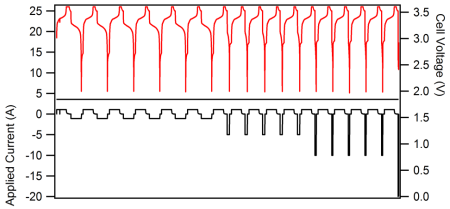
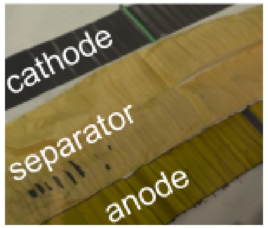
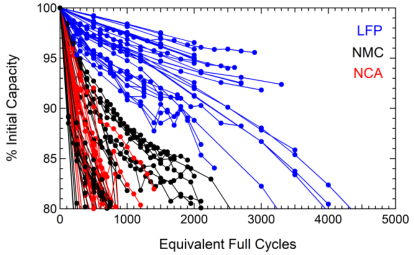
SAND2021-12000C

Sandia National Laboratories

A mechanism-based assessment of 'knees' in lithium-ion battery aging trajectories







PRESENTED BY

Yuliya Preger

IAPG Chemical Working Group Safety Panel

October 1, 2021

U.S. DEPARTMENT OF ENERGY NNSA

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SNL grid energy storage program overview

Develop advanced energy storage technologies and systems, in collaboration with industry, academia, and government institutions, that will increase the reliability, performance, and competitiveness of electricity generation and transmission in the electric grid and in standalone systems.

Materials

Advancing battery chemistries through development and commercialization

Safety & Reliability

Testing, Analysis, Standards, Protocols

Power Electronics

Reduce installed cost and footprint

Improve control capability

Increase reliability

Regulatory Outreach

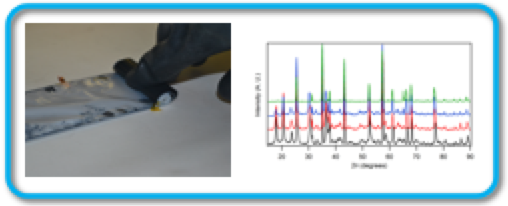
Collaborating with States and other National Labs

State Policy Analysis

Demonstration Projects

Support, Analysis, Implementation, Monitoring

Energy storage safety and reliability focus areas

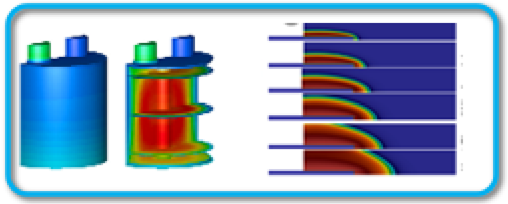


Materials R&D

- Thermal stability and impact of aging on battery components
- Vent gas composition

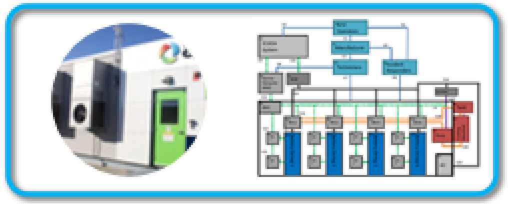
Cell and Module Testing

- High precision cell cycling and degradation
- Electrical, thermal, mechanical abuse testing
- Failure propagation testing on batteries/systems



Simulations and Modeling

- Multi-scale models for understanding thermal runaway
- Fire Dynamic Simulations to predict the size, scope, and consequences of battery fires



System Level Design and Analysis

- Hazard analysis methods to avoid fire and explosion
- Predictive maintenance
- Power electronics control

Outreach, Codes, and Standards

- Energy storage safety working group
- IEEE battery management system standard
- EPRI data submission guidelines

System operation and safety prediction: closing the data gap between cells and systems

We built labs and software to collect and consolidate data from all levels of battery operation for rapid technology iteration. The testing conditions are informed by environmental and system-level effects we have observed in field applications.

BLC[1]

Open-source repository to consolidate cell and system data (Dedicated SNL labs in parentheses)

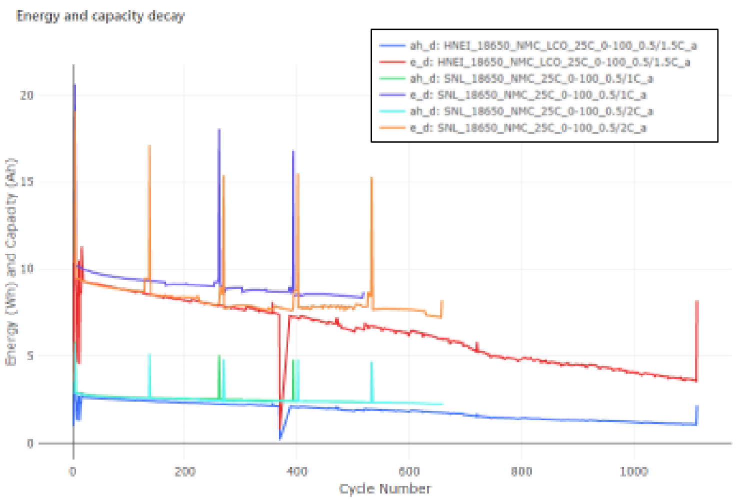
Field Application Data (ESTP, Demonstrations, NITE[2])
Collect normal & abuse data and environmental effects (T, humidity) from field systems (EPRI/SNL Report[3])

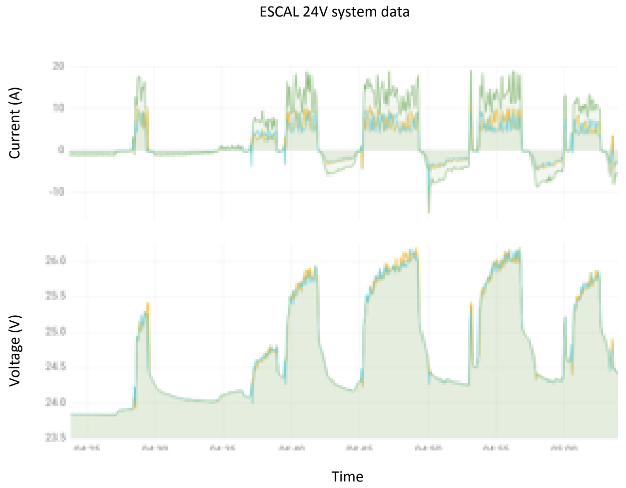
DC-Rack Data with Power Electronics (ESCAL, APEX)
Determine the impact of DC power quality (pulses and harmonics) on cell behavior

Module-Level Data (BEST, BATLab)
Assess the effect of cell-to-cell variation on safety and performance

Lab Cells Data (BTF, BATLab)
Design industry-relevant performance & abuse testing and quality assurance checks using data from all layers

Cell and system data in one dashboard





BTF

BEST

APEX

ESCAL

Prosperity (PNM)

(1) V. De Angelis, Y. Preger, B. Chalamala "Battery Lifecycle Framework: A Flexible Repository and Visualization Tool for Battery Data from Materials Development to Field Implementation" ECSarXiv, 2021
(2) B. Chalamala, D. Rosewater, Y. Preger, J. Lamb, R. Wittman, A. Kashiwakura "Ensuring Safety of Grid-scale Energy Storage Systems" IEEE Electrification, Vol. 9, No. 4, Dec. 2021
(3) D. Rosewater, Y. Preger, J. Mueller, S. Atcitty, S. Willard, M. Smith, J. Thompson, D. Long, "Electrical Energy Storage Data Submission Guidelines, v 2" Electric Power Research Institute & SNL, 2021. 3002022119.

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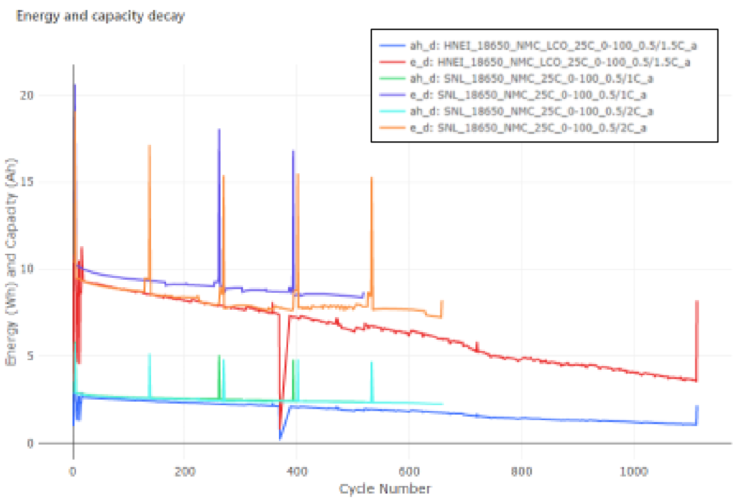

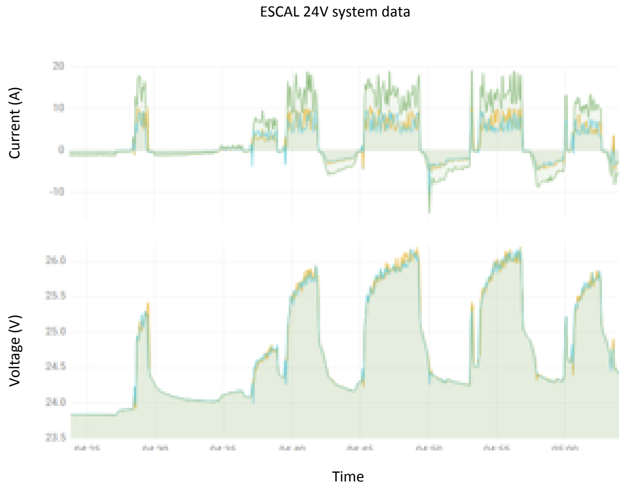

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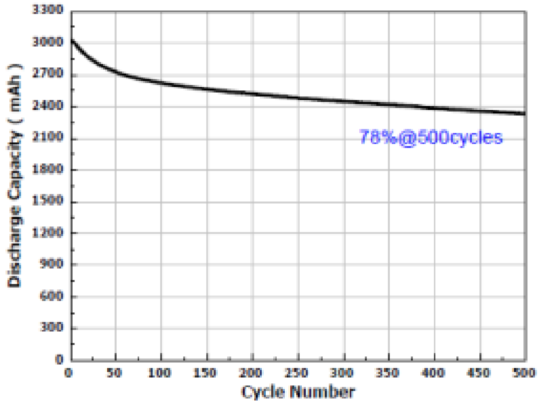
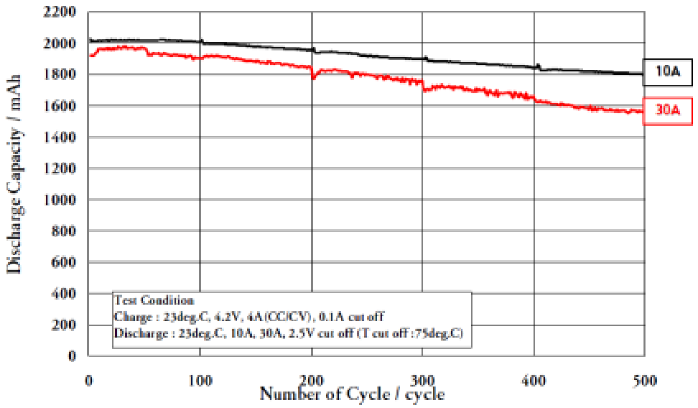
What is the remaining useful life (RUL) of a battery?

- 80% capacity is a common reference point in manufacturer spec sheets

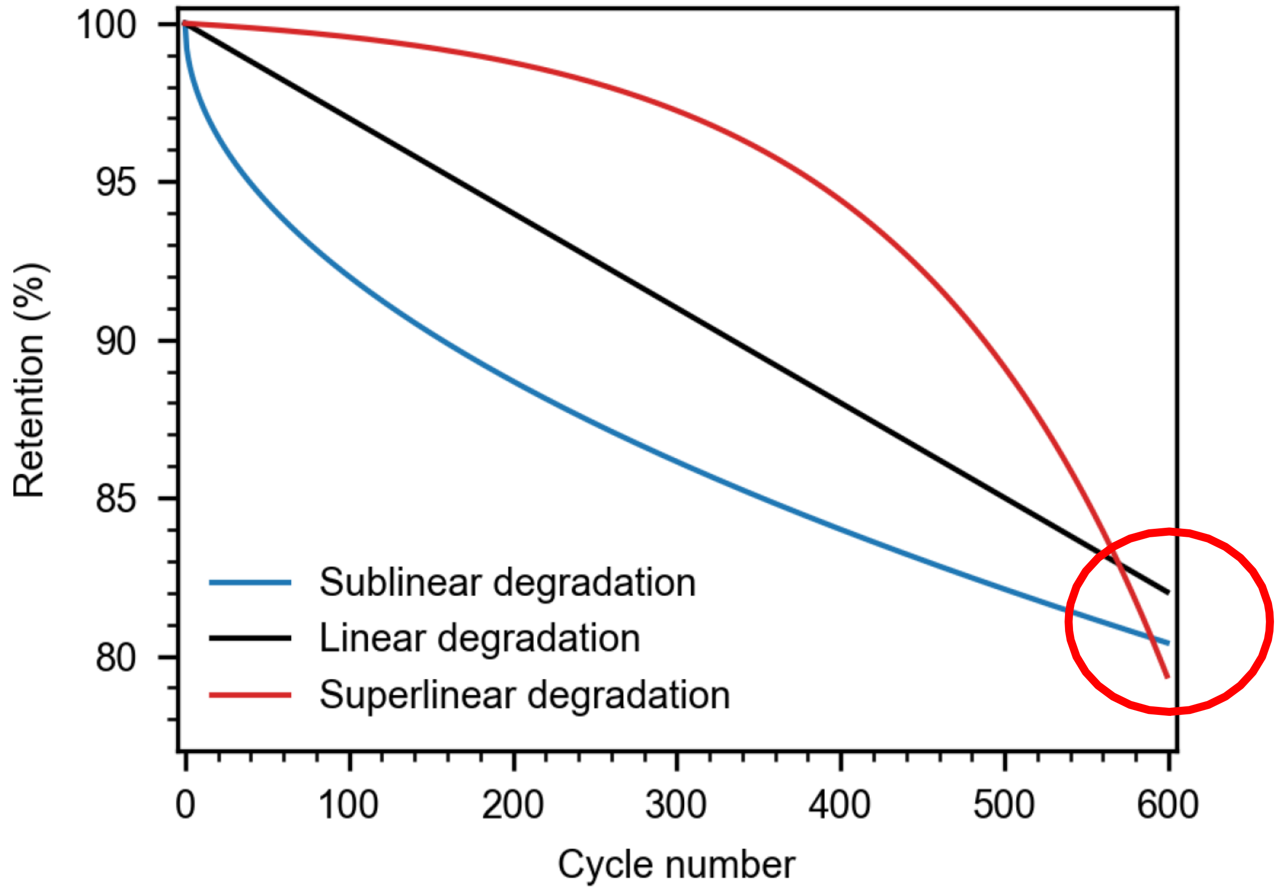




- 80% capacity retention is a holdover from early EV days
  - USABC 1996: "*EV batteries should be removed from automotive use when **current battery capacity is 80% of initial battery capacity** and current battery power capability is 80% of initial battery power capability*"
  - At this time, EVs were primarily powered by Ni-based batteries

- Understanding RUL is critical for first life valuation and a deal-breaker for second life applications

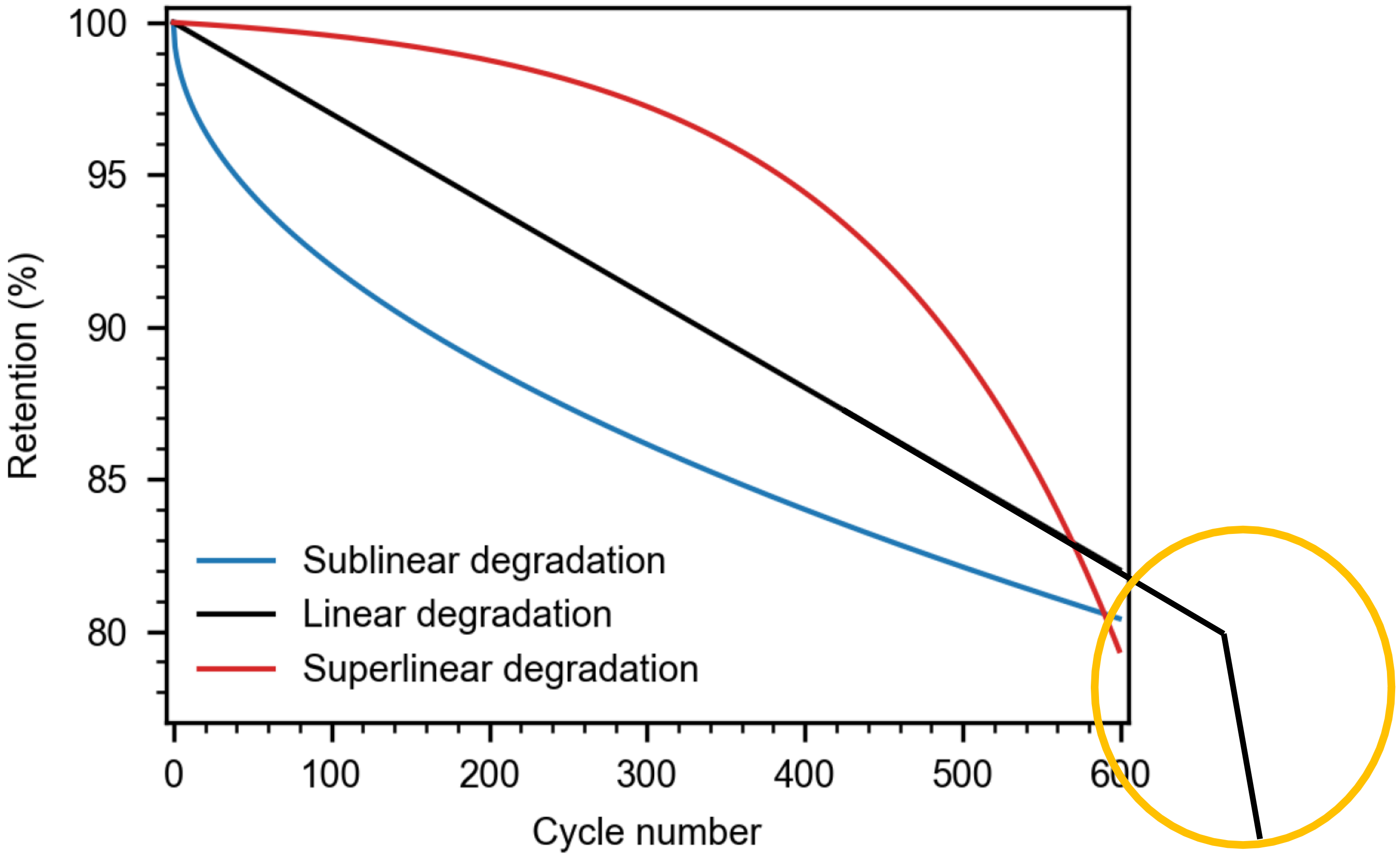
Remaining useful life depends on the aging trajectory



Batteries with identical SOH have different RUL

What causes superlinear degradation (aka knee, rollover failure, nonlinear aging, two phase degradation, etc.) and how do you avoid it?

Remaining useful life depends on the aging trajectory



How do you avoid this?

Multi-institution team reviewing empirical causes and mechanisms of knee points

Stanford (Peter Attia)
Sandia (Yuliya Preger)
Carnegie Mellon University (Shashank Sripad, Alec Bills)
Hawai'i Natural Energy Institute (Matthieu Dubarry)
NREL (Paul Gasper)
University of Cincinnati (Abhishek Soni)

University of Michigan (Anna Stefanopoulou, Valentin Sulzer)
RWTH Aachen University (Philipp Dechent)
University of Edinburgh (Goncalo dos Reis, Richard Gilchrist)
University of Warwick (Ferran Brosa Planella)
University of Oxford (David Howey, Sam Greenbank)
A*STAR (Edwin Khoo, Ouyang Liu)

Project approach

1) Review all literature on knees: every experimental example + modeling explanation

2) Identify classes of degradation pathways

3) Determine how these pathways lend themselves to predictive capability

"Perturbation" of Any Variable Can Induce Knees – Cell Design

Variable	Knee Acceleration	Reference
Electrode loading	Higher positive electrode loading	Ma et al. 2019
Positive electrode coating	Uncoated positive electrode	Ma et al. 2019
Graphite type	Natural graphite	Ma et al. 2019
Additive package and concentration	FEC consumed	Petibon et al. 2016
	FEC consumed	Jung et al. 2016
	Higher methyl acetate concentration	Ma et al. 2019
Salt concentration	Higher salt concentration	Aiken et al. 2020
	Lower salt concentration	Ma et al. 2019
	Higher salt concentration	Wang et al.

"Perturbation" of Any Variable Can Induce Knees – Testing Conditions

Variable	Knee Acceleration	Reference
Charging rate	Higher charging rate	Lewerenz et al. 2017
	Higher charging rate	Petzl et al. 2015
	Higher charging rate	Burns et al. 2015
	Higher charging rate, constant voltage	Waldmann et al. 2015
	Higher charging rate	Schuster et al. 2015
	Higher charging rate	Severson et al. 2019
	Higher charging rate	Schindler et al. 2018
	Higher charging rate	Keil et al. 2019
Discharging rate	Lower discharging rate	Keil et al. 2016
	Lower discharging rate	Keil et al. 2019
	Lower discharging rate	Atalay et al. 2020
	Higher discharging rate	Omar et al. 2014
	No difference at 10-45 °C	Diao et al. 2019

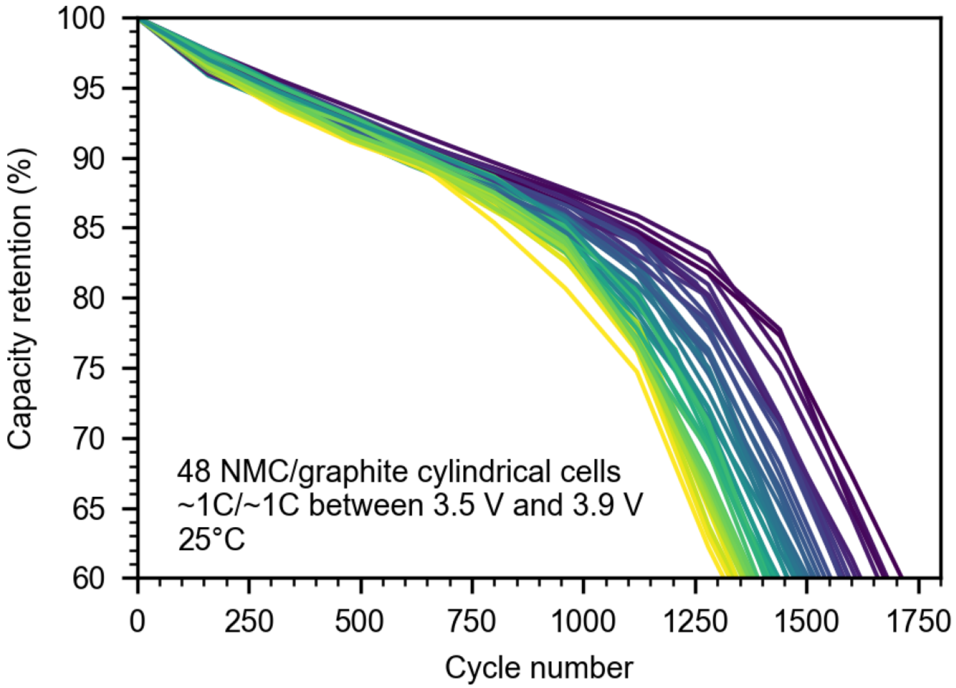
"Perturbation" of Any Variable Can Induce Knees – Testing Conditions

Variable	Knee Acceleration	Reference
Voltage limits	Higher SOC	Broussely et al. 2005
	Higher voltage	Aiken et al. 2020
	1) Higher DOD 2) Extreme midpoints	Ecker et al. 2014, Pfrang et al. 2018
	Higher DOD	Klett et al. 2014
	Higher DOD	Schuster et al. 2015
	1) Higher DOD 2) Higher midpoint SOC	Ma et al. 2019
	Higher DOD	Petzl et al. 2015
	Lower SOC	Zhu et al. 2021
Rests	Longer rest time	Keil et al. 2019
	Longer rest time	Ma et al. 2019
	Shorter rest time	Epding et al. 2019

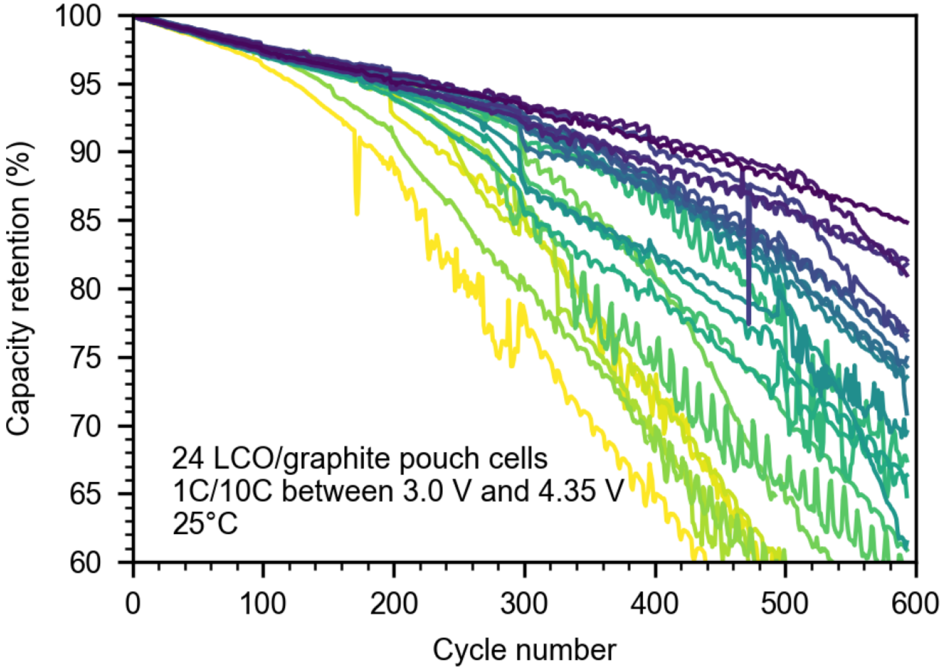
"Perturbation" of Any Variable Can Induce Knees – Testing Conditions

Variable	Knee Acceleration	Reference
Temperature	Temperature above and below 25 °C	Zhang et al. 2019
	Higher temperature	Broussely et al. 2005
	Temperature above and below 35 °C	Schuster et al. 2015
	Higher temperature	Safari et al. 2011
	Temperature above and below 25 °C	Waldmann et al. 2014
	Lower temperature	Coron et al. 2020
	Temperature below 25 °C	Waldmann et al. 2015
Pressure	More rigid bracing or zero bracing	Wunsch et al. 2019
	Higher stack pressure or zero pressure	Cannarella et al. 2014
	Heterogeneous compression	Bach et al. 2016

Impact of cell to cell variability



Baumhofer et al. *J. Power Sources*, **2014**, *247*, 332.



Harris et al. *J. Power Sources*, **2017**, *342*, 589.

General assessment of experimental studies

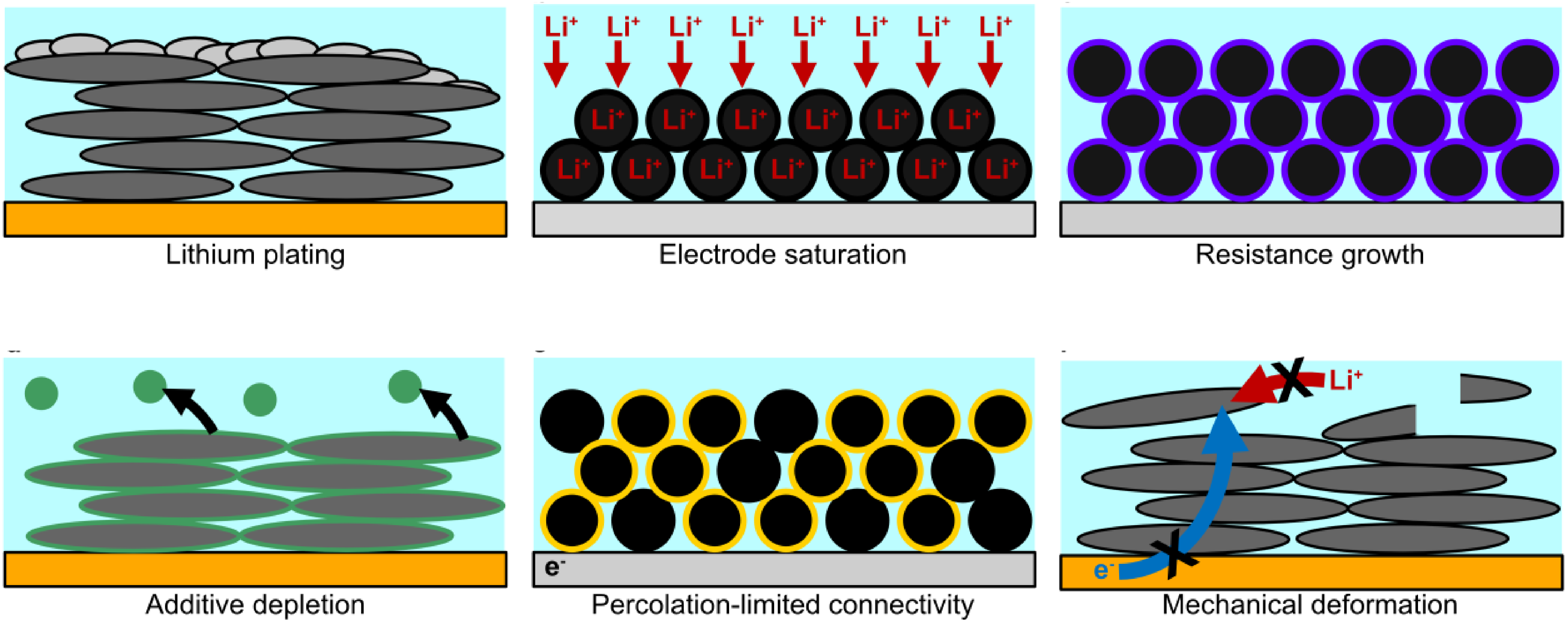
Knees are complex and occur under many conditions

- Higher charging rate and wider DOD consistently accelerate knees
- Temperature/pressure have a ‘sweet spot’ outside of which knee is accelerated
- Discharge rate/rest time – it varies

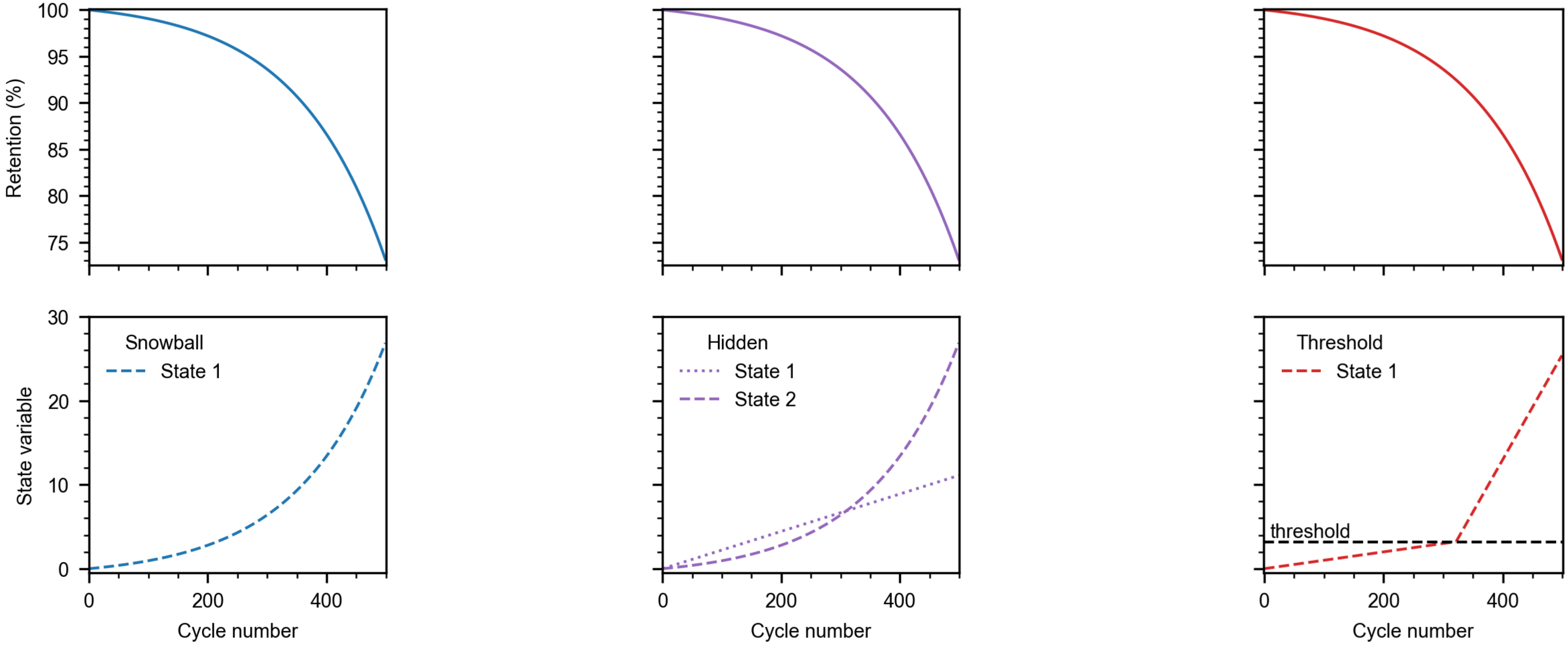
- Knees can occur during cycling within manufacturer specifications
- Knees observed as high as 90% remaining capacity and as low as 40%
- No specific range of values to avoid – specific value depends on the other variables

Next step: link all experimental observations to broader classes of degradation pathways

Six pathways to knees



Defining internal state trajectories



Ex. Mechanical deformation

Extrapolation of exponential function difficult if there's noise

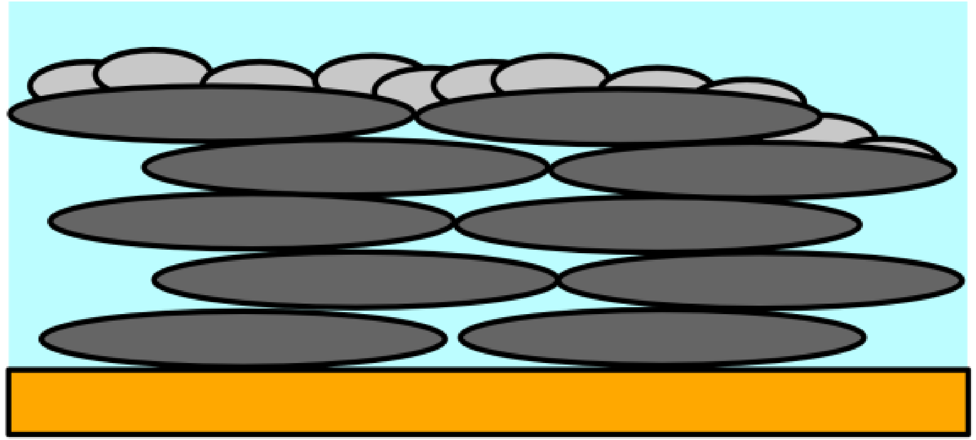
Ex. Electrode saturation

Need to track two internal states

Ex. Additive depletion

Requires knowledge of internal state trajectory AND threshold

Pathway 1: Li plating



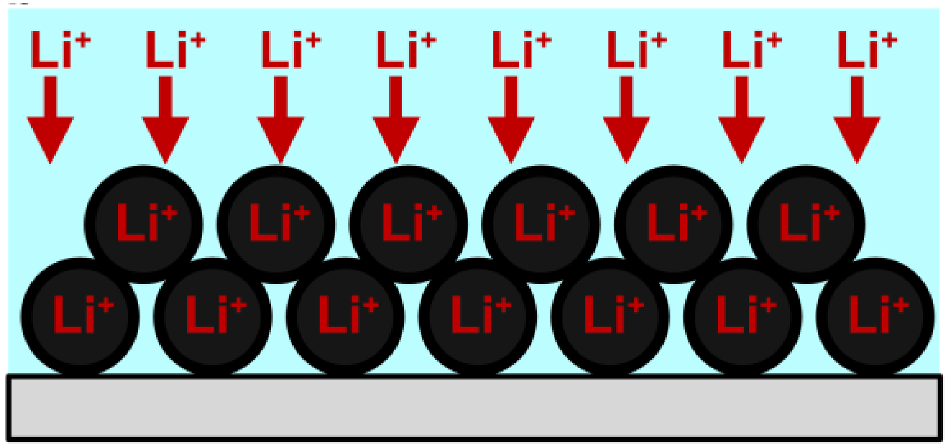
What is it: Li ions form metallic lithium on surface of negative electrode rather than intercalating

Cause

- Rate independent: Loss of active material from delithiated negative electrode
- Rate dependent: High transport/reaction overpotentials cause local electrode potential to drop below Li/Li^+
  - salt depletion, low temperature, high charge rate
  - mechanical compression reduces porosity
  - LAM increasing local current density
  - pore clogging from SEI build-up

Trajectory: snowball, hidden, threshold

Pathway 2: Electrode saturation



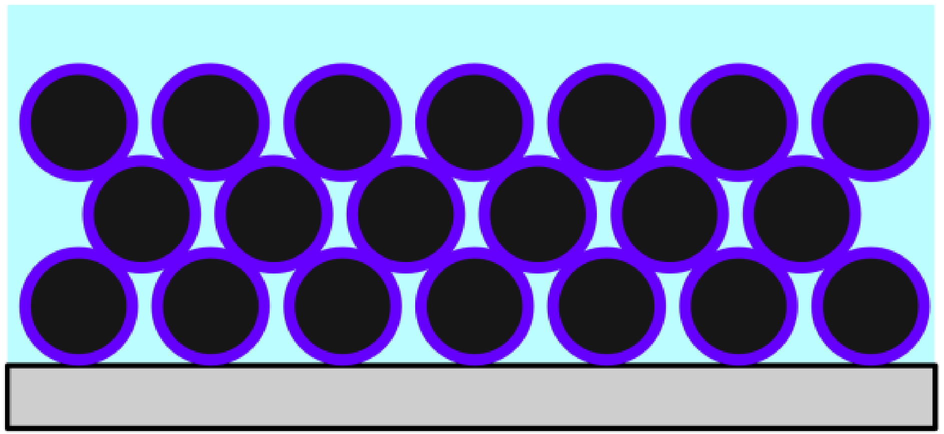
What is it: electrode “saturates” and reaches cutoff potential before all Li transferred

Cause

- Rate of active material loss for one electrode outpaces lithium inventory loss
- Applicable to both electrodes (can be hidden for some time by oversized negative electrode)

Trajectory: threshold, hidden

Pathway 3: Resistance growth



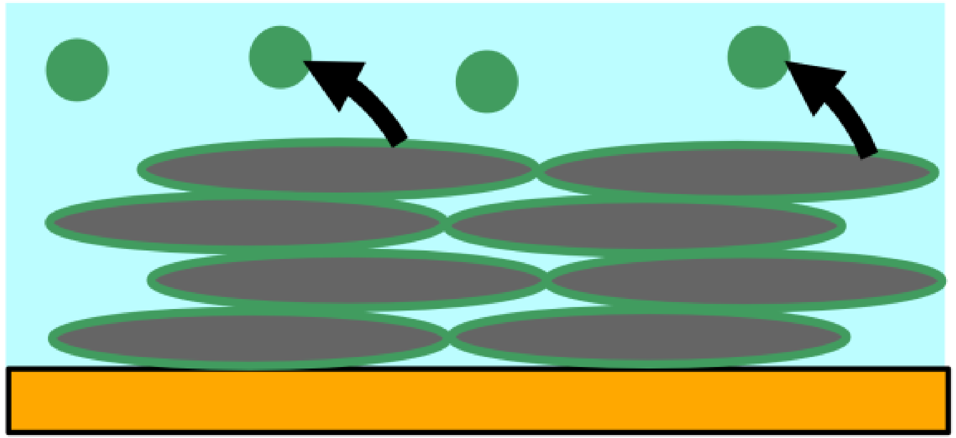
What is it: cell internal resistance increases, with additional overpotential causing cell to reach cutoff voltage quicker

Cause

- Growth of side reaction products (electrolyte oxidation/reduction) on surface of electrode particles

Trajectory: threshold

Pathway 4: Additive depletion



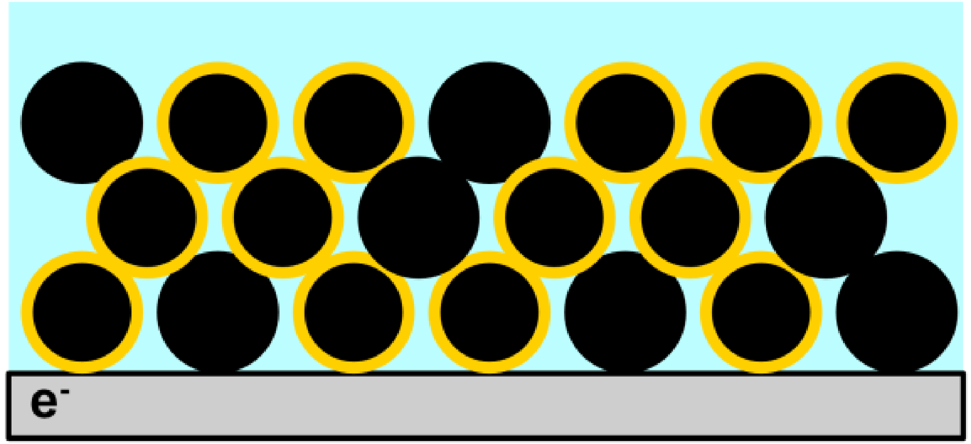
What is it: quantity of electrolyte additive in cell reduced over time

Cause

- Additive consumed in side reactions
- More likely in commercial cells without excess electrolyte

Trajectory: threshold

Pathway 5: Percolation-limited connectivity



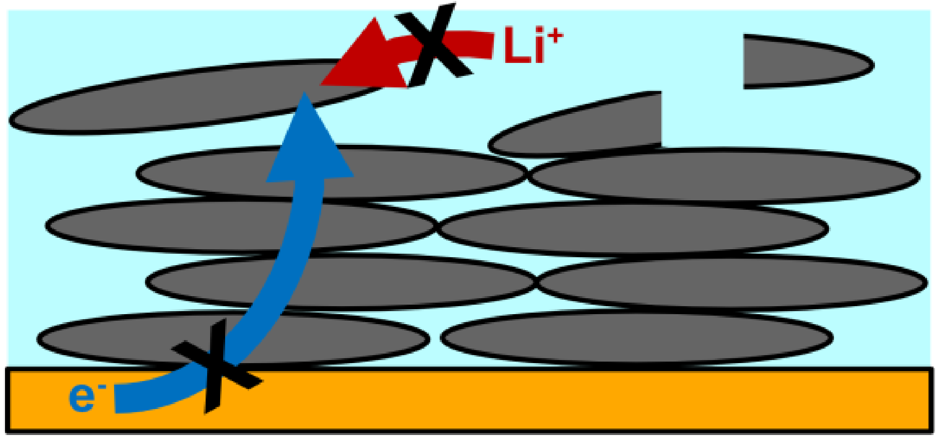
What is it: electronic/ionic conductive network does not span the full electrode

Cause

- Electrode dry-out results in loss of ionic contact between active material and electrolyte, leading to loss of active material

Trajectory: threshold

Pathway 6: Mechanical deformation



What is it: physical changes at the micro- and macro-scale due to mechanical processes

Cause

- Micro-scale
  - particle cracking due to (de)intercalation stress
  - delamination
- Macro-scale
  - heterogeneous internal pressure distribution from cell components (e.g. tab)
  - jelly roll deformation causes loss of active material
  - uneven external pressure causes plating

Trajectory: snowball, threshold

Implications for modeling and prediction

- Goal of knee pathways evaluation: provide fundamental understanding of physics of knees to assess limits of today's models

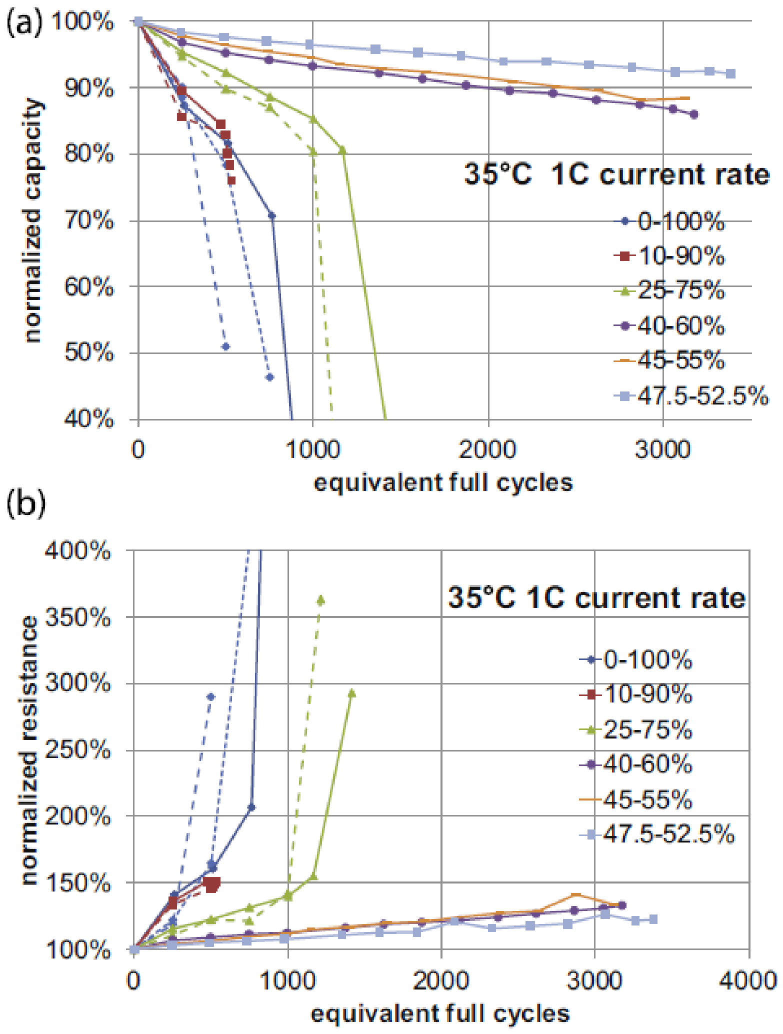
- Lithium plating, electrode saturation, resistance growth
  - dependent on bulk internal states (LLI, LAM, etc.), so they are straightforward to detect and model via electrochemistry

- Additive depletion, percolation-limited connectivity, microscale mechanical deformation
  - involve subtle effects that are challenging to measure (e.g. porosity decrease, remaining additive amount)

Value of resistance measurements for knee prediction in the field

- Capacity knee onset is nearly always correlated to onset of rapid resistance growth (elbow)
  - many intertwined degradation mechanisms

- Correlation is important because measuring capacity in the field can be hard, but measuring resistance at various SOCs is not



Ecker et al. *J. Power Sources*, **2014**, *248*, 839.

Role of data-driven methods in knee prediction

- Methods are well-suited for knee pathways with bulk electrochemical signals
- Models trained on cycling data are poorly suited for knee pathways with signals that are challenging to measure via electrochemistry
- Datasets that span many pathways for various cell designs + use cases are needed for training generalizable models

Conclusions

- Reviewed all examples of knees in the literature
  - Knees are complex and occur under many cycling + design conditions
  - No specific range of values to avoid – specific value depends on the other variables
- Identified classes of degradation pathways and underlying state trajectories
  - Li plating, electrode saturation, resistance growth, additive depletion, percolation-limited connectivity, mechanical deformation
  - Internal state trajectories (snowball, hidden, threshold) each pose unique challenges for monitoring
- Determined how pathways lend themselves to predictive capability
  - Need to consider which pathways have bulk electrochemical signals
  - Resistance is a useful value for field predictions

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