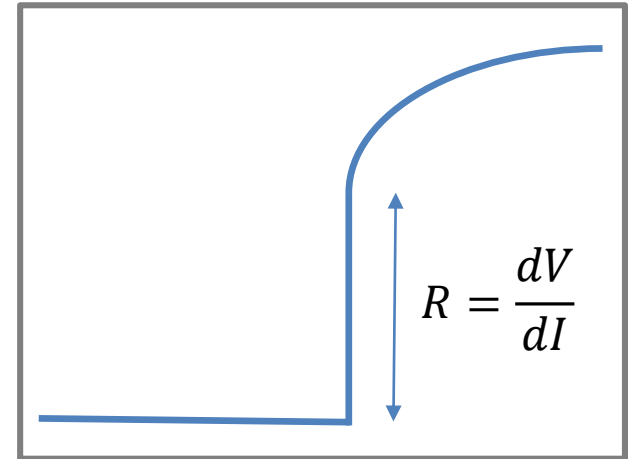
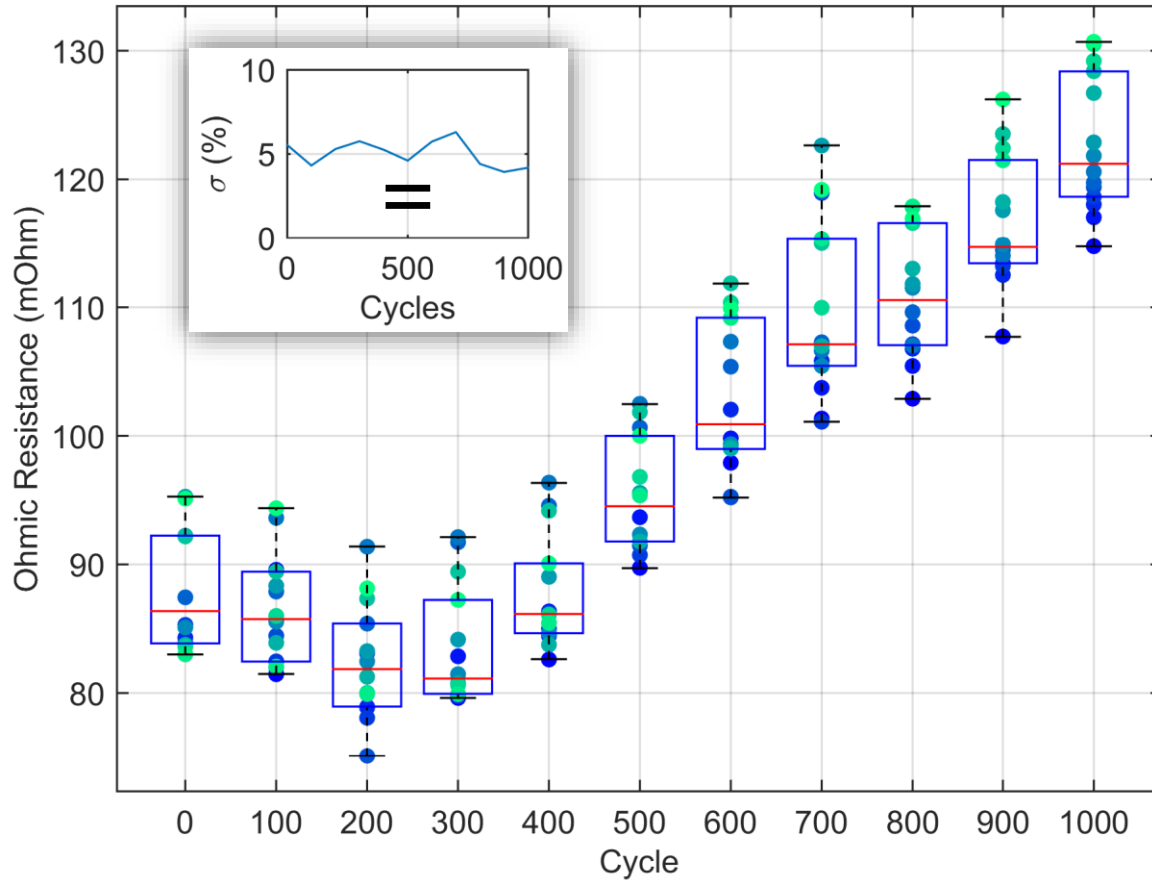
Calibration across channels

Evolution of the cell-to-cell variations ?



# Metric 1: Resistance

## Ohmic resistance (R)



Outliers

Ohmic resistance rose  
ca. 50% over 1000 cycles

Stable statistical dispersion

50%

Whisker

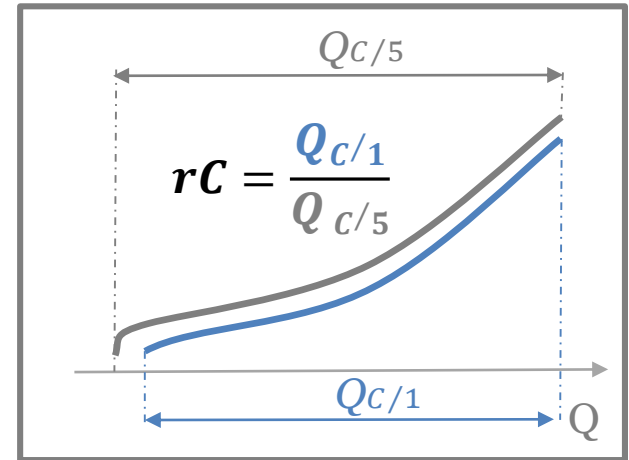
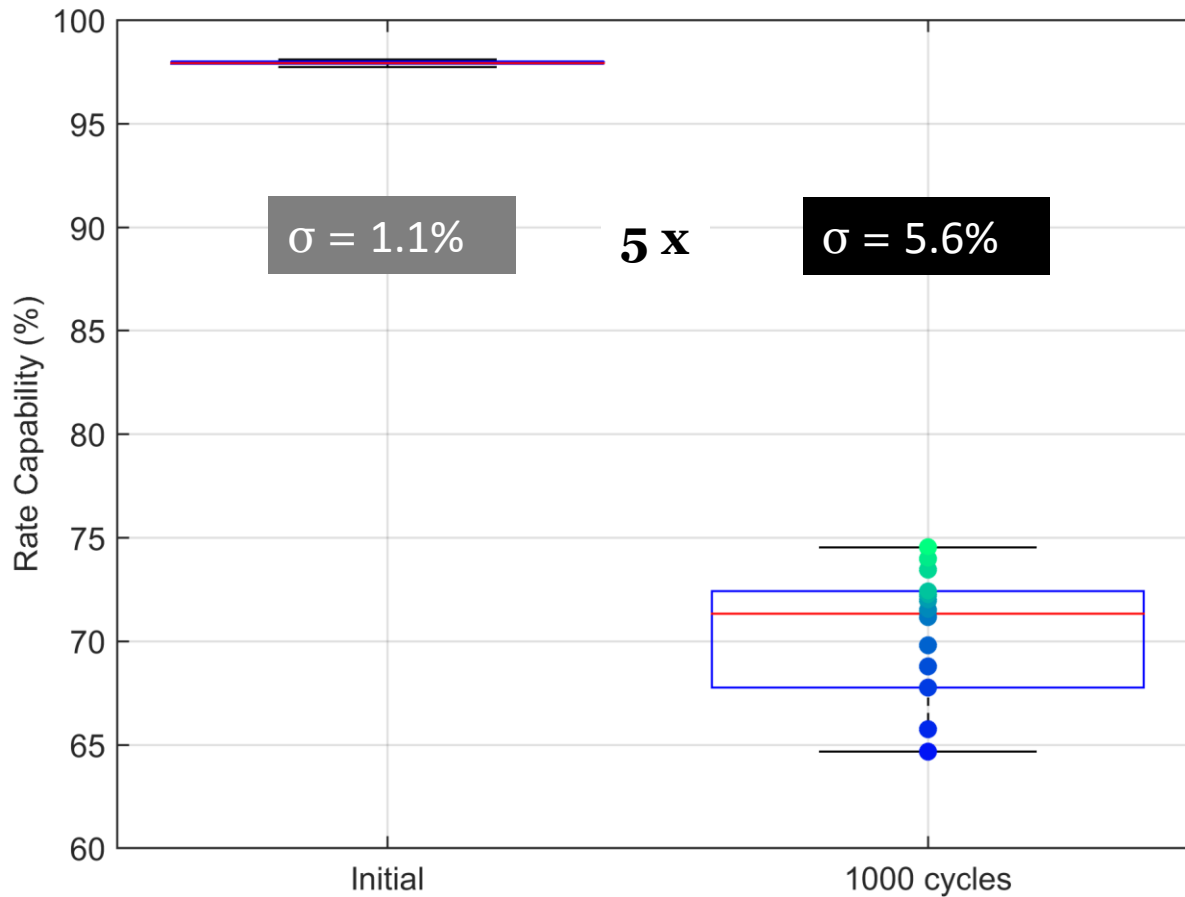
Lower Quartile

Lower Extreme



# Metric 2: Kinetics

## Rate Capability (rC)



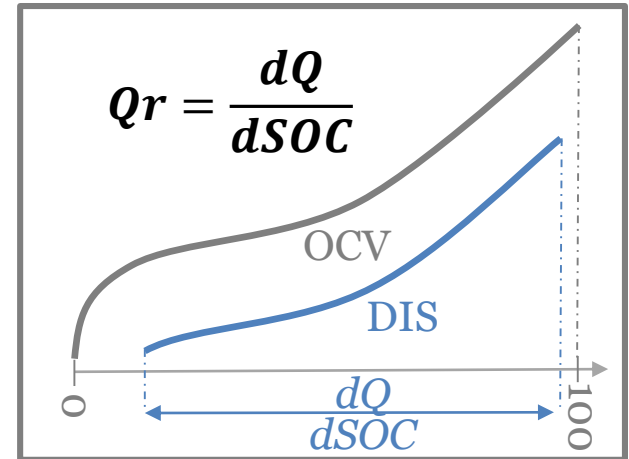
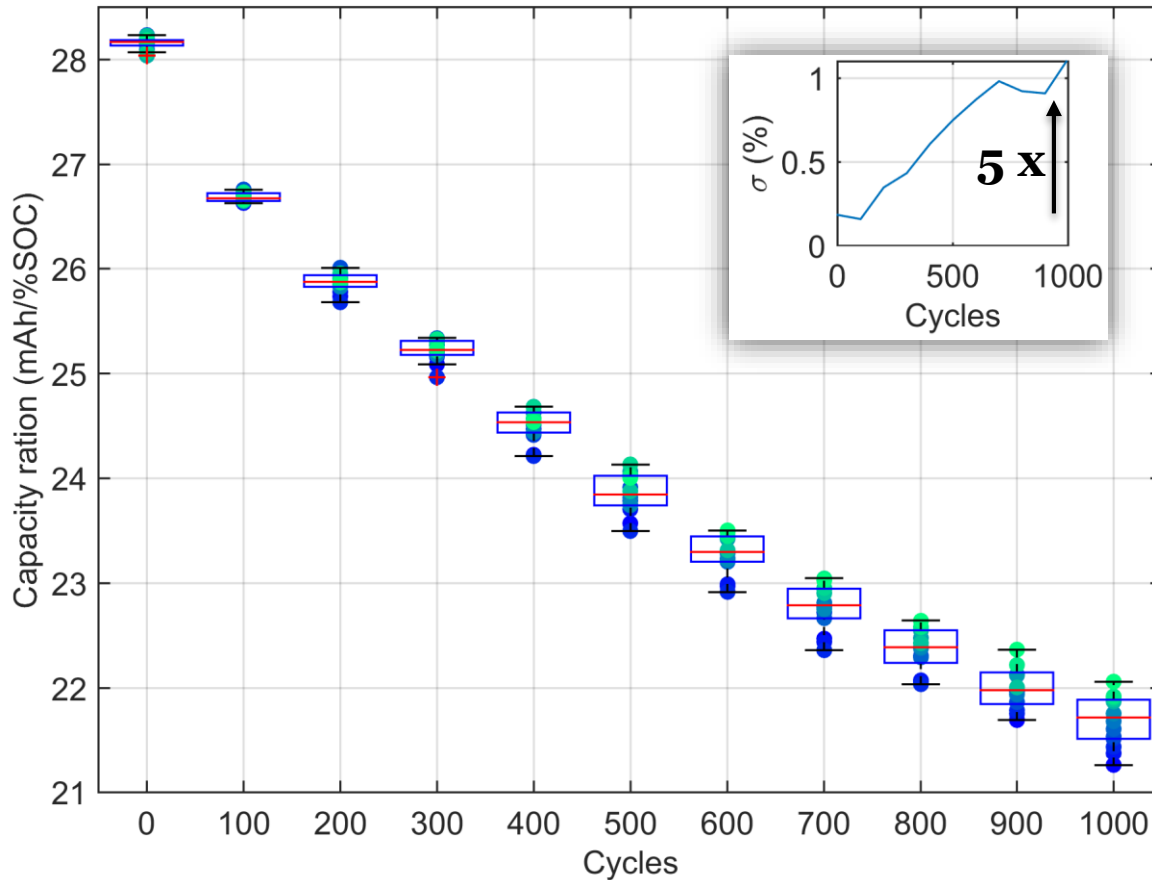
Significant degradation of  
the rate capability

Statistical dispersion rose  
5X!



# Metric 3: Thermodynamic Capacity

## Capacity ration (Qr)

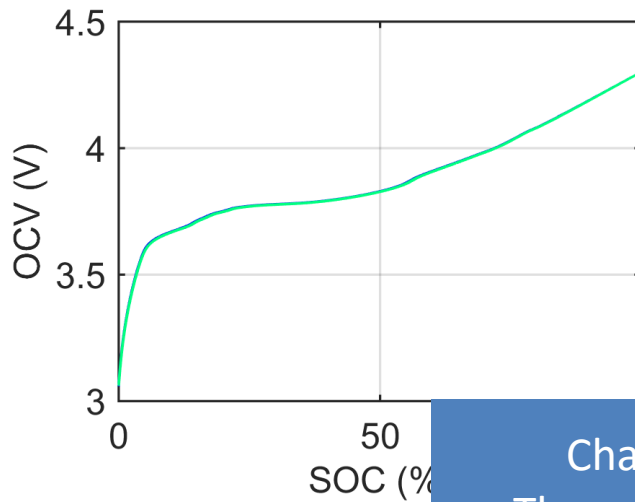


Capacity ration decreased regularly

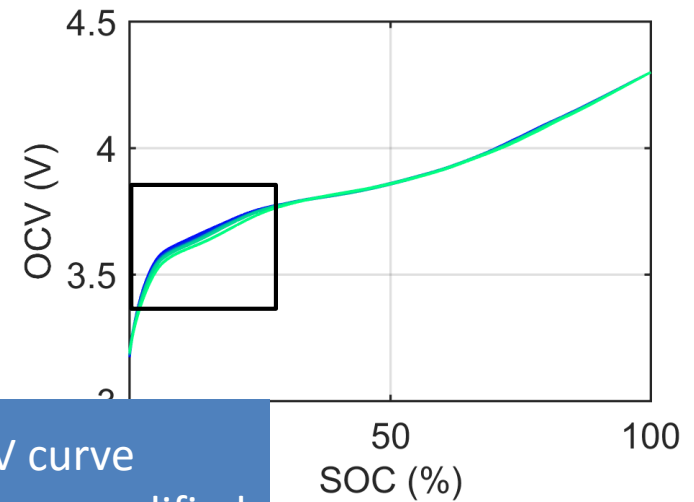
Statistical dispersion rose 5X!

# OCV Curves

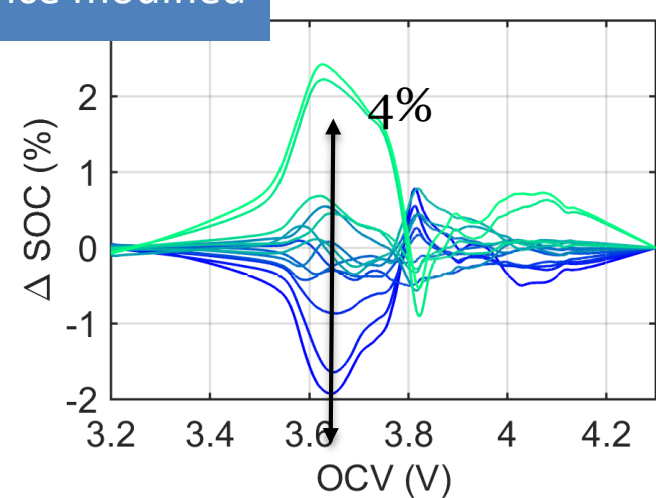
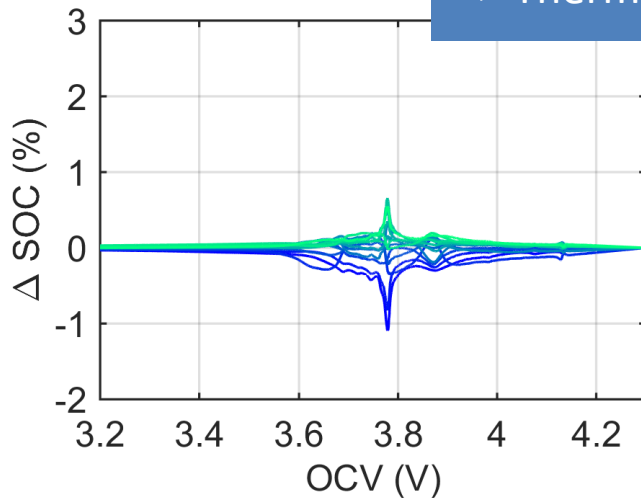
Initial

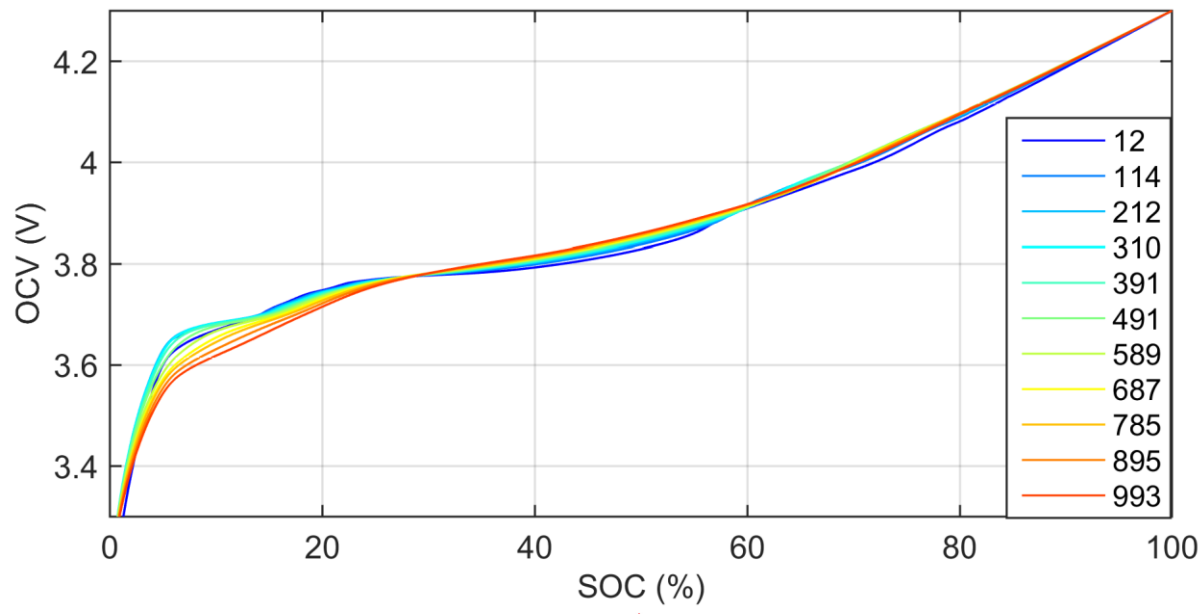


1000 cycles

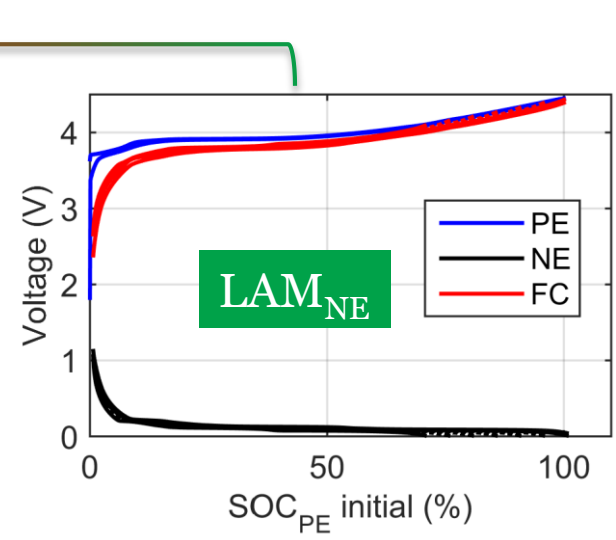
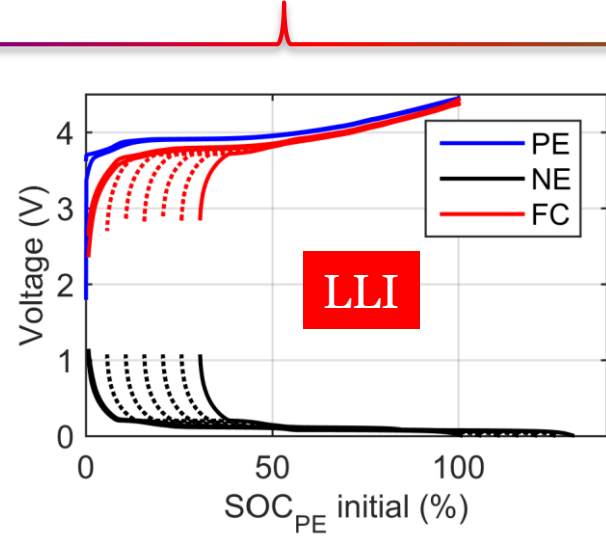
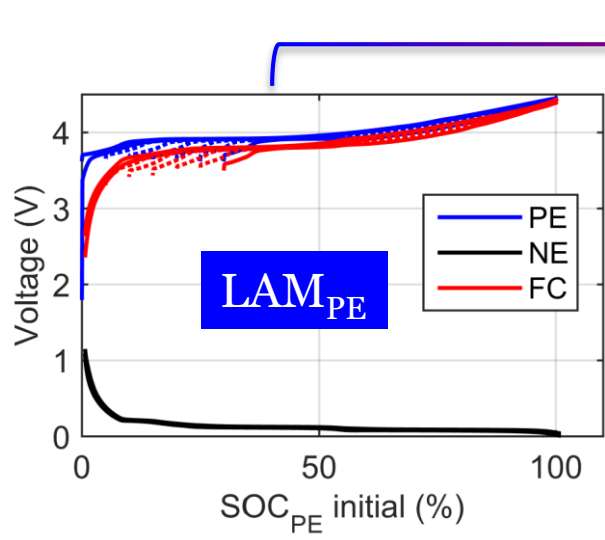


Changes in the OCV curve  
 => Thermodynamic balance modified



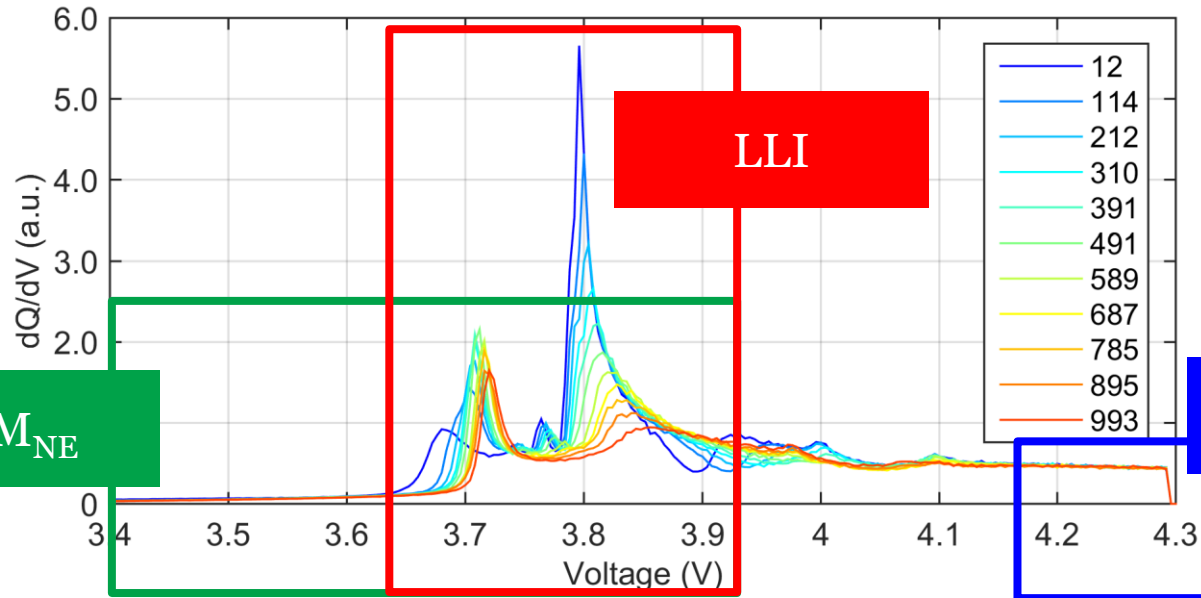
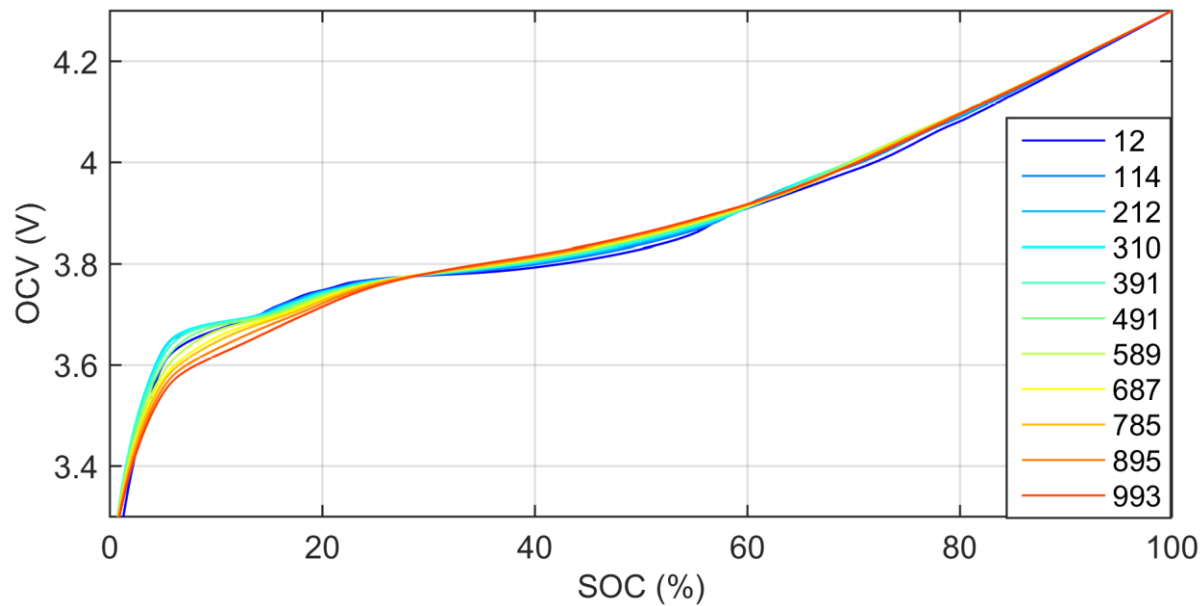


Variation in thermodynamic balance =  $f(\text{LAM}_{\text{PE}}, \text{LAM}_{\text{NE}}, \text{LLI})$





# Incremental Capacity Analysis



Switch to  $dQ/dV$

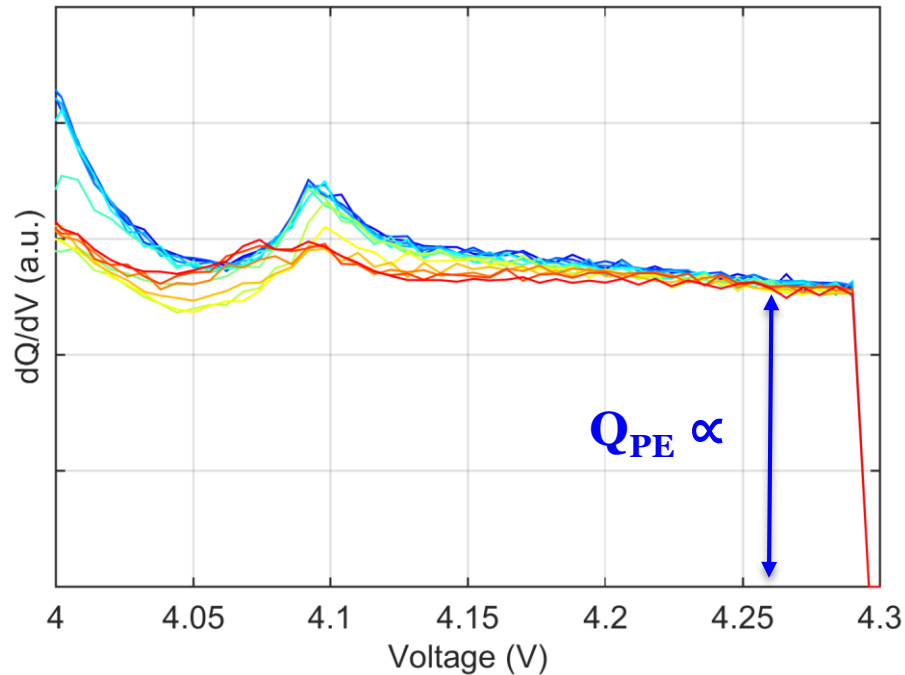
A more intuitive representation

$LAM_{NE}$

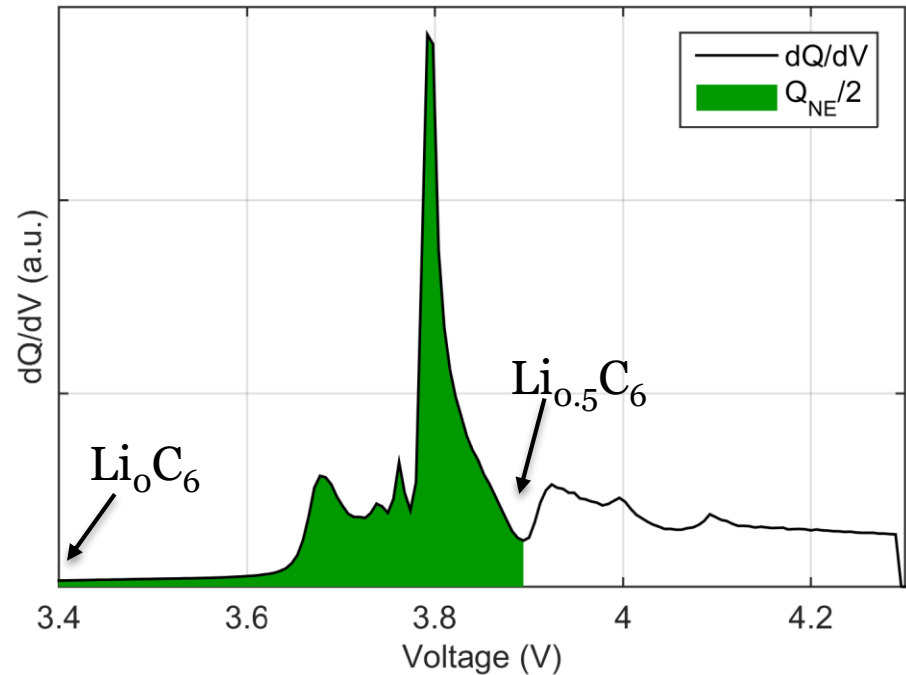
$LAM_{PE}$



# Loss of Active Material (LAM)

 $LAM_{PE}$ 


Stable Positive Electrode Capacity  
 $LAM_{PE}$  is not detectable (ca. 0%)

 $LAM_{NE}$ 


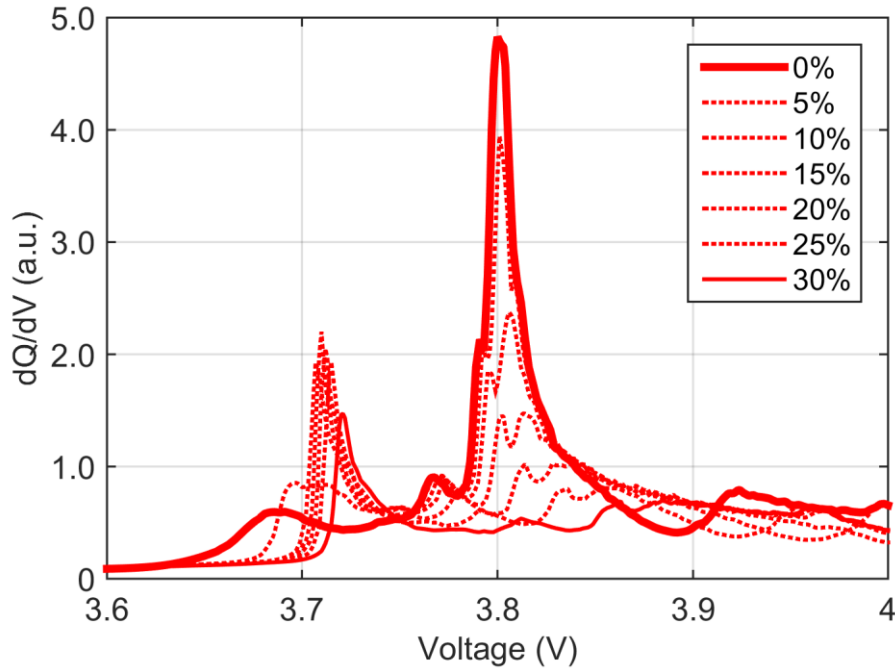
Stable Negative Electrode Capacity  
 $LAM_{NE}$  is not detectable (ca. 0%)


**HNEI**

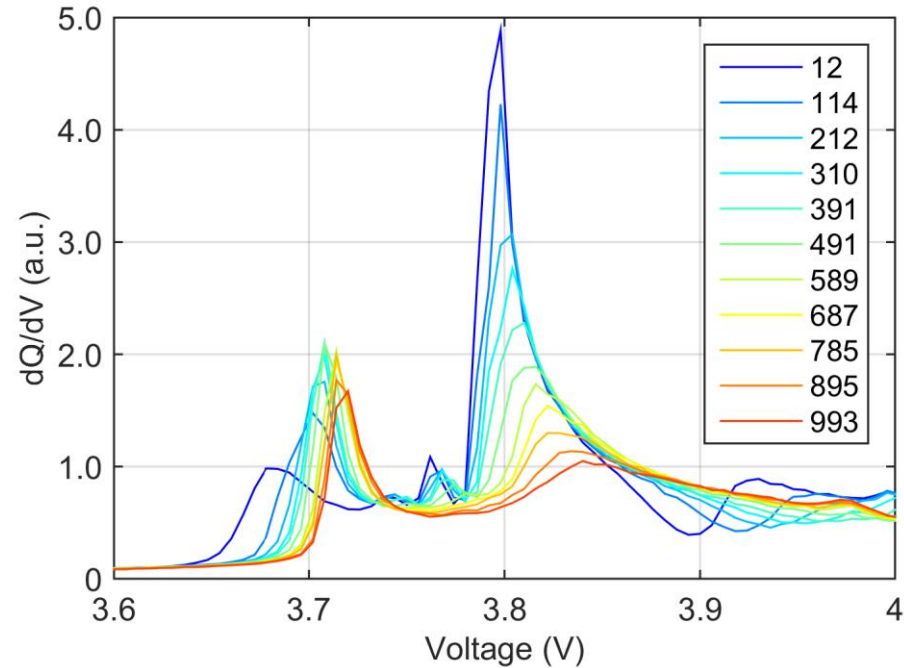
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# Loss of Lithium Inventory (LLI)

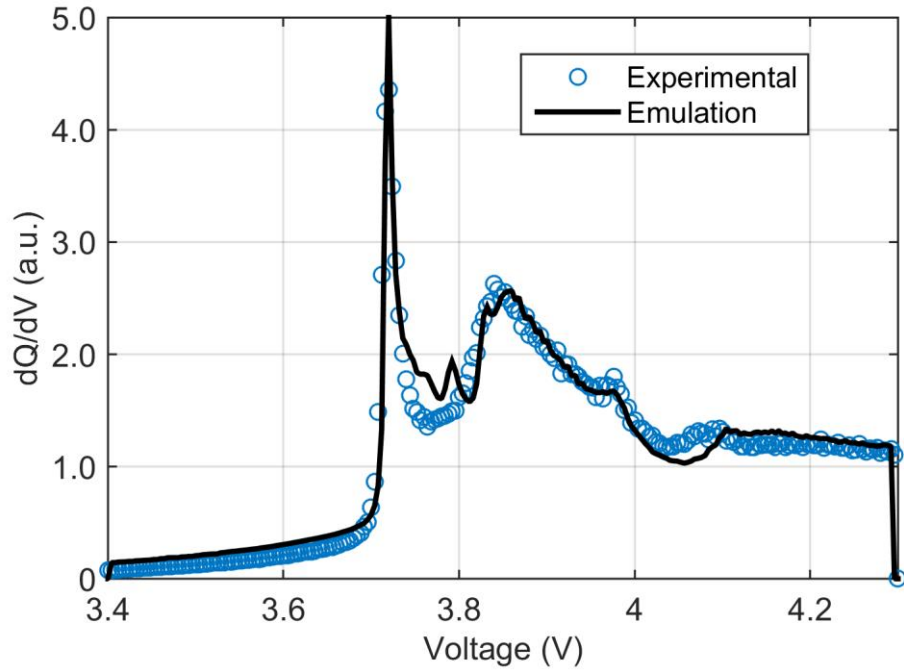
**LLI**


Results of 'alawa emulation

**Exp. dQ/dV**

 Experimental  $dQ/dV$  consistent with up to 25% LLI

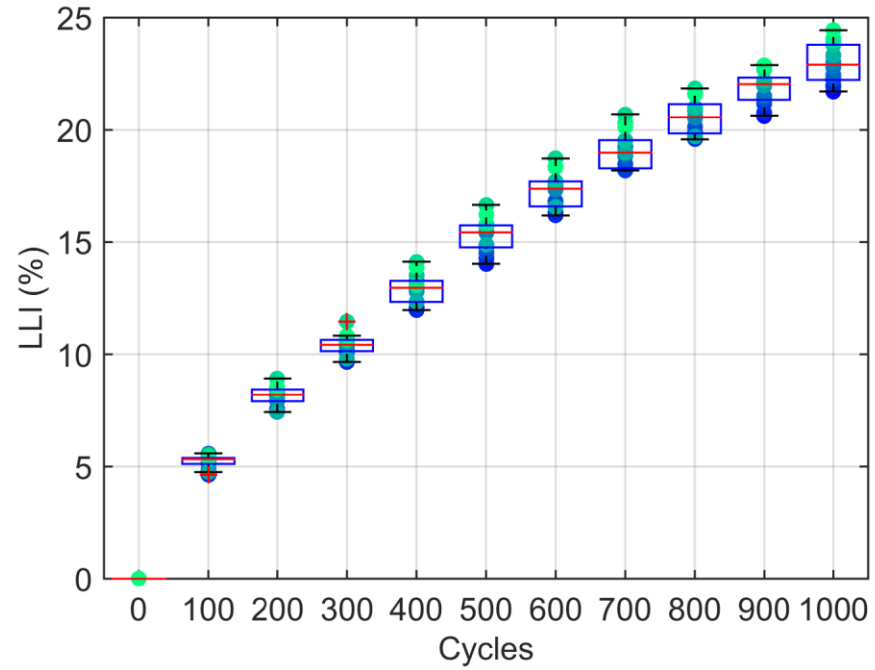
# Loss of Lithium Inventory (LLI)

alawa toolbox



Comparison of emulated and experimental  $dQ/dV$  after 1000 cycles with LLI as the degradation mode

LLI



Gradual increase of LLI  
Statistical dispersion rose

# Conclusion

Many sources of variability in the manufacturing of lithium-ion cells

Tight control over the cell-to-cell variations can be achieved at the end of the assembly line

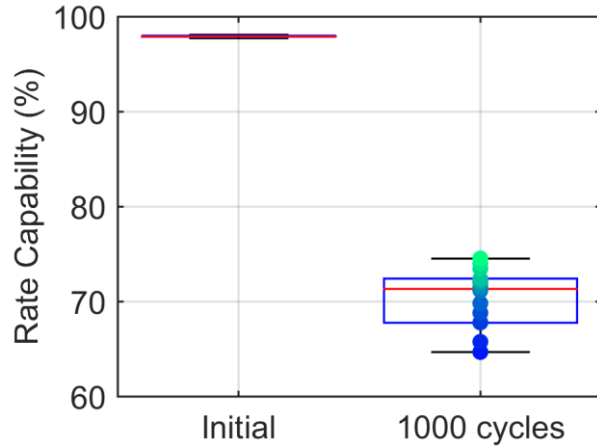
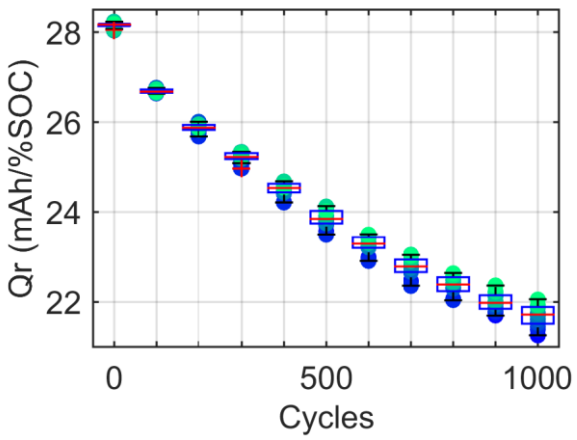
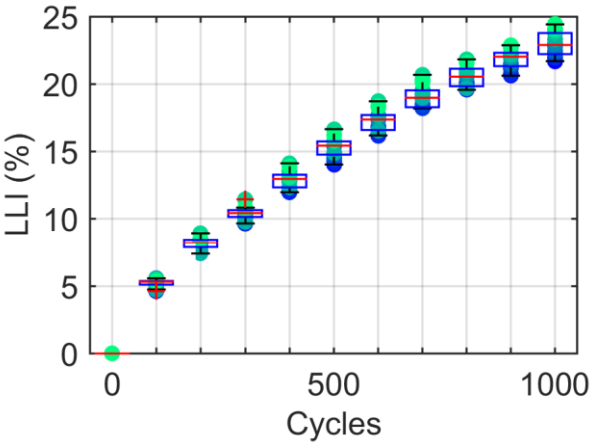
Grading & Matching

But, it is not sufficient to achieve tight control over the cycle life of these cells

Capacities & Kinetics diverged

We uncovered a possible thermodynamic origin to this variability

Main driver: spread in susceptibility to Loss of Lithium Inventory (LLI)





# Acknowledgement

## Funding:

Idaho National Laboratory  
US DOE EERE ABR  
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*Mahalo for your attention! Questions ?*

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