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Stationary
Energy Storage:
Engineering Battery Utility into the Grid
TRACK 3: APRIL 18-19, 2016

EV Cell Degradation under Electric Utility Grid Operations: Impact of Calendar Aging & Vehicle to Grid Strategies

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HiSERF

Objectives & Motivations

Battery degradation is extremely sensitive to usage and chemistry.

This raises concerns over battery monitoring and durability in the rollout of electric vehicles (EVs).

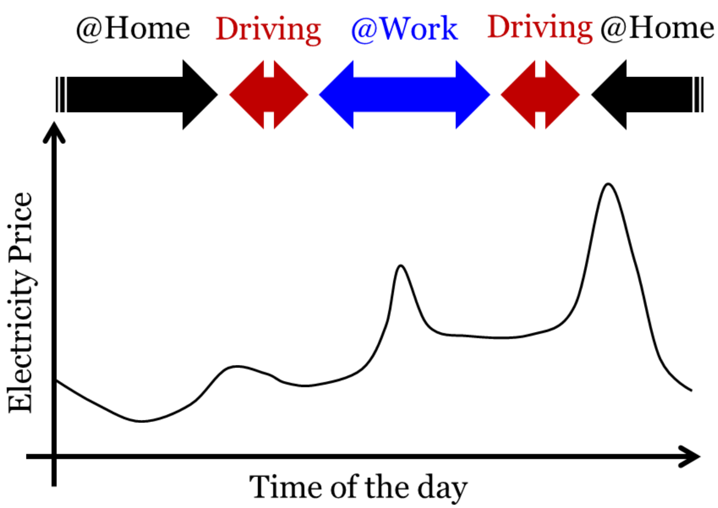
- Range anxiety, battery lifetime,
- Participation in V2G/G2V programs,
- …

In most studies on the impact of EVs on the grid, the battery is viewed as a black box and therefore there is no real understanding on the actual long-term impact of V2G profiles on batteries.

The goal of this research is to assess such impact and to propose solutions to monitor changes *in-operando* via the BMS.

Experimental approach

Matrix of experiments based on daily commute vs. electricity price



@Home or @Work
4 possible scenarios:

V2G

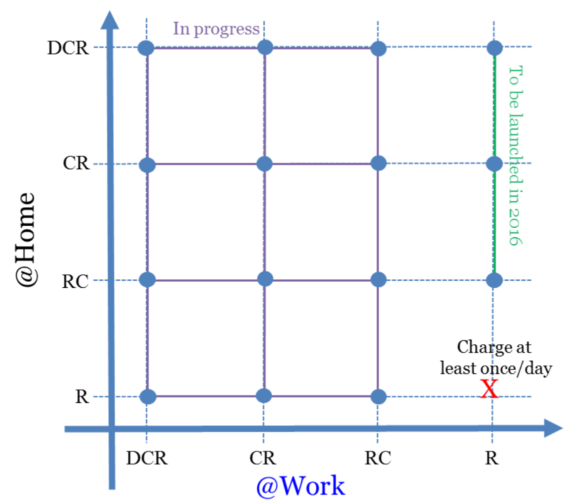
- Discharge, charge and rest (DCR)
- Charge then rest (CR)
- Rest then charge (RC)
- Resting (R)

G2V

Consumer side:
Electricity more expensive @ peak hours

Selling it when expensive and buying when cheap could provide income when the battery is sitting (cars are parked 95% of the time).

Is it worth it?



Assumptions:

- Driving data: 20 mi round trip,
- At least 1 charge/day,
- V2G step: 1 hour @ 7kW
- EV battery pack: ~ 25 kWh,
- @Work battery charger:
  - Max power to grid ~ 7kW
  - Fast charger (4h/full charge)
- @Home battery charger:
  - Max power to grid ~ 4kW
  - Regular charger (8h/full charge)

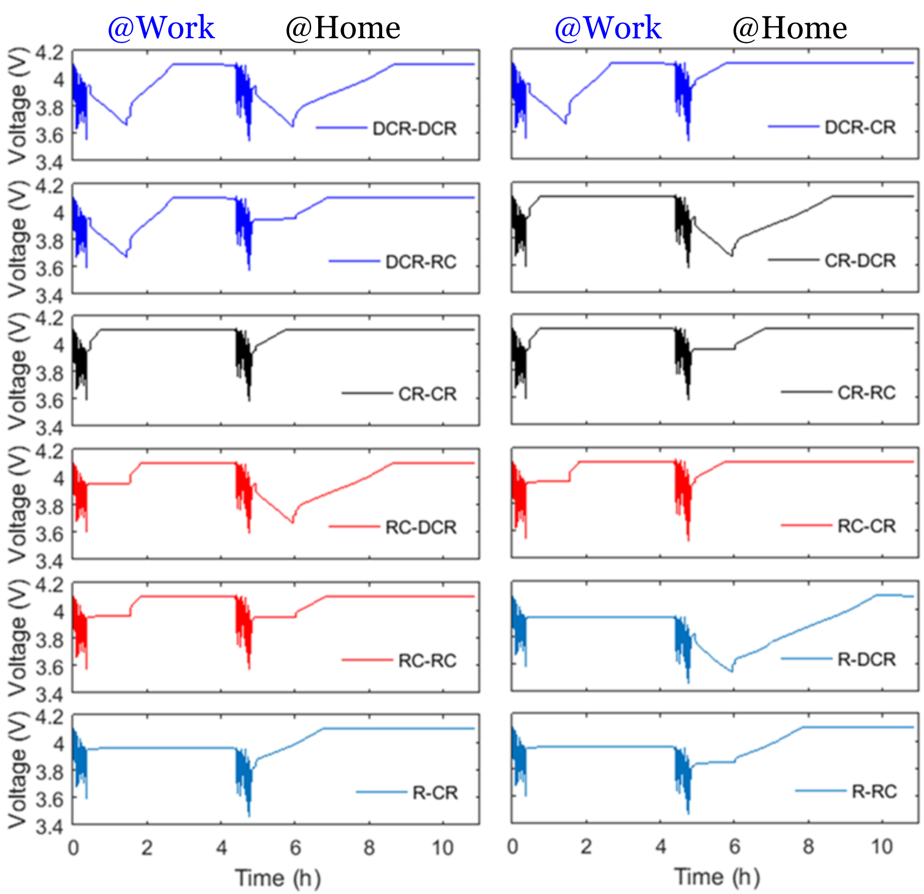
More details @ http://evtc.fsec.ucf.edu/research/project9.html

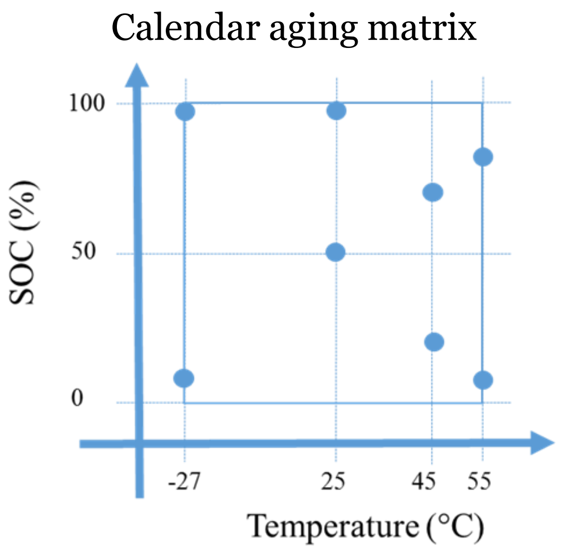
Experimental approach

Matrix of experiments based on daily commute vs. electricity price

Schedule can be compressed to 11h: Test accelerated > x2

Need for calendar aging experiment to assess impact of the skipped 13 h/day





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

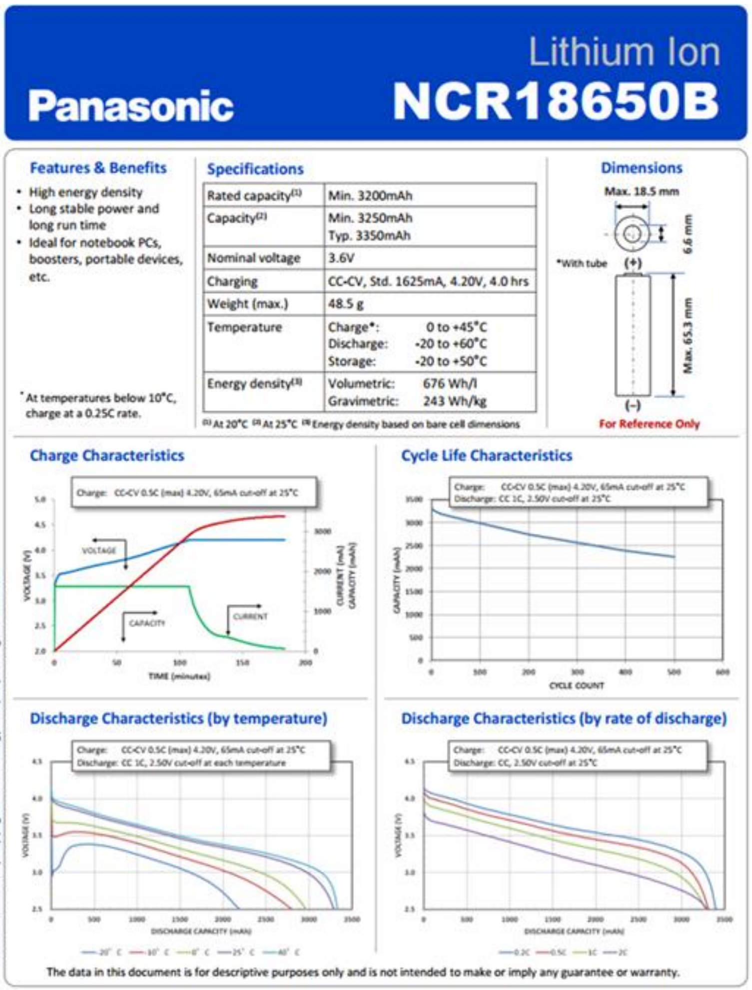
Unique set of protocols
Shall yield unique insight in real effect of V2G/G2G strategies on battery degradation

Cell selection

Assess cell-to-cell variations

High quality Graphite//NCA cells

Reported to be used in some EVs today



Lithium Ion

Panasonic NCR18650B

Features & Benefits

- High energy density
- Long stable power and long run time
- Ideal for notebook PCs, boosters, portable devices, etc.

*At temperatures below 10°C, charge at a 0.25C rate.

Specifications

Rated capacity[1]	Min. 3200mAh
Capacity[2]	Min. 3250mAh Typ. 3350mAh
Nominal voltage	3.6V
Charging	CC-CV, Std. 1625mA, 4.20V, 4.0 hrs
Weight (max.)	48.5 g
Temperature	Charge*: 0 to +45°C Discharge: -20 to +60°C Storage: -20 to +50°C
Energy density[3]	Volumetric: 676 Wh/l Gravimetric: 243 Wh/kg

[1] At 20°C [2] At 25°C [3] Energy density based on bare cell dimensions

Dimensions

Max. 18.5 mm; 6.6 mm; *With tube; (+); Max. 65.3 mm; (−)

For Reference Only

Charge Characteristics

Charge: CC-CV 0.5C (max) 4.20V, 65mA cut-off at 25°C

Cycle Life Characteristics

Charge: CC-CV 0.5C (max) 4.20V, 65mA cut-off at 25°C
Discharge: CC 1C, 2.50V cut-off at 25°C

Discharge Characteristics (by temperature)

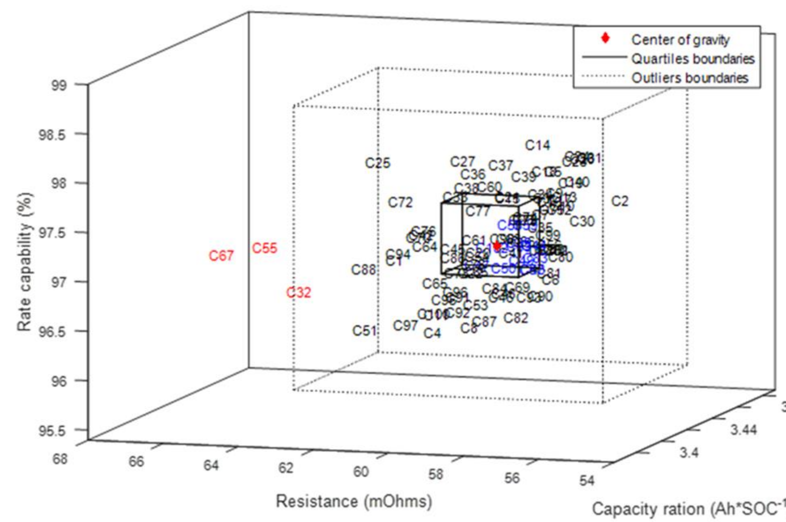
Charge: CC-CV 0.5C (max) 4.20V, 65mA cut-off at 25°C
Discharge: CC 1C, 2.50V cut-off at each temperature

Discharge Characteristics (by rate of discharge)

Charge: CC-CV 0.5C (max) 4.20V, 65mA cut-off at 25°C
Discharge: CC, 2.50V cut-off at 25°C

The data in this document is for descriptive purposes only and is not intended to make or imply any guarantee or warranty.

Cell-to-cell variations assessment:
100 cells purchased
< 0.5% rate capability variations
< 0.5% capacity ration variations
< 3% resistance variations
3 outliers



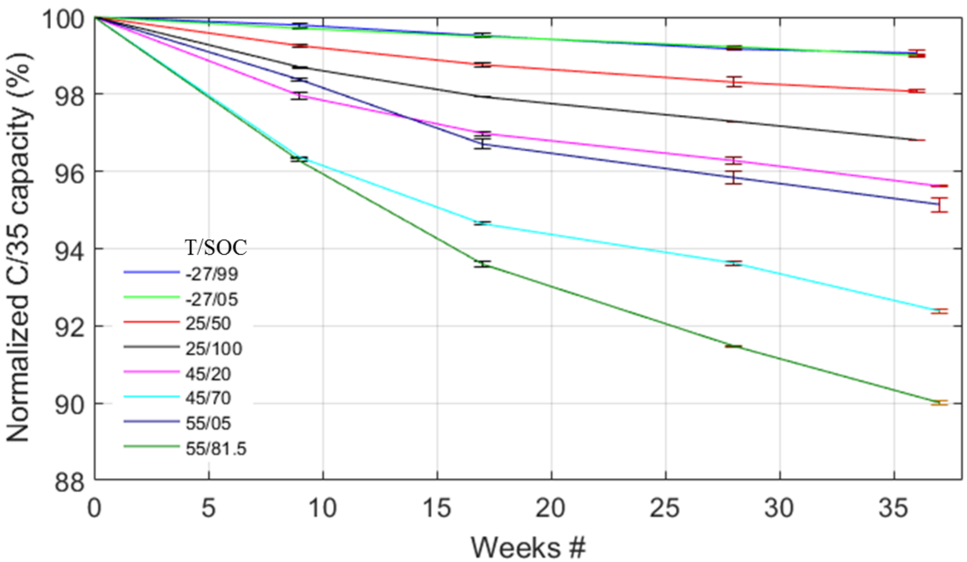
High quality cell selected
For additional confidence in results:
3 cells tested / cycle aging conditions
2 cells tested / calendar aging conditions

Methodology in Dubarry M., Vuillaume N., Liaw B. Y. "Origins and accommodation of cell variations in Li-ion battery pack modeling", Int. J. Energ. Res. 34, pp. 216-31, (2010)

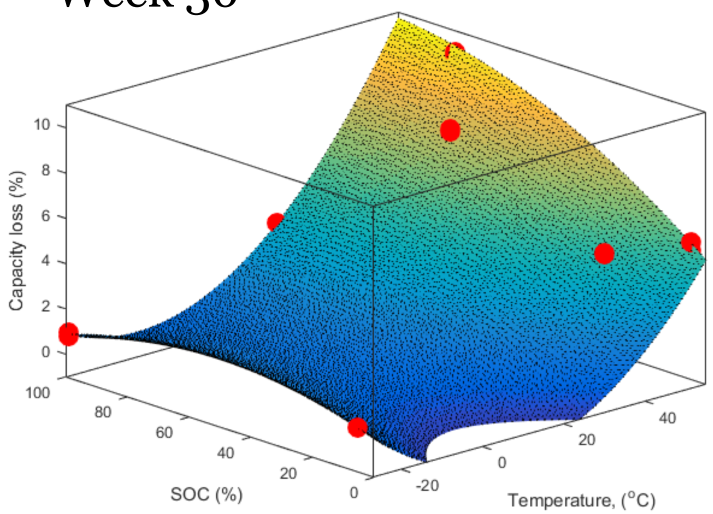
Calendar aging results

Capacity vs. storage weeks

Testing still in progress, 37 weeks in,



Week 36



Capacity loss influenced by both temperature and SOC.

Most impact above RT, little loss below.

Calendar aging at high temperature and high SOCs can induce more than 10% loss after 37 weeks.
Loss up to 3% at RT after 37 weeks.

Calendar aging results

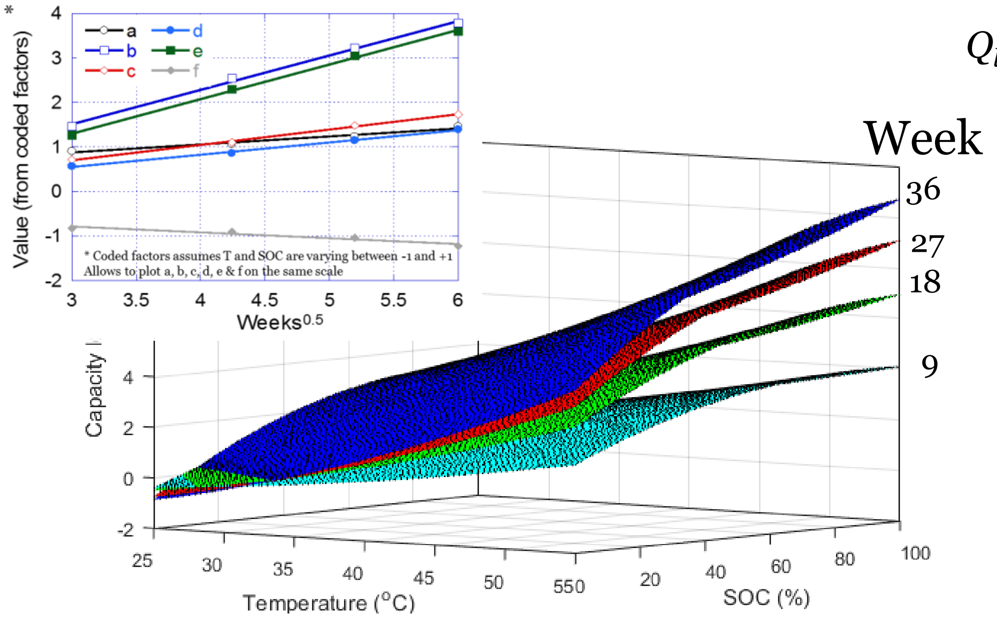
Capacity vs. storage weeks

For all weeks, data can be fitted with a quadratic model:

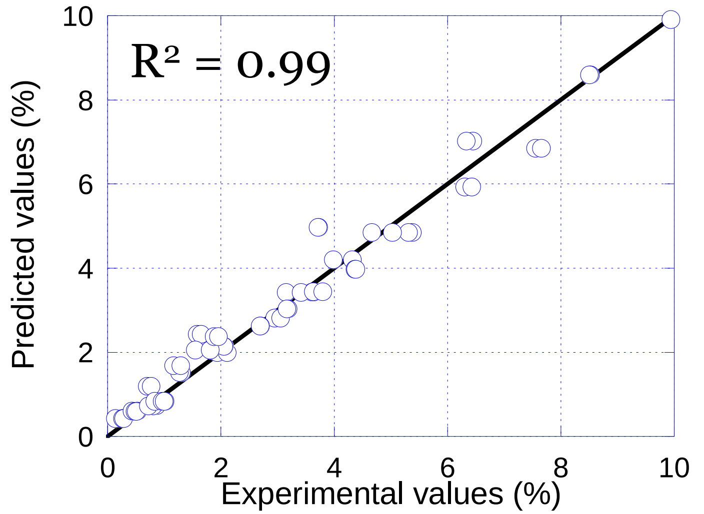
$Q_{loss} = a + b\,T + c\,SOC + d\,T\,SOC + e\,T^2 + f\,SOC^2$ ($R^2 = 0.99$)

Parameters *a* to *f* of all quadratic models can be fitted in function of time:

a, *b*, *c*, *d*, *e* & *f* seems to mostly vary linearly with $Weeks^{0.5}$



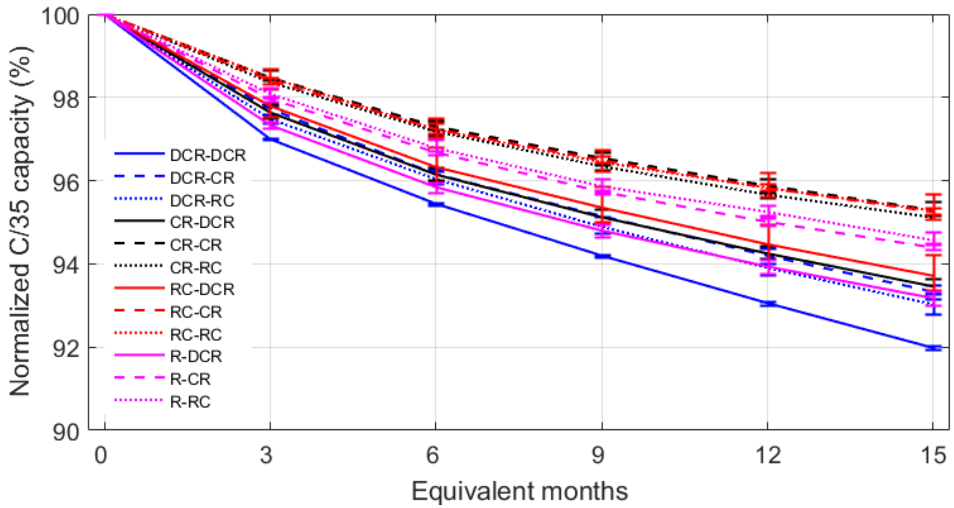
$Q_{loss} = W^{0.5}(a + bT + cSOC + dTSOC + eT^2 + fSOC^2)$:

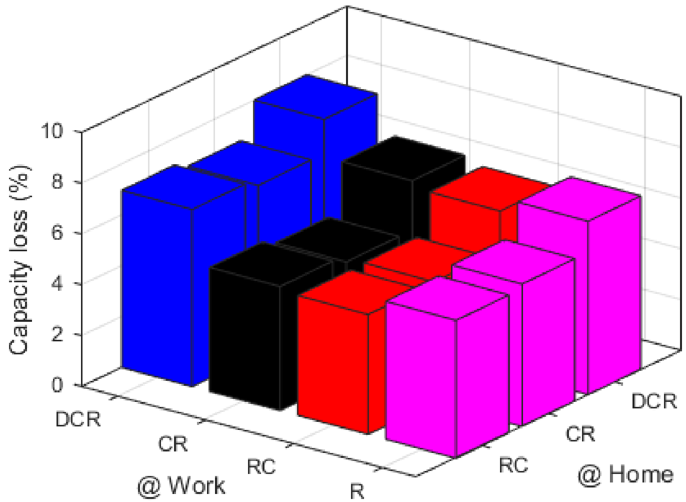


Capacity fading associated with calendar aging can be predicted.
Cars are parked 95% of their time: this will be the main degradation.

Cycling results

Testing still in progress – 15 equivalent months done





Cells lost between 4.5 and 8% capacity after equivalent of 15 months driving.

11h schedule, needs to add about 3% for additional calendar aging at 25°C

V2G strategy: 2% additional capacity loss / daily occurrence after 15 months.

RC/CR strategies have similar capacity loss

2 charges / day strategy degraded cells the least

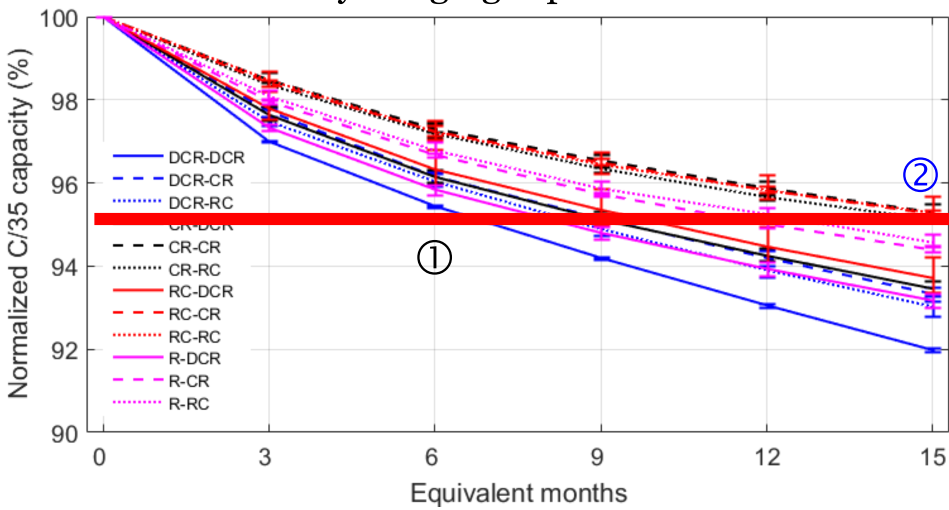
Sustained V2G usage (1h @ 7kW, 1/4th of the car nominal power) seems to induce some additional capacity loss, 0.13%/month.

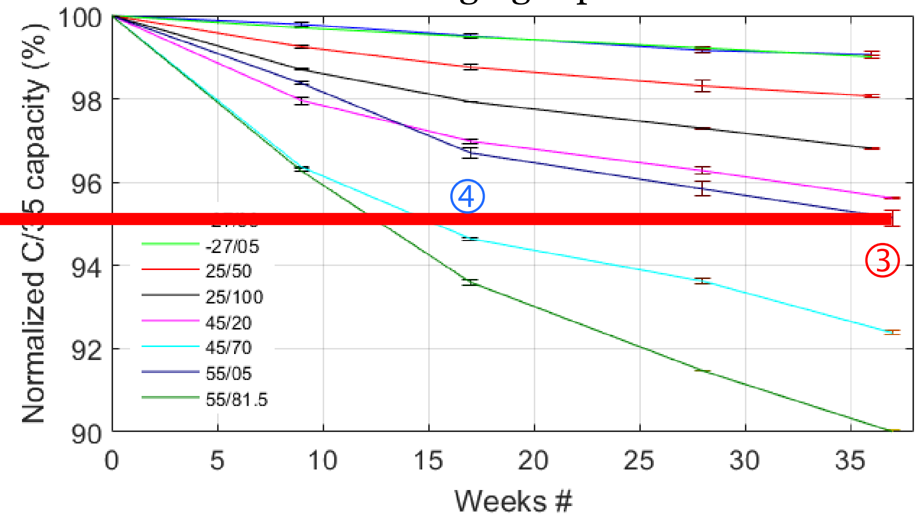
Degradation mechanisms

Battery degradation is extremely sensitive to usage and chemistry.

Is it the case here?

4 different paths to 5% capacity loss





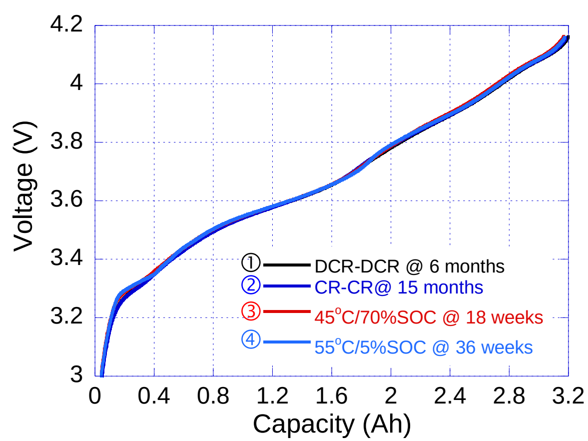
Study voltage response

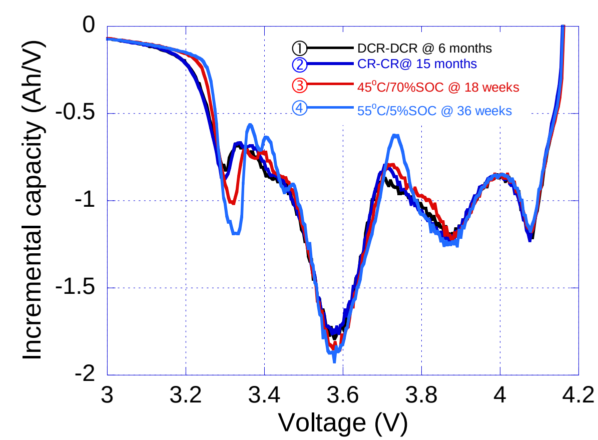
Traditional V vs. Q:

Hard to visualize

Incremental capacity:

Differences visible





Degradation mechanisms

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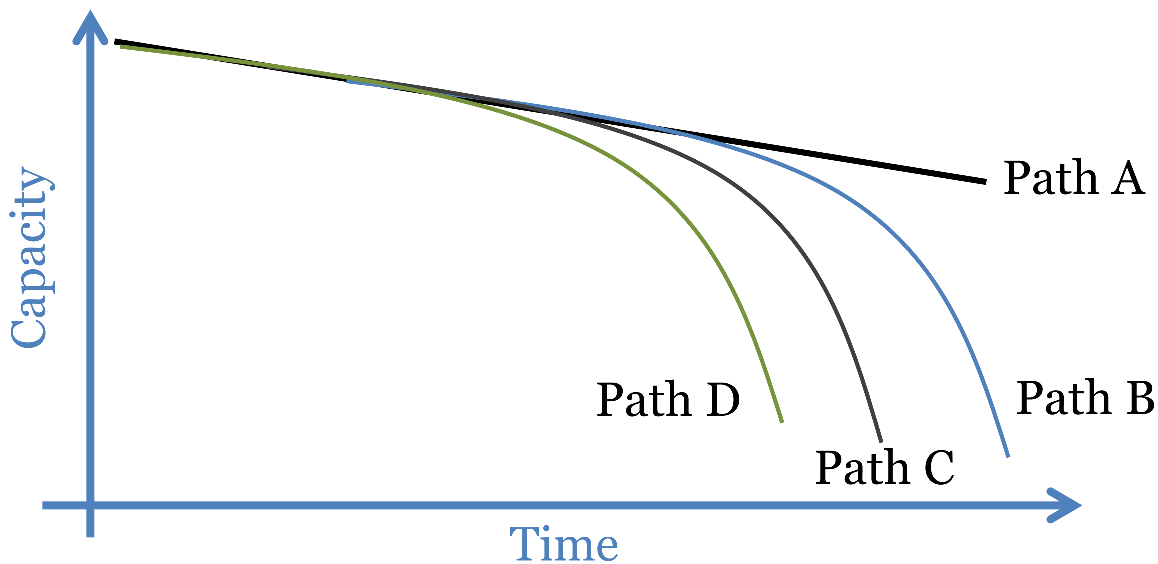
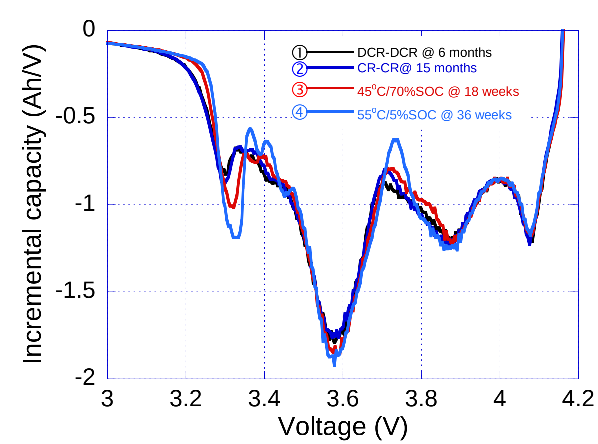
Is it the case here?



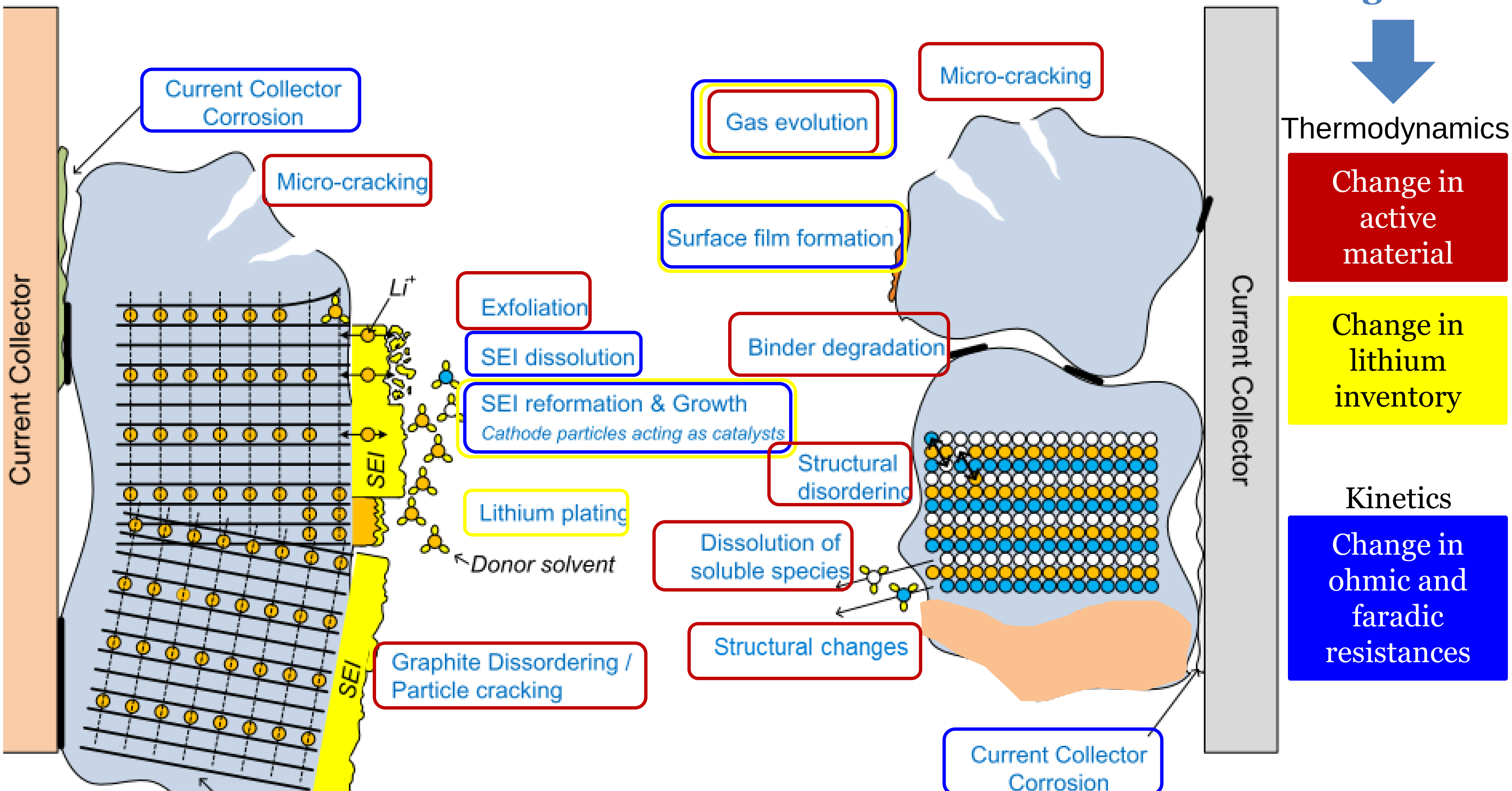
Cells followed different paths to 5% capacity loss.
⇨ Impact on lifetime?
⇨ Need to diagnose cell degradation



Li-ion battery degradation mechanisms

Multiple of possible degradation mechanisms

Useful categorization for diagnostics



Extremely difficult to test or have a model to handle all the processes simply
BUT can we only emulate their effects on the cell?

Quantifying the three diagnostic categories

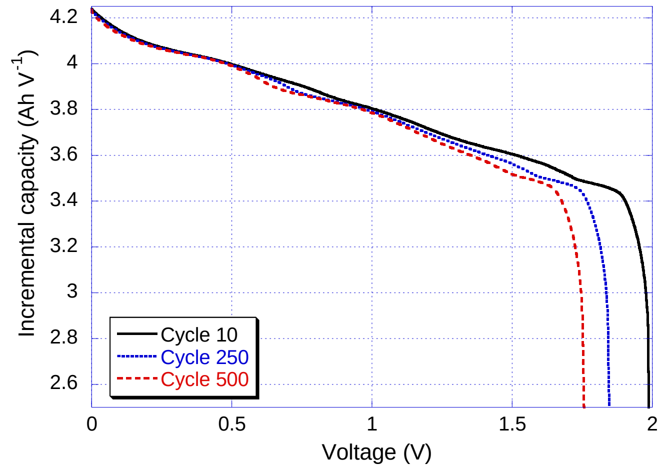
Use of available sensors: voltage, current and temperature.

Voltage is the best candidate

Study evolution of voltage response

How can we extract degradation information?

How can we put it in equation for a model?

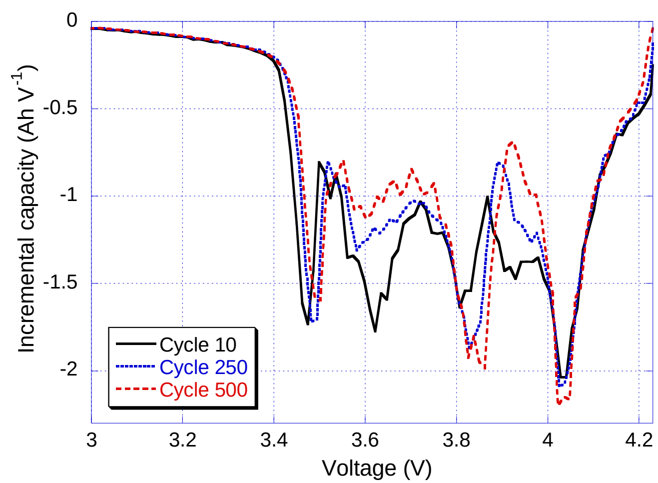


Use derivative method (highlight changes): IC

Link every feature to corresponding

reactions in the PE and the NE

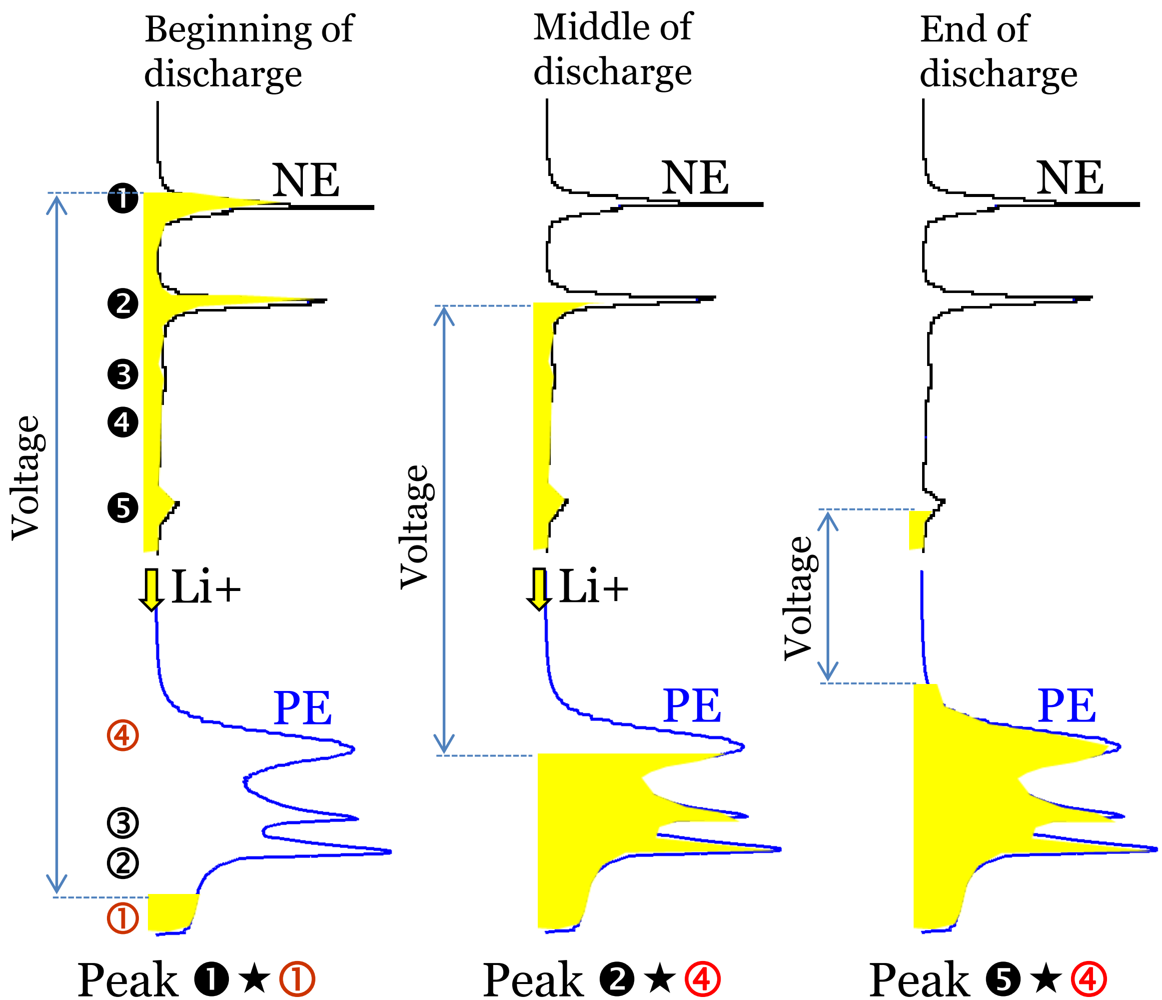
Follow peak evolution to deduce the origin

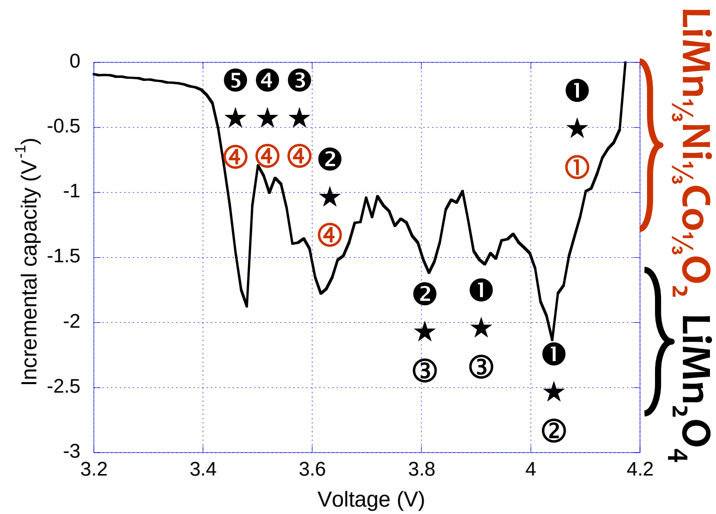


Understanding the IC signature

Peak indexation: The clepsydra analogy

Use individual electrode response





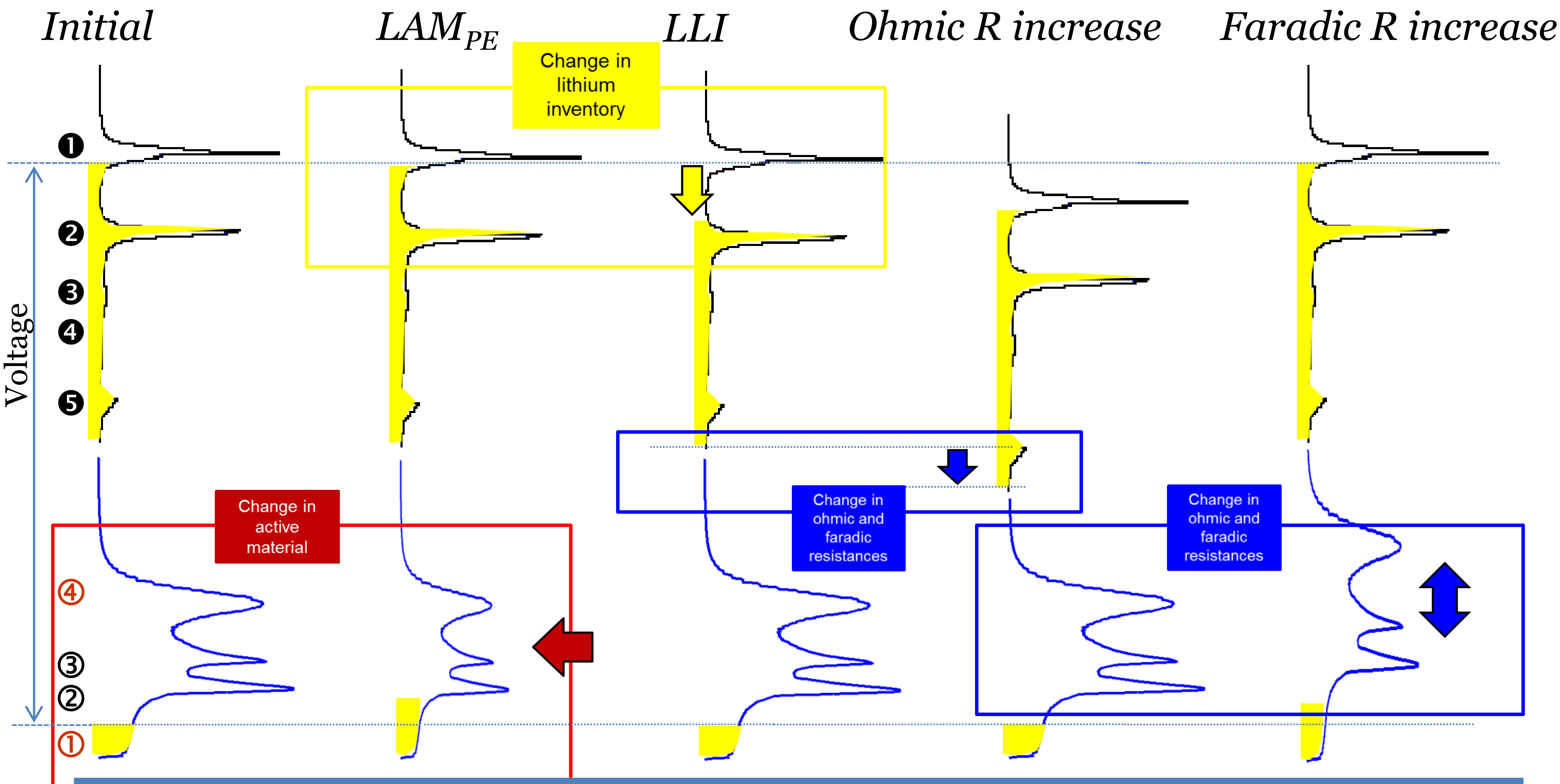
IC curves contains information on every component of the cell

The clepsydra analogy enables the indexing of IC curves

M. Dubarry *et al.*, *J. Power Sources*, **196** (2011) 10328.
M. Dubarry, A. Devie and B.Y. Liaw, *JEPS* **1(5)** (2014) 242
Water clock concept: M. Dubarry *et al.* *ECS222/PRIME2012* (2012) abs# 885

Understanding changes in the IC signature

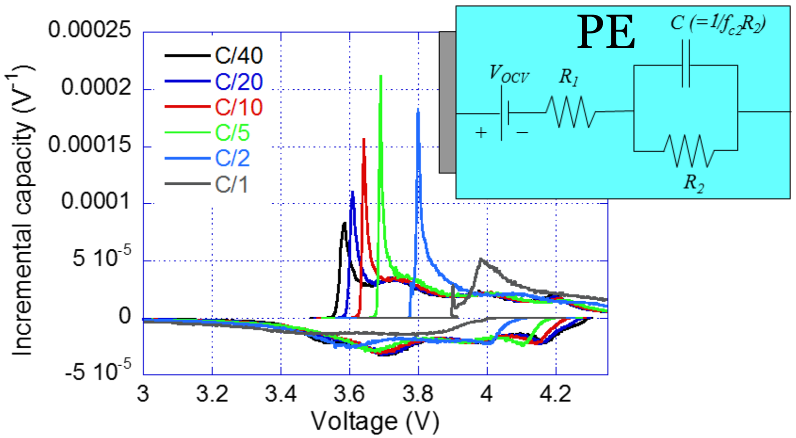
Clepsydra analogy: Visualize effect of categories of degradation



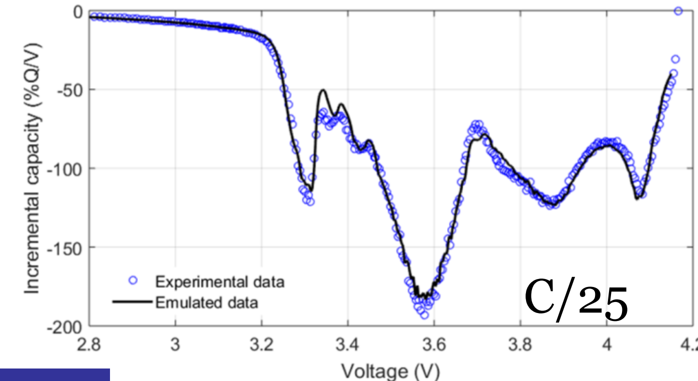
Different degradation categories will have different voltage signatures
Diagnostic possible w/o post-mortem analyses
No need to be an electrochemist

The clepsydra in equations: the 'alawa approach

Half cell data obtained from commercial electrode sheets



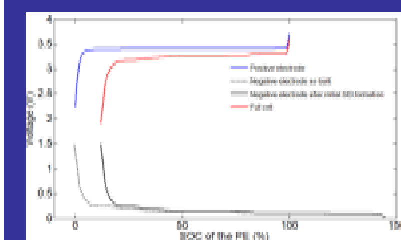
$V_{PE}(SOC_{PE})$



Input from degradation mechanisms

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

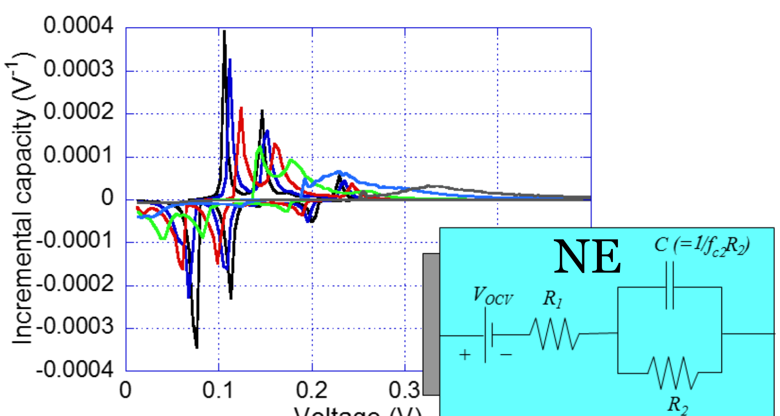
Full cell module



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

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

'alawa



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

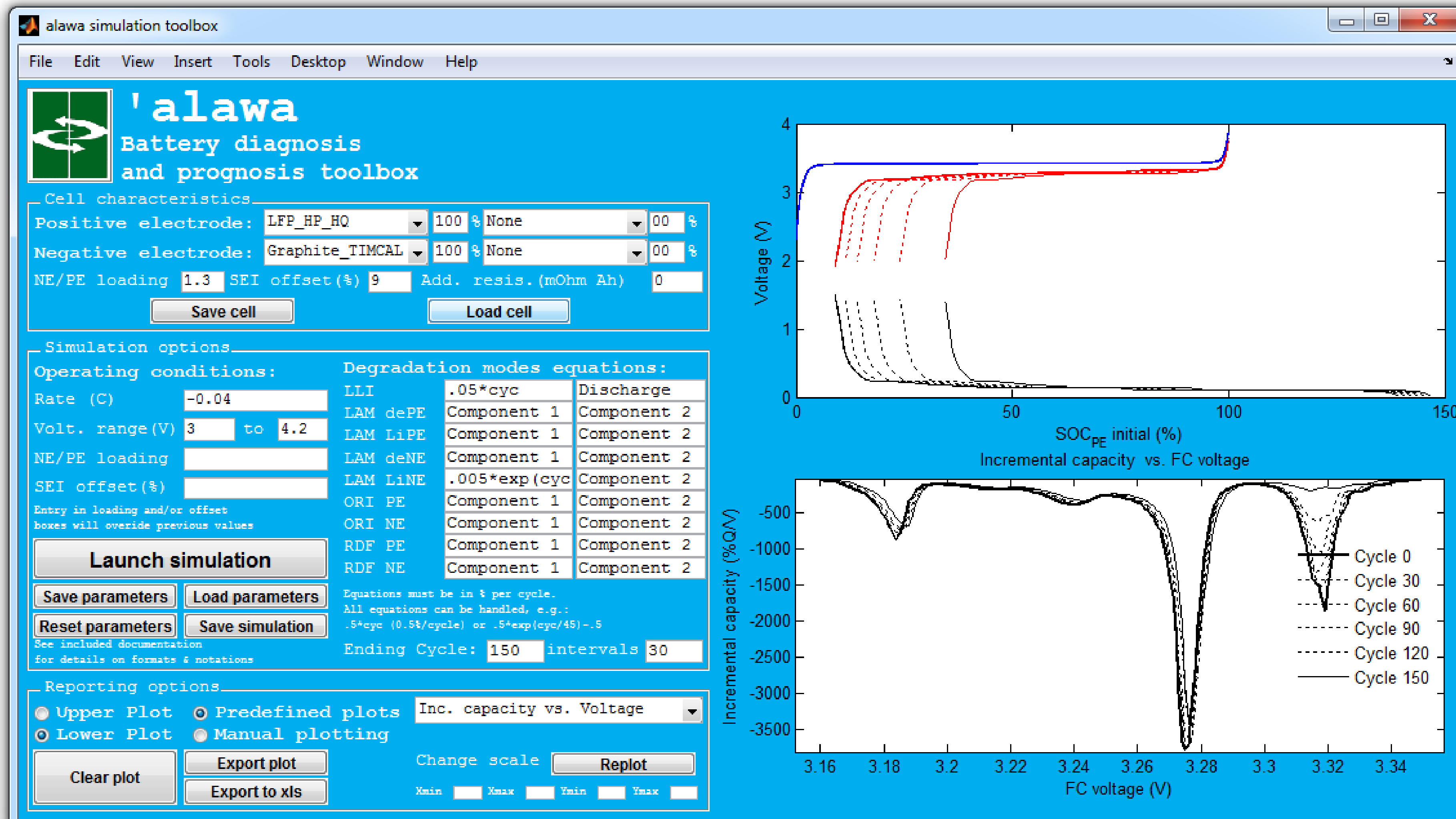
Emulate every possible degradation mode and study effect on full cell (capacity and voltage)

M. Dubarry et al. J. Power Sources 219 (2012) 204-216

'alawa - Mechanistic diagnosis and prognosis

Graphical user interface

Simple, fast, powerful and accurate diagnosis and prognosis tool

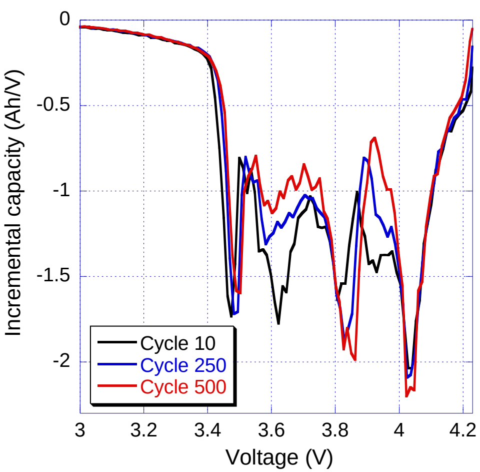


Stand alone GUI available for license or collaboration

Li-ion battery diagnosis and prognosis
Understanding changes in the IC signature

Use ‘alawa toolbox to analyze data *operando*

Incremental capacity curves from maintenance cycles

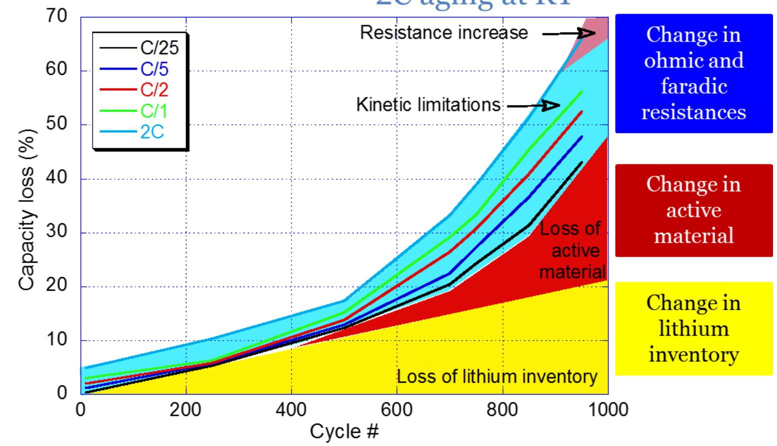


SOH determination

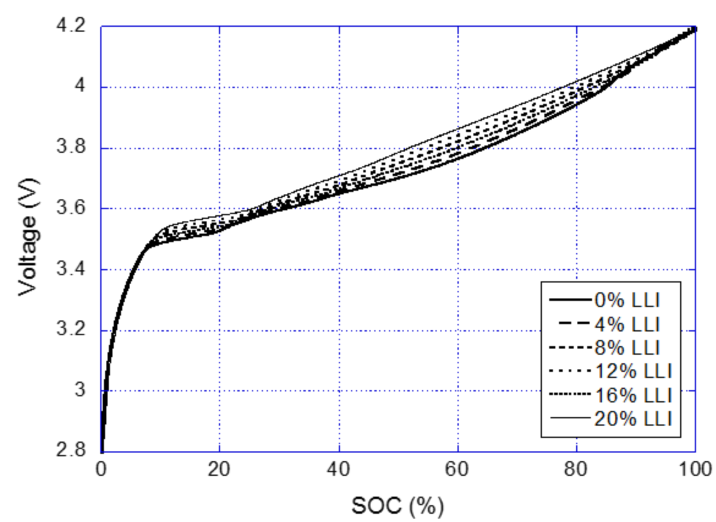
‘alawa

Update OCV vs. SOC curve

2C aging at RT



Enables prognosis



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

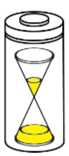
M. Dubarry et al. J. Power Sources, 196(7), (2011) 3420

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

Scale-up to pack level: on board pack SOC and SOH tracking

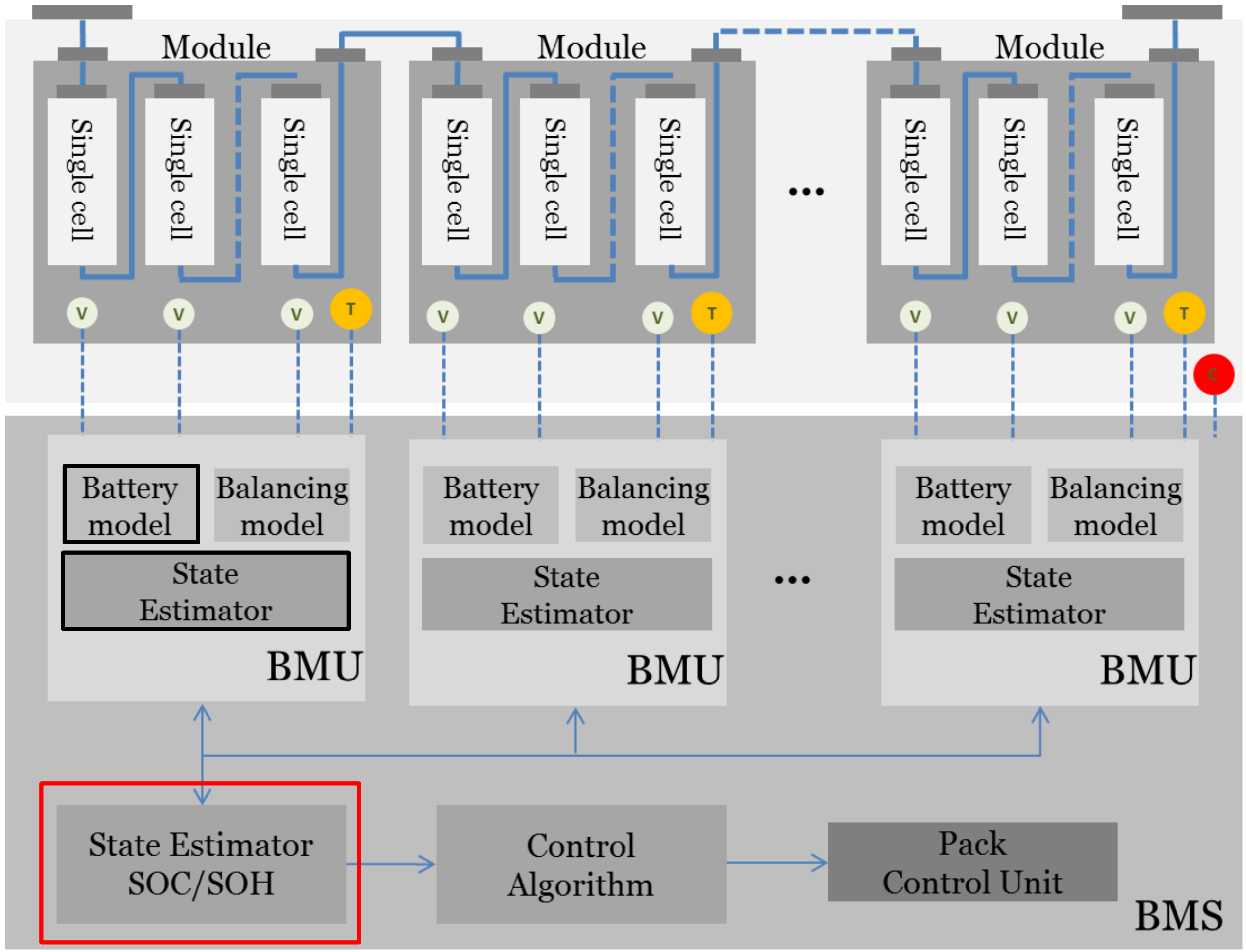
Battery Diagnosis is only half of the problem:

Need for a pack level State Estimator



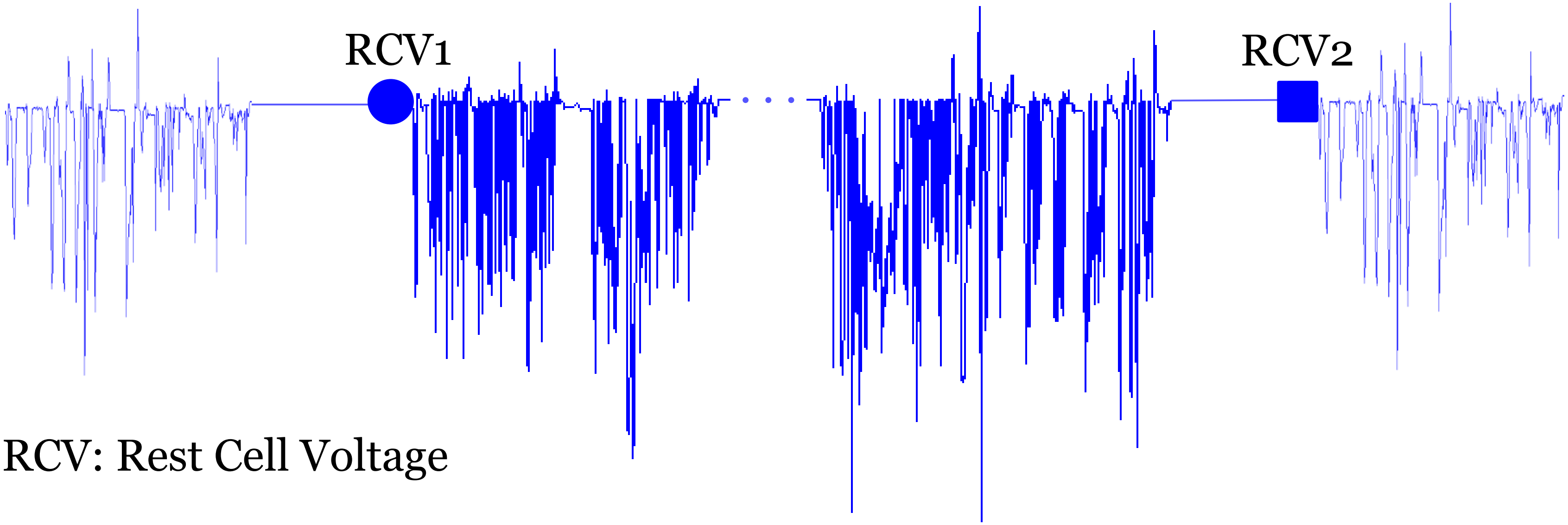
‘alawa

anakonu



Anakonu approach: Single cell/Pack correlation

Full SC/pack correlation:



RCV: Rest Cell Voltage

$$_{\mathrm{SC}i}\mathrm{sf} = \frac{_{SCi}SOC(\mathrm{RCV}_1) - {}_{SCi}SOC(\mathrm{RCV}_2)}{_{SC1}SOC(\mathrm{RCV}_1) - {}_{SC1}SOC(\mathrm{RCV}_2)} \qquad _{\mathrm{SC}i}\mathrm{tf} = {}_{SC1}SOC(\mathrm{RCV}_1) - {}_{SCi}SOC(\mathrm{RCV}_1)$$

$$OPV({}_{SC1}SOC) = {}_{SC1}OCV({}_{SC1}SOC) + \sum_{i=2}^{n} {}_{SCi}OCV\left({}_{\mathrm{SC}i}\mathrm{sf}({}_{SC1}SOC + {}_{\mathrm{SC}i}\mathrm{tf})\right)$$

$$_{\mathrm{pack}}\mathrm{Qr} = \frac{({}_{SCi}SOC(\mathrm{RCV}_1) - {}_{SCi}SOC(\mathrm{RCV}_2))\,{}_{\mathrm{SC}i}\mathrm{Qr}}{_{pack}SOC(\mathrm{RCV}_1) - {}_{pack}SOC(\mathrm{RCV}_2)} = \frac{\mathrm{Q}}{\Delta_{\mathrm{pack}}\mathrm{SOC}}$$

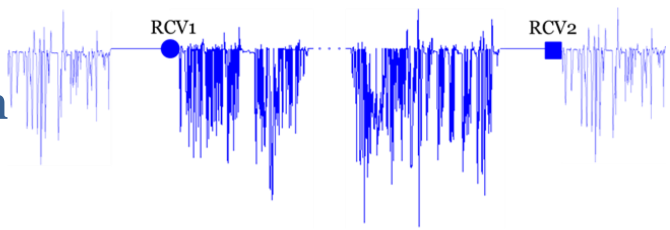
With **2 sets of RCVs** we can calculate the **full pack characteristics**

M. Dubarry, C. Truchot, A. Devie and B.Y. Liaw, *J. Electrochem. Soc.* 162(6), p. A877 (2015).

Anakonu approach: Single cell/Pack correlation

Full SC/pack correlation:

- *OPV* is a function of *OCV* of all single cells within assembly
  - Not directly proportional: need 2 adjustments for every single cell
  - A scaling factor *sf (“SC capacities ratio”)*
  - A translation factor *tf (“SC SOC imbalance”)*
  - Both calculable from RCV gathered information



  - Their evolution characterize pack imbalance.

$$ {}_{\mathrm{sc}i}\mathrm{sf} = \frac{{}_{sci}SOC(\mathrm{RCV}_1) - {}_{sci}SOC(\mathrm{RCV}_2)}{{}_{sc1}SOC(\mathrm{RCV}_1) - {}_{sc1}SOC(\mathrm{RCV}_2)} \qquad {}_{\mathrm{sc}i}\mathrm{tf} = {}_{sc1}SOC(\mathrm{RCV}_1) - {}_{sci}SOC(\mathrm{RCV}_1) $$

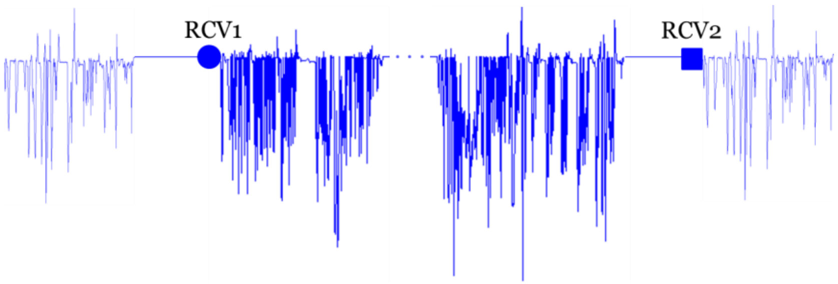
$$ \boldsymbol{OPV}({}_{sc1}SOC) = {}_{sc1}\boldsymbol{OCV}({}_{sc1}SOC) + \sum_{i=2}^{n} {}_{sci}\boldsymbol{OCV}\left(\boxed{{}_{\mathrm{sc}i}\mathrm{sf}}\left({}_{sc1}SOC + \boxed{{}_{\mathrm{sc}i}\mathrm{tf}}\right)\right) $$

M. Dubarry, C. Truchot, A. Devie and B.Y. Liaw, *J. Electrochem. Soc.* 162(6), p. A877 (2015).

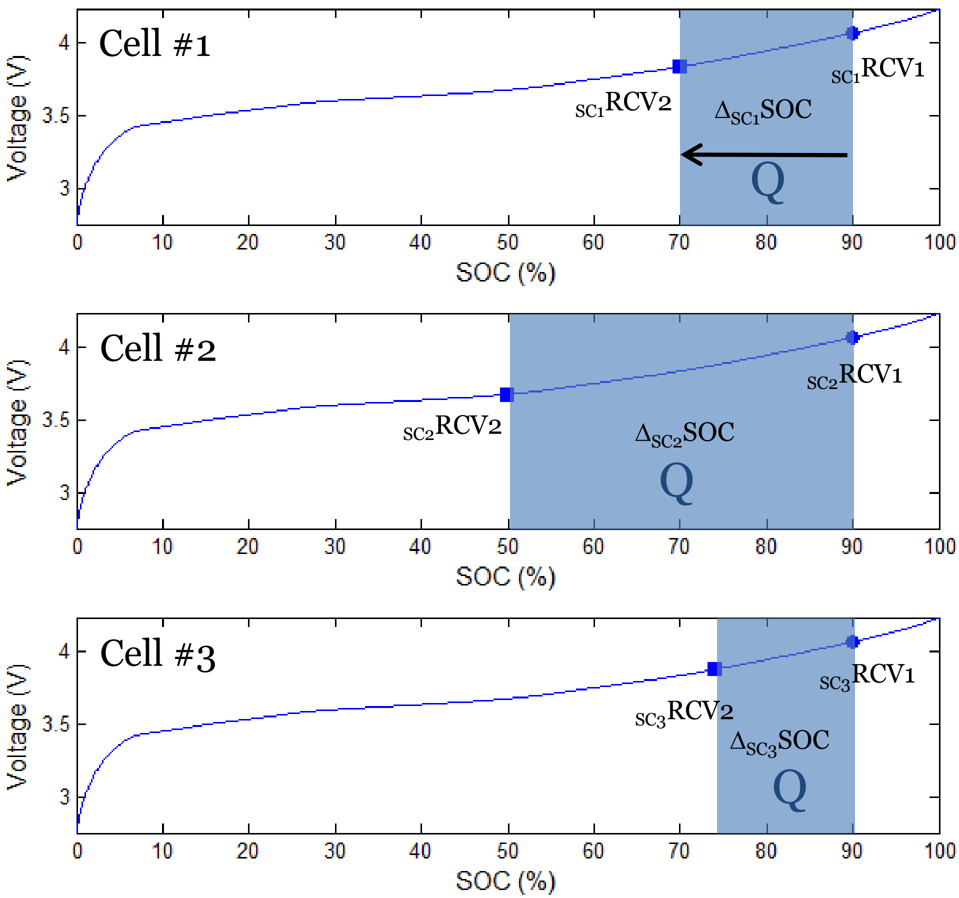
Anakonu approach: SC/Pack correlation

Cells with different capacity ration

Graphical analogy:



Align all the single cell OCV data using the 2 RCVs points as anchors



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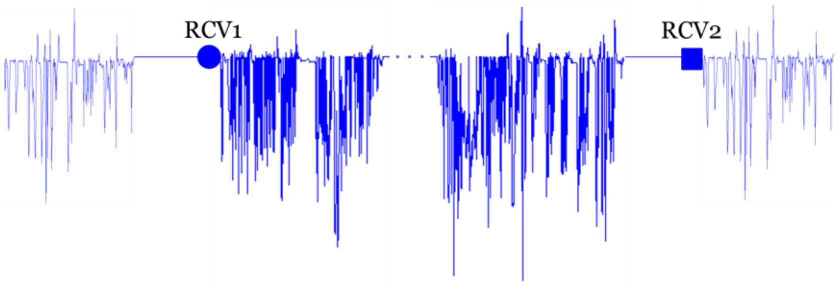
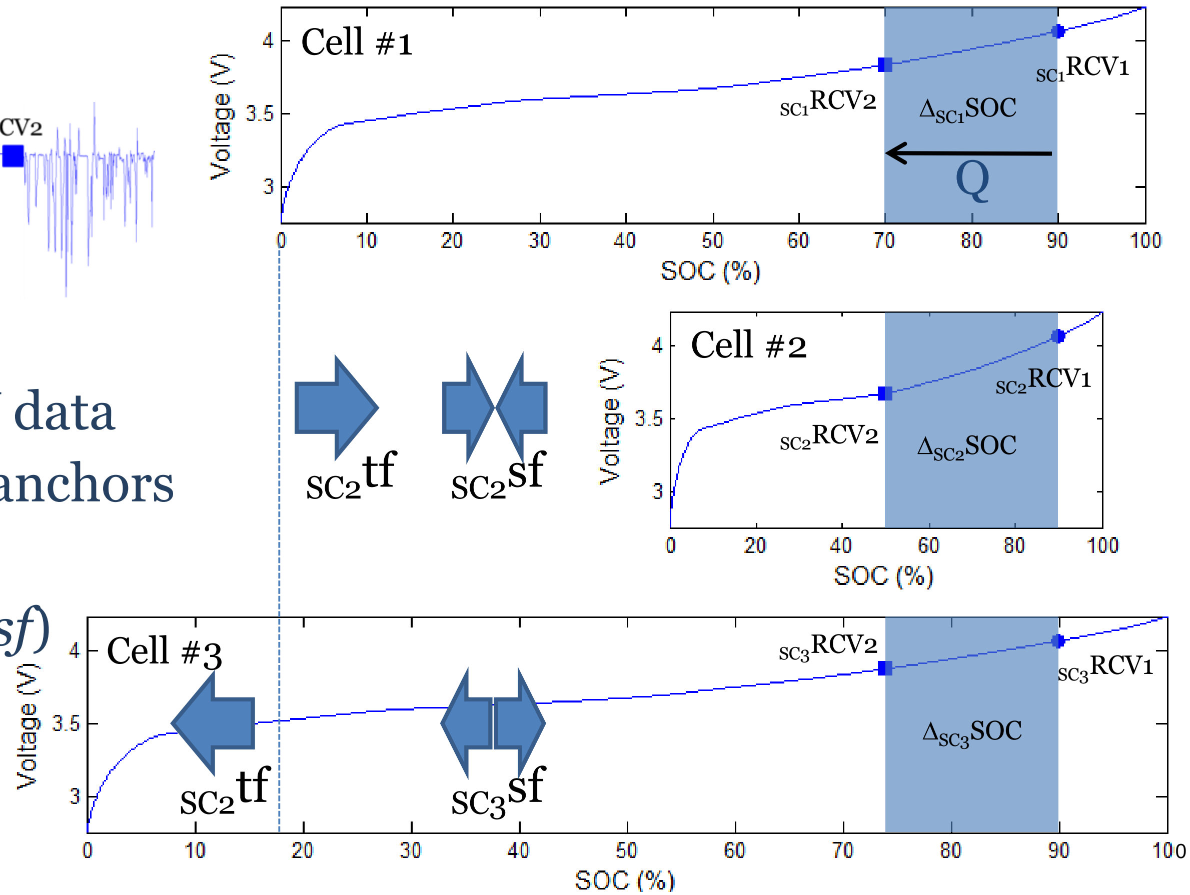




Align all the single cell OCV data using the 2 RCVs points as anchors

Introducing scaling factor (*sf*) and translation factor (*tf*)

All Qr and SOC mismatches can be accommodated with simple scalings and translations

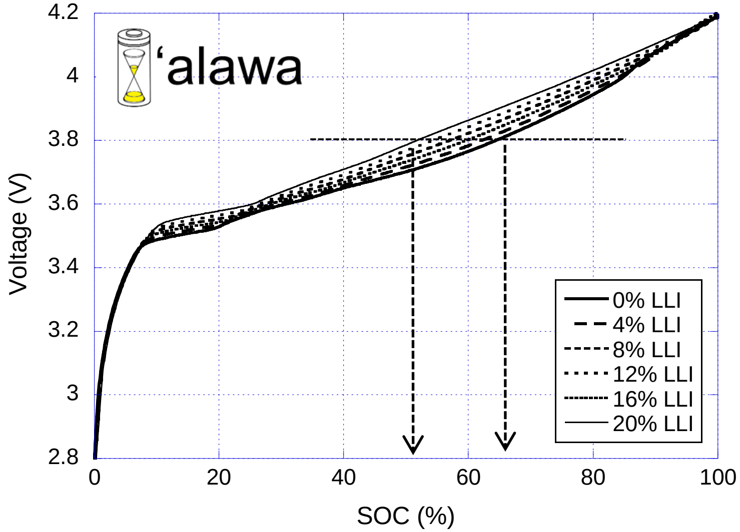
M. Dubarry, C. Truchot, A. Devie and B.Y. Liaw, *J. Electrochem. Soc.* 162(6), p. A877 (2015).

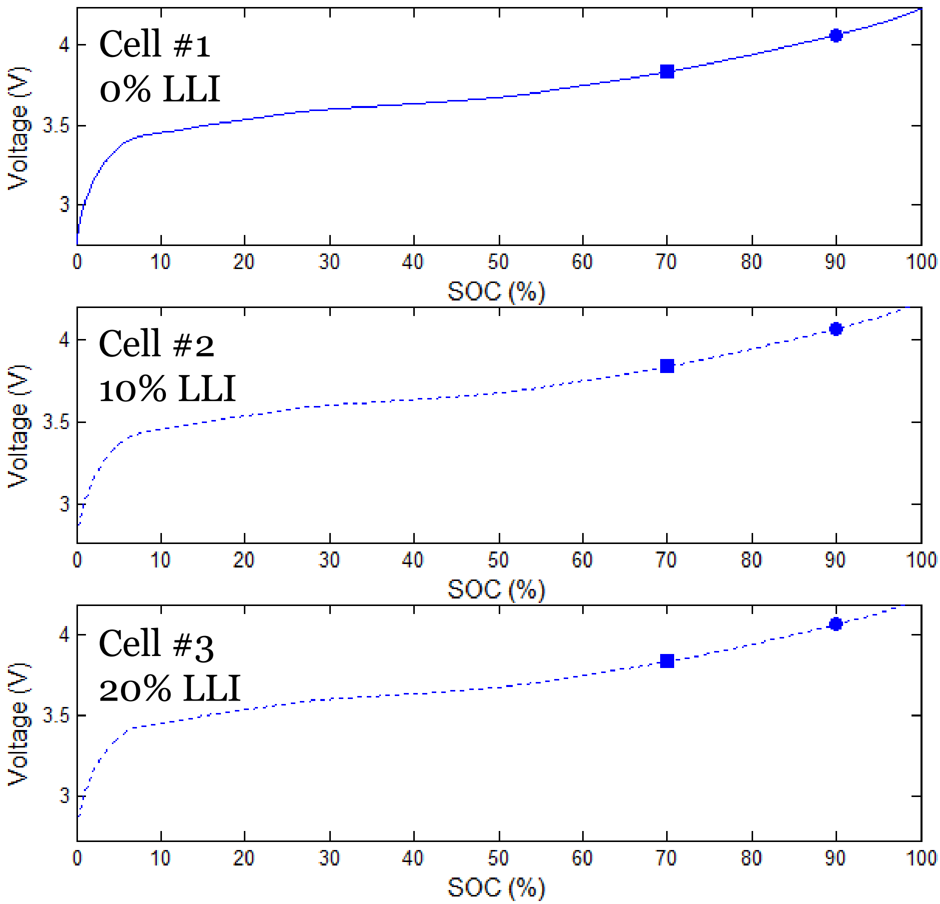
Anakonu approach: SC/Pack correlation
Cells with different SOH

Graphical analogy:

Cell degradation modifies the cells

Same RCV1 but different *OCV* and Qr





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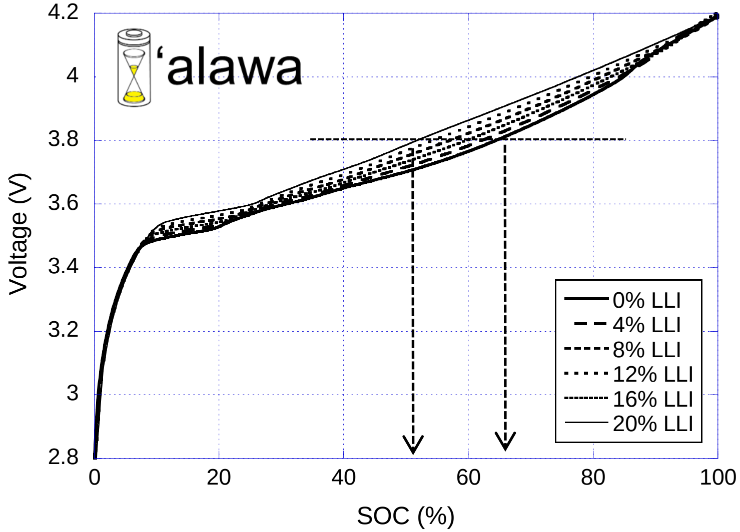
Anakonu approach: SC/Pack correlation

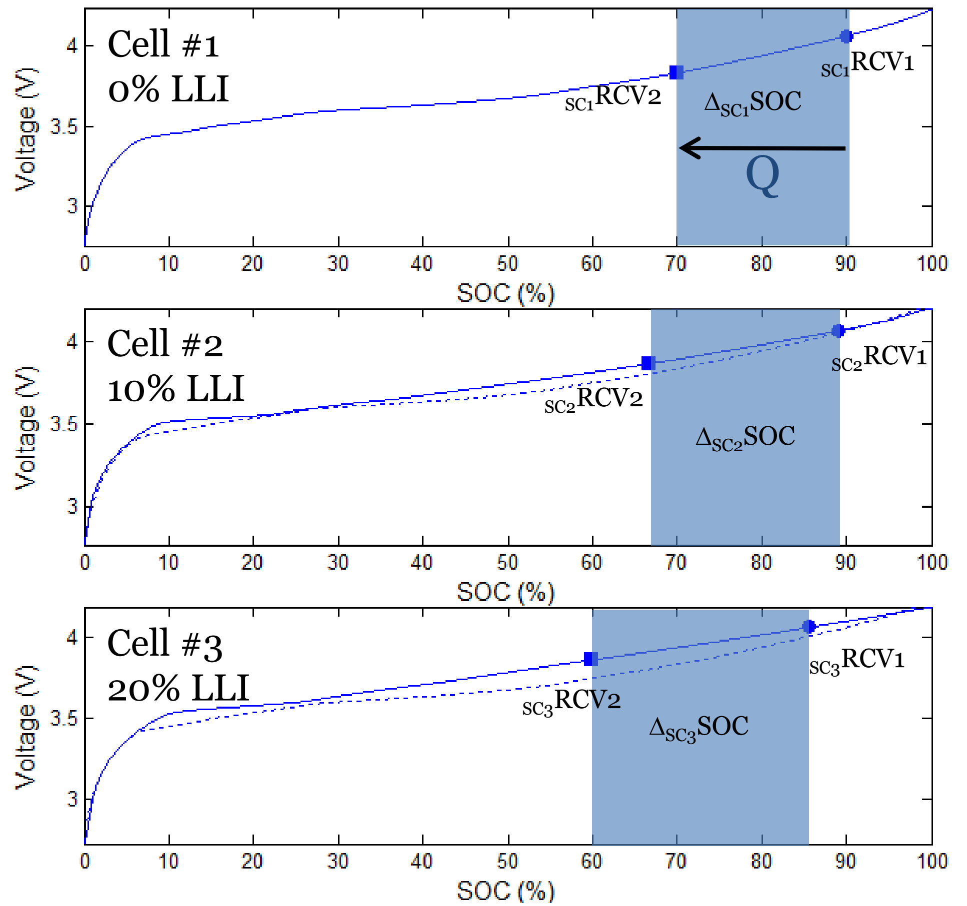
Cells with different SOH

Graphical analogy:

Cell degradation modifies the cells

Same RCV1 but different *OCV* and Qr





M. Dubarry, C. Truchot and B.Y. Liaw, *J.Power Sources*, **219** (2012) 204-216

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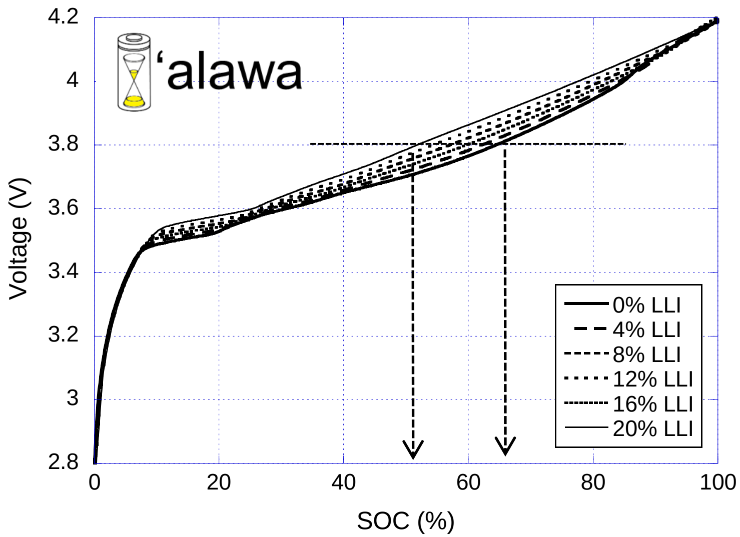

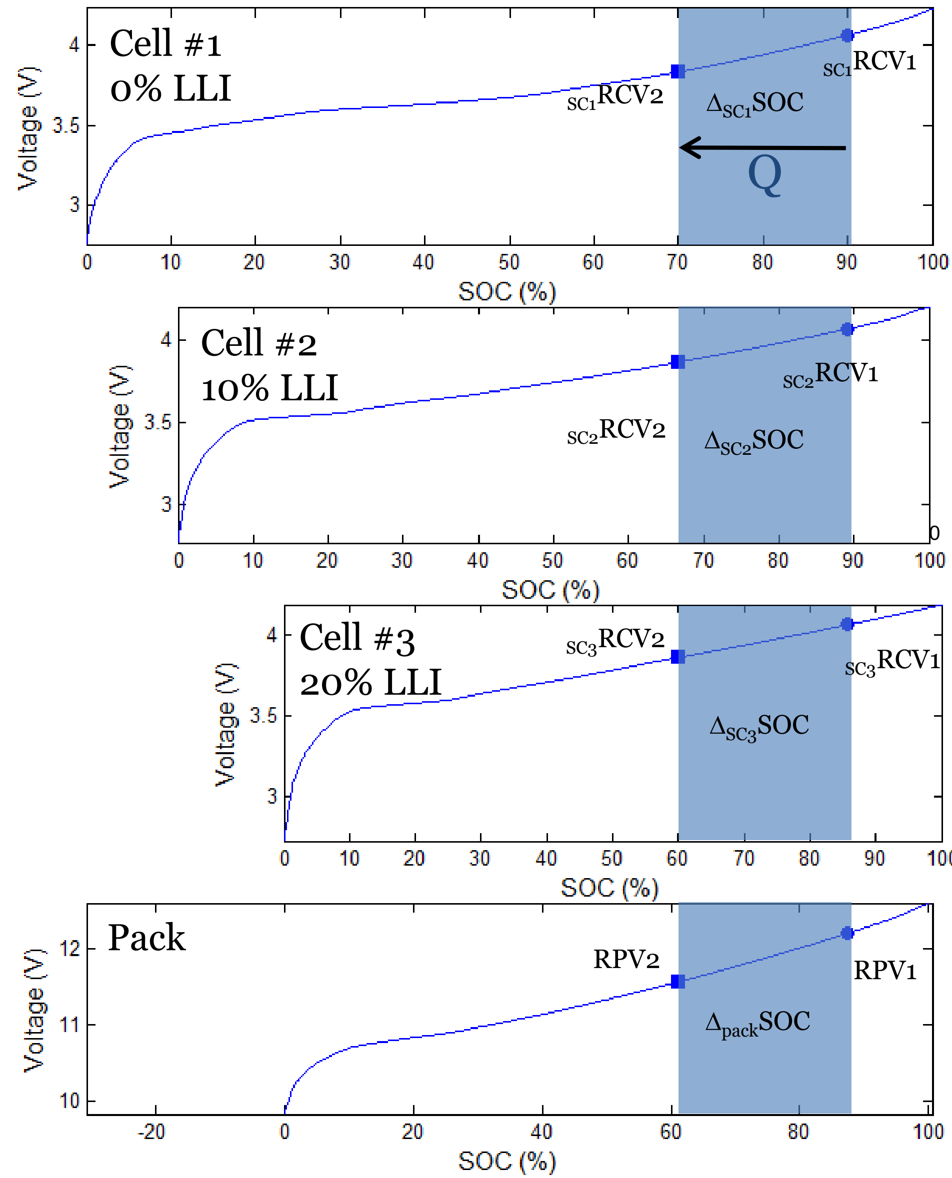

All aging mismatches can be accommodated with an update of the SC OCV curves and simple scaling and translation operations

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Conclusions

HNEI is testing commercial Li-ion cells to assess the impact of V2G and G2V scenarios on battery degradation.

Sustained V2G usage (1h @ 1/4th of the car nominal power) seems to induce some additional capacity loss, 0.13%/month. Interestingly, it also appears that charging twice a day is beneficial to the cells.

Regarding calendar aging, the **high temperature and high SOC are aggravating factors** with losses up to 10% after 36 weeks under harsh conditions. Cells stored at 25°C experienced a 0.05 to 0.1% loss per week depending on SOC.

A quadratic model accounting for time, temperature and SOC was proposed.

Conclusions

The *anakonu* approach is an efficient way to recalibrate the SOC scale for battery packs.

- Based only on the measurement of 2 sets of relaxation potentials

Coupled with the *'alawa* approach, the SOC scale can also be recalibrated at different SOH.

- Based on premeasured half-cell data
- Main drawback is that the *'alawa* approach requires some maintenance cycles at constant current.

HNEI recently developed a new approach that removes this restriction and allows SOC recalibration, imbalance quantification and SOH estimation without the need for maintenance cycles.

- Provisional patent filed in February
- Licensing available
- http://universityofhawaii.technologypublisher.com/technology/21496

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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