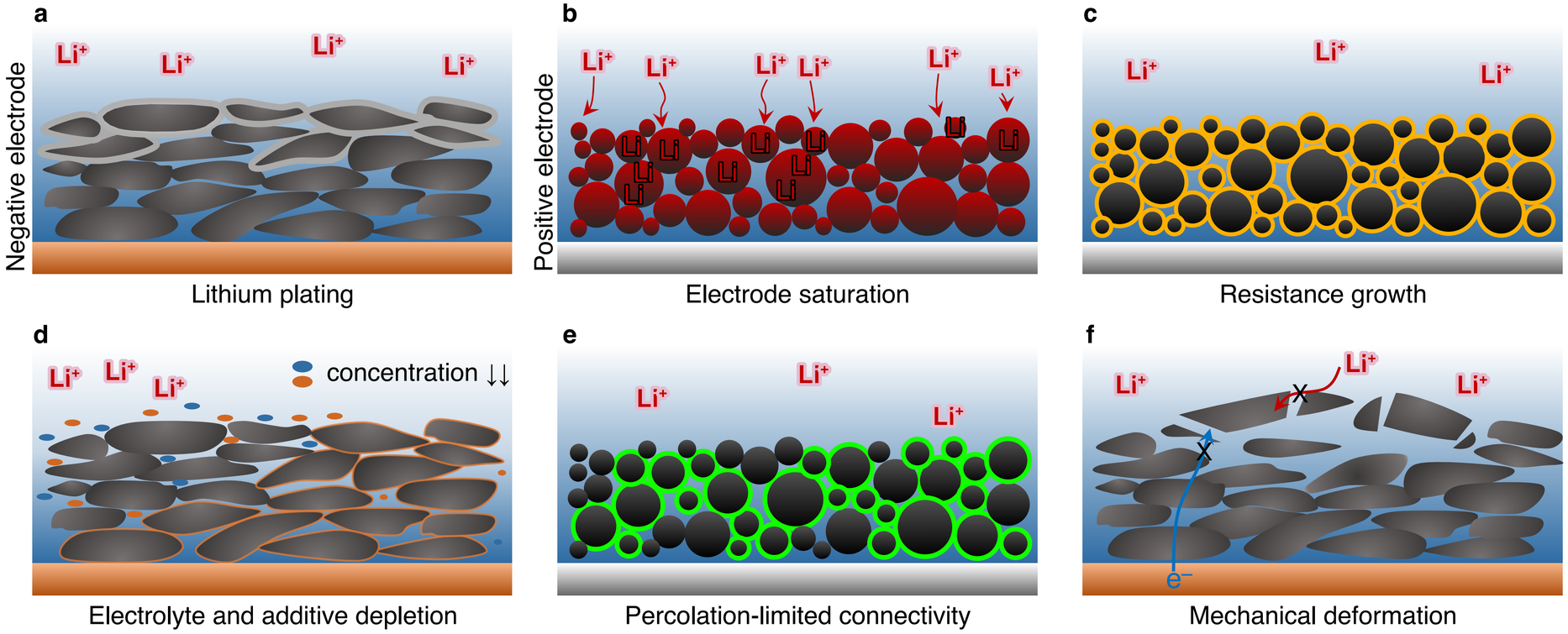
“Knees” in lithium-ion battery aging trajectories



Peter Attia (and many others!)

December 7, 2021

Disclaimer

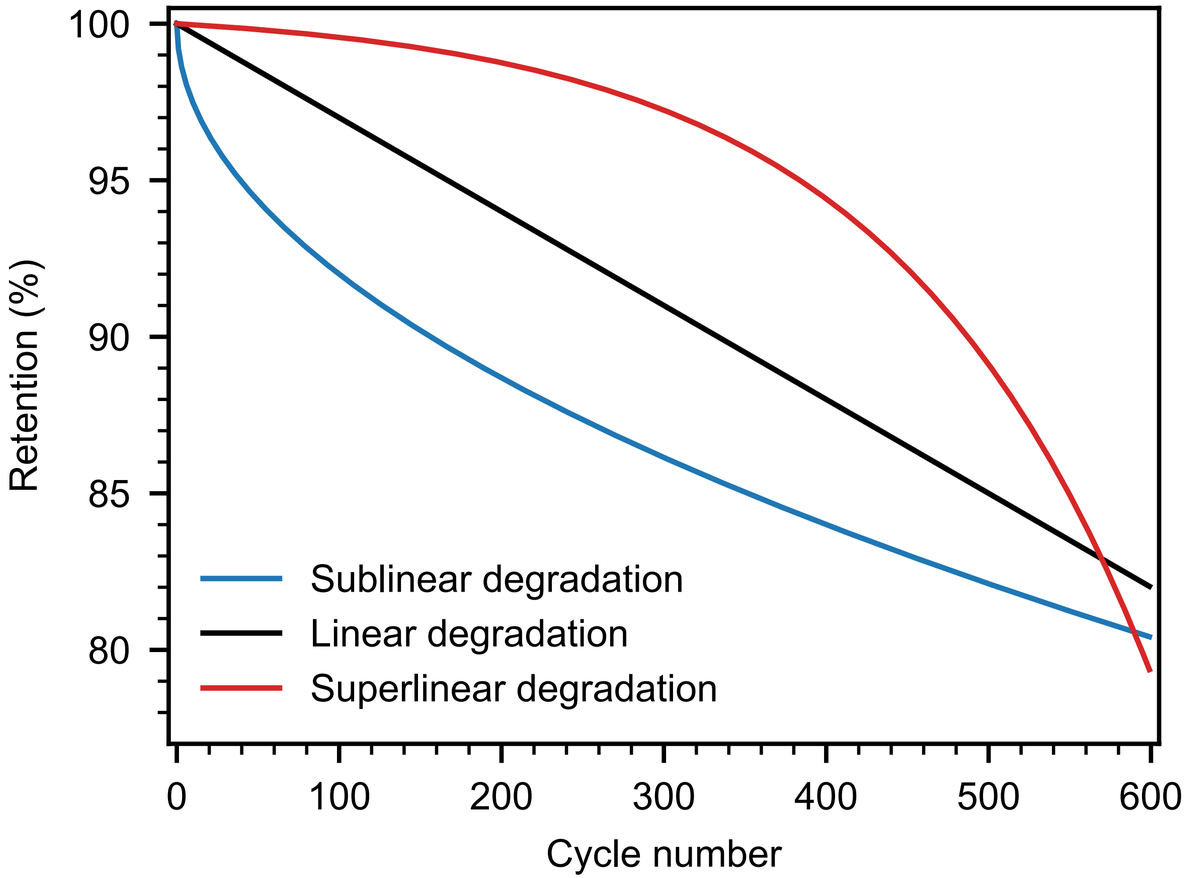
This work is not affiliated with Tesla Inc. and was solely performed during personal time.

Any insights from this presentation are solely synthesized from published academic literature.

P. M. Attia et al., *in preparation*

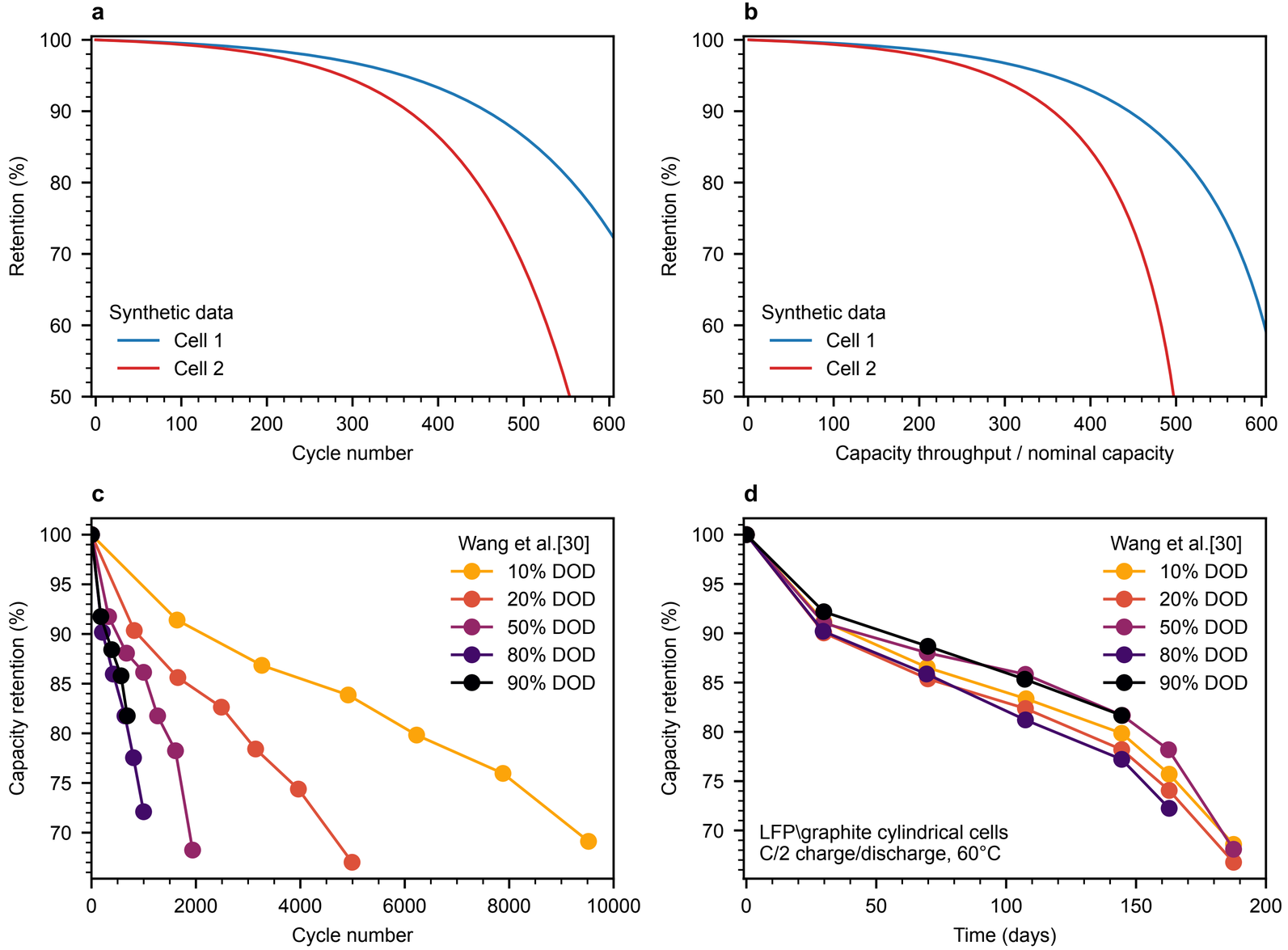
What are “knees”?

- Battery lifetime can be linear, sublinear, or **superlinear** (knees)
- Also known as “rollover failure”, ”nonlinear aging”, “sudden death”, “capacity plunge”, etc.
- Avoiding knees = extended lifetime for first or second use, before recycling



Visualization choices matter!

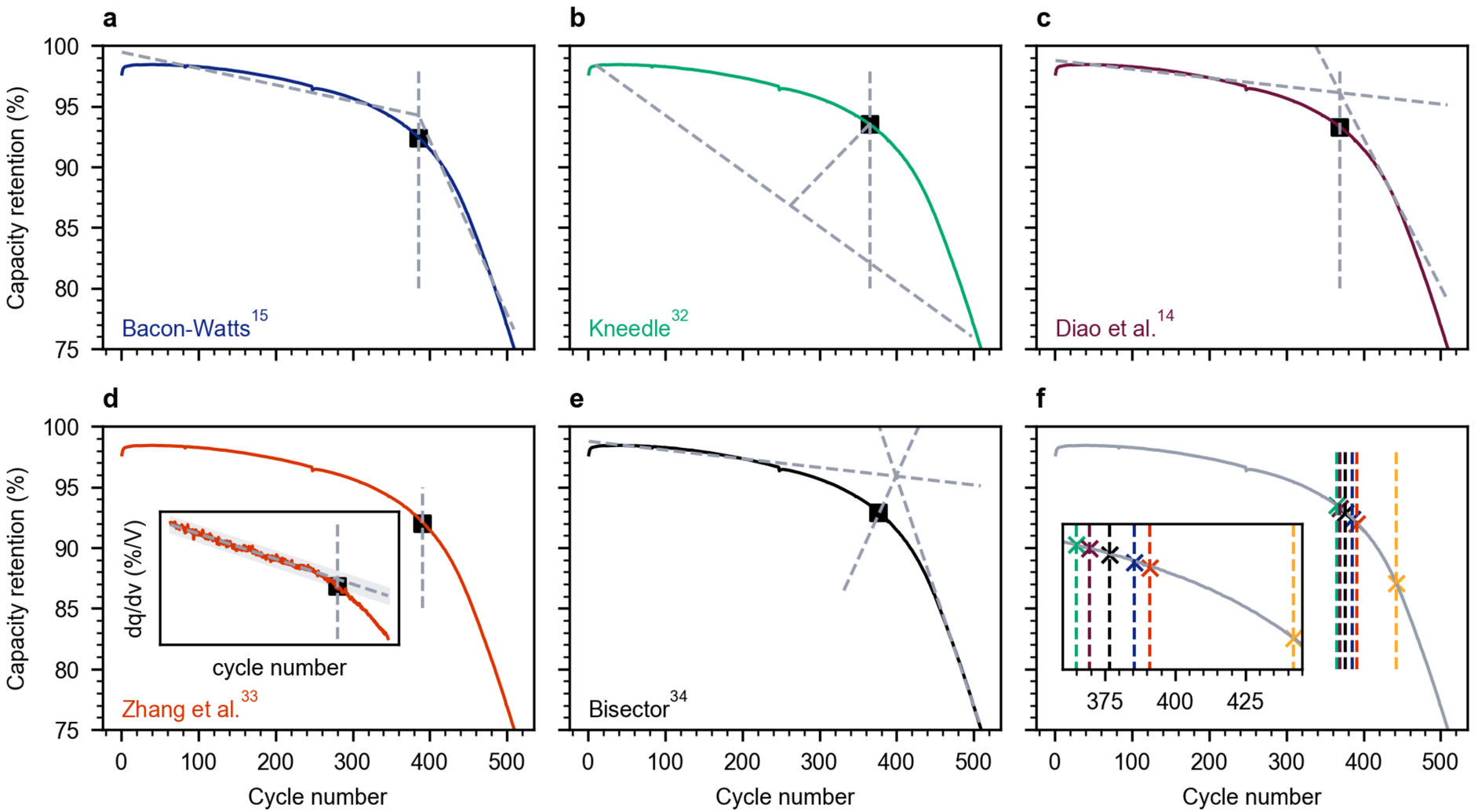
- Cycle number vs. throughput vs. time
- On y axis: Capacity vs. energy vs. power; absolute vs. normalized
- Resistance “elbows” also reported



Wang et al., *Journal of Power Sources* (2011)

Defining the knee

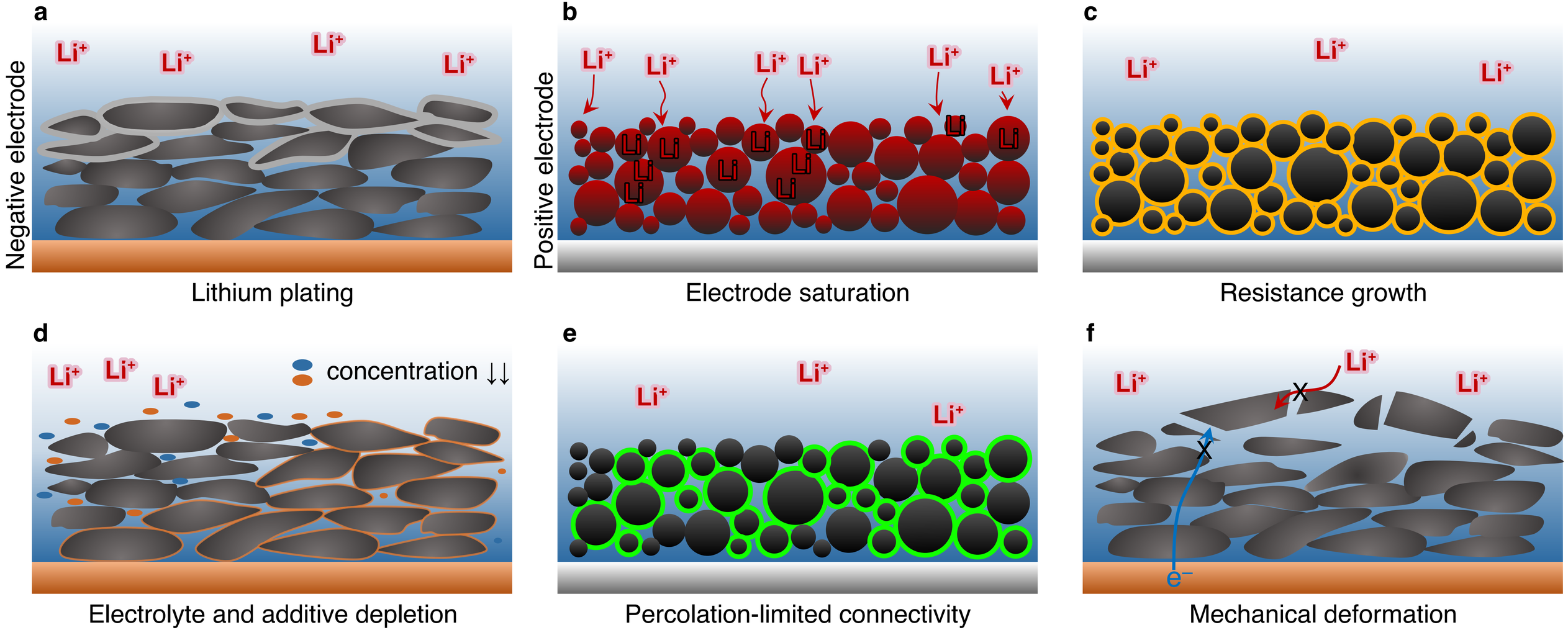
- Formally: A knee is the max of curvature
- Literature methods produce similar results
- Online detection much harder



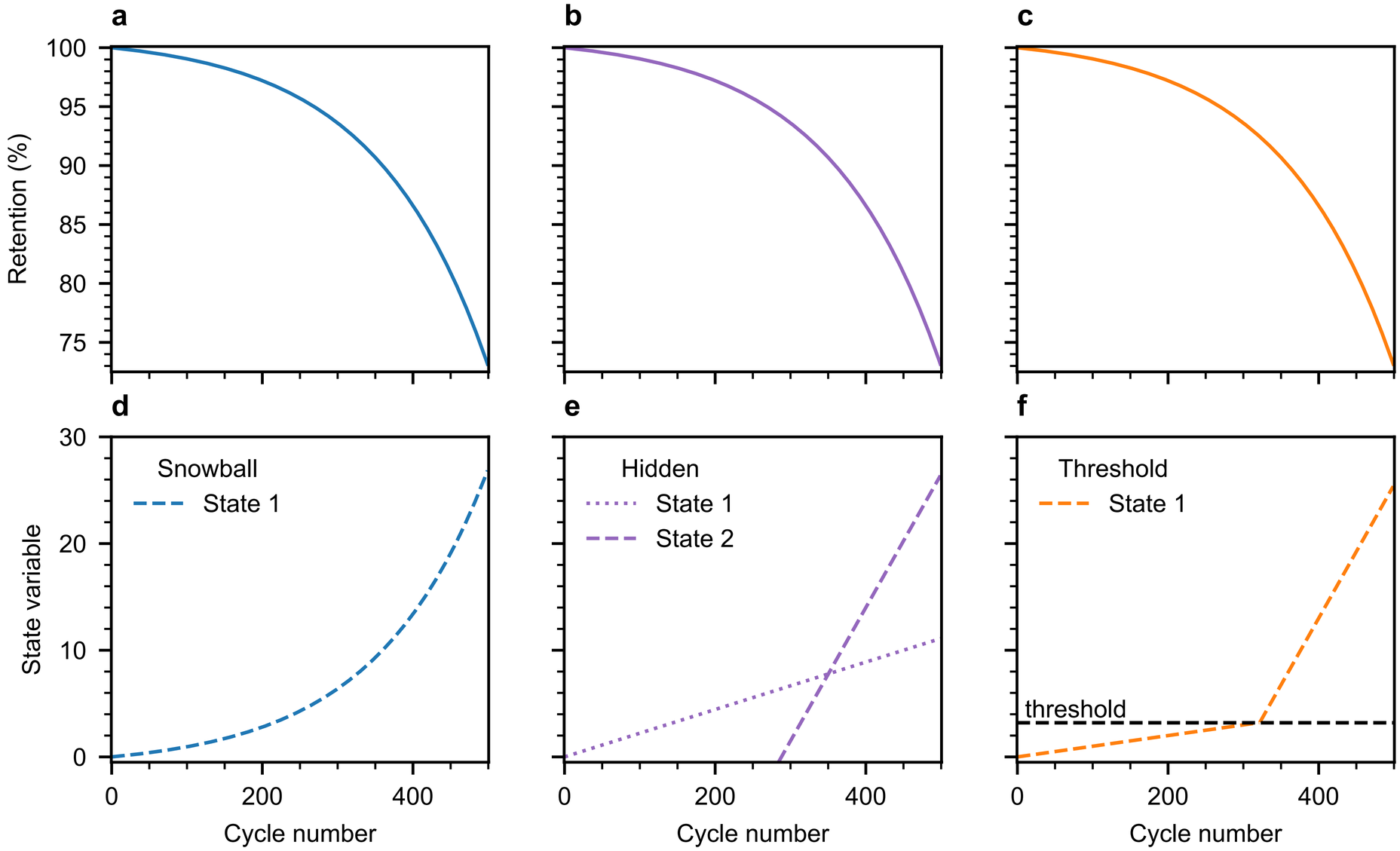
Knees in the literature

- Six knee pathways: What fundamental mechanism leads to the knee?
- Three internal state trajectories: What non-observable variable leads to the knee in the observable variable?

Six knee pathways



Three internal state trajectories

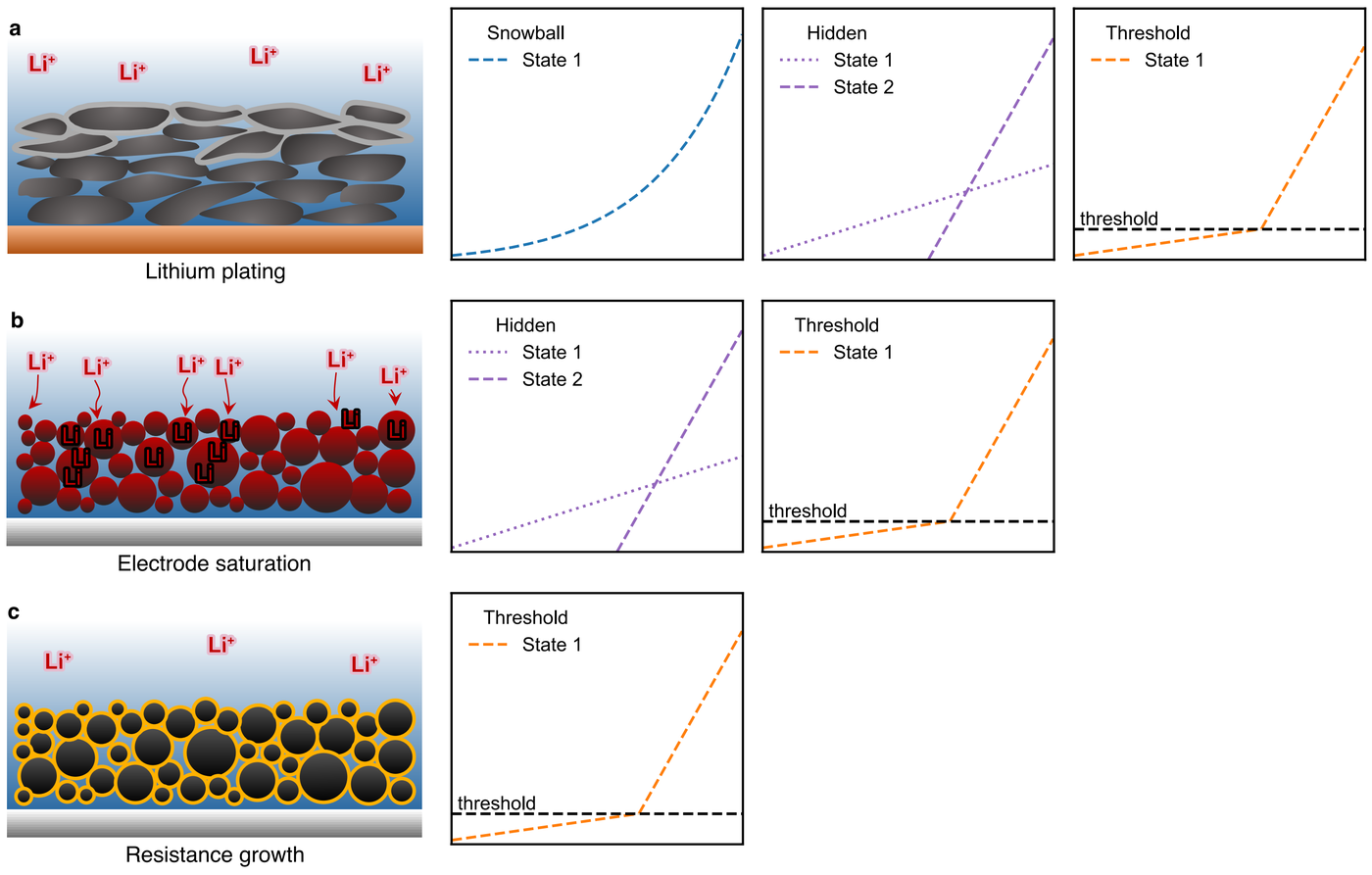


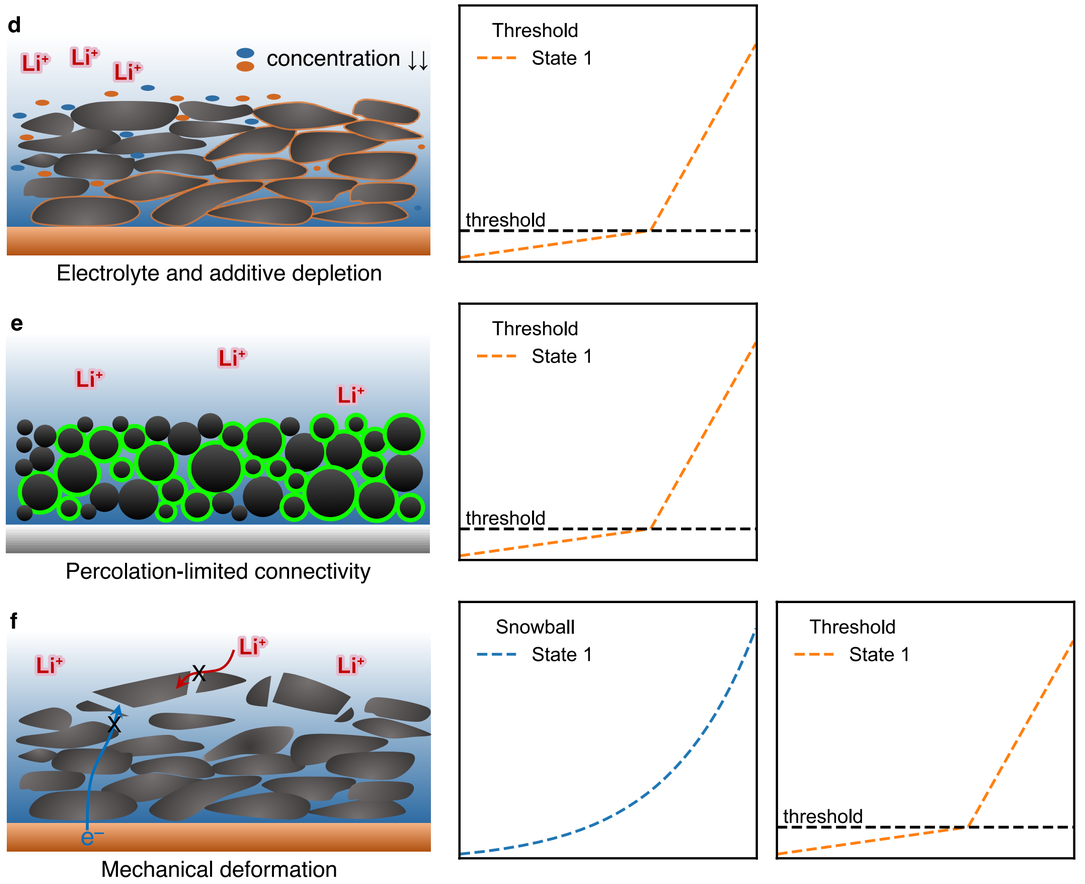
Internal state trajectories?

- Implications for modeling, detection, and prediction
  - Prediction: Given a *new* cell, when will knee occur?
- Snowballs: Need to extrapolate noisy exponential curve
- Hidden: Need to simultaneously track two variables
- Threshold: Need to know the threshold

- All have unique challenges

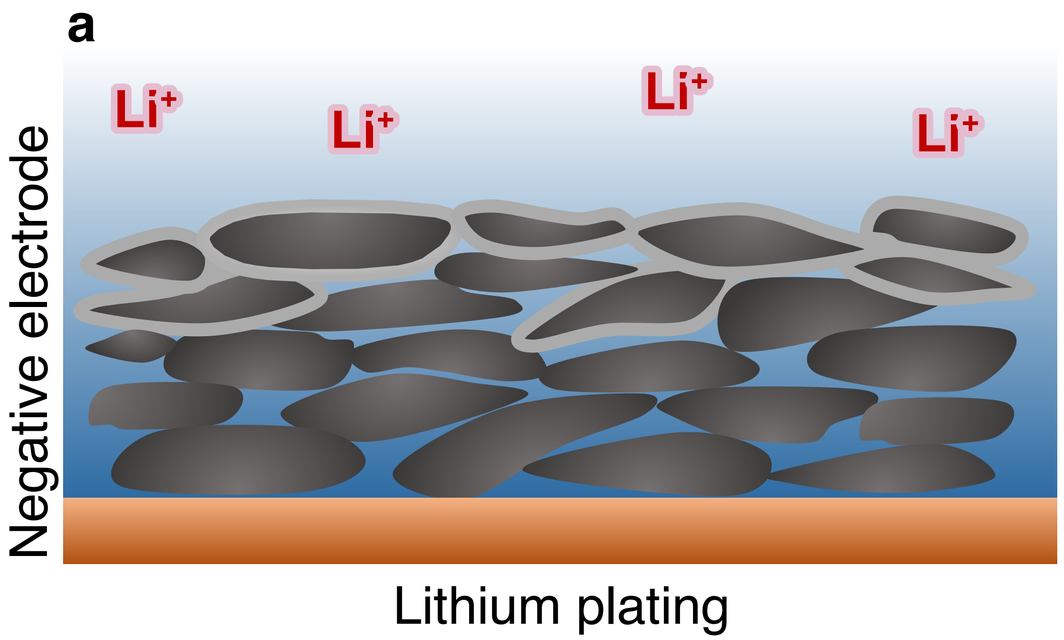
Pathways + internal state trajectories





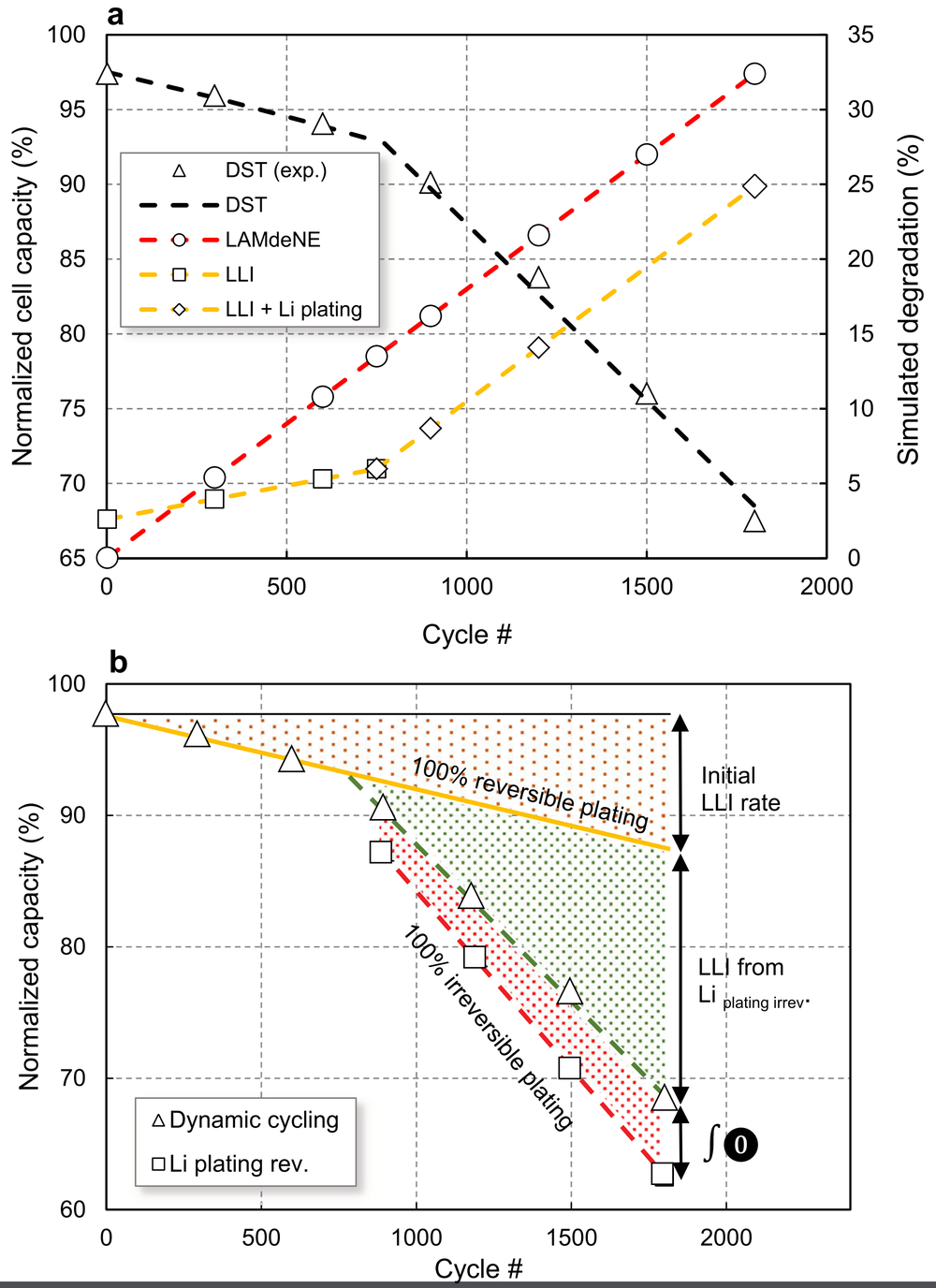
1. Lithium plating

- Complex pathway, many possibilities
- Nucleation and growth kinetics = snowball
- We consider *rate-independent* and *rate-dependent* plating
- Also fresh (boring) vs. aged (interesting) plating



1. Lithium plating

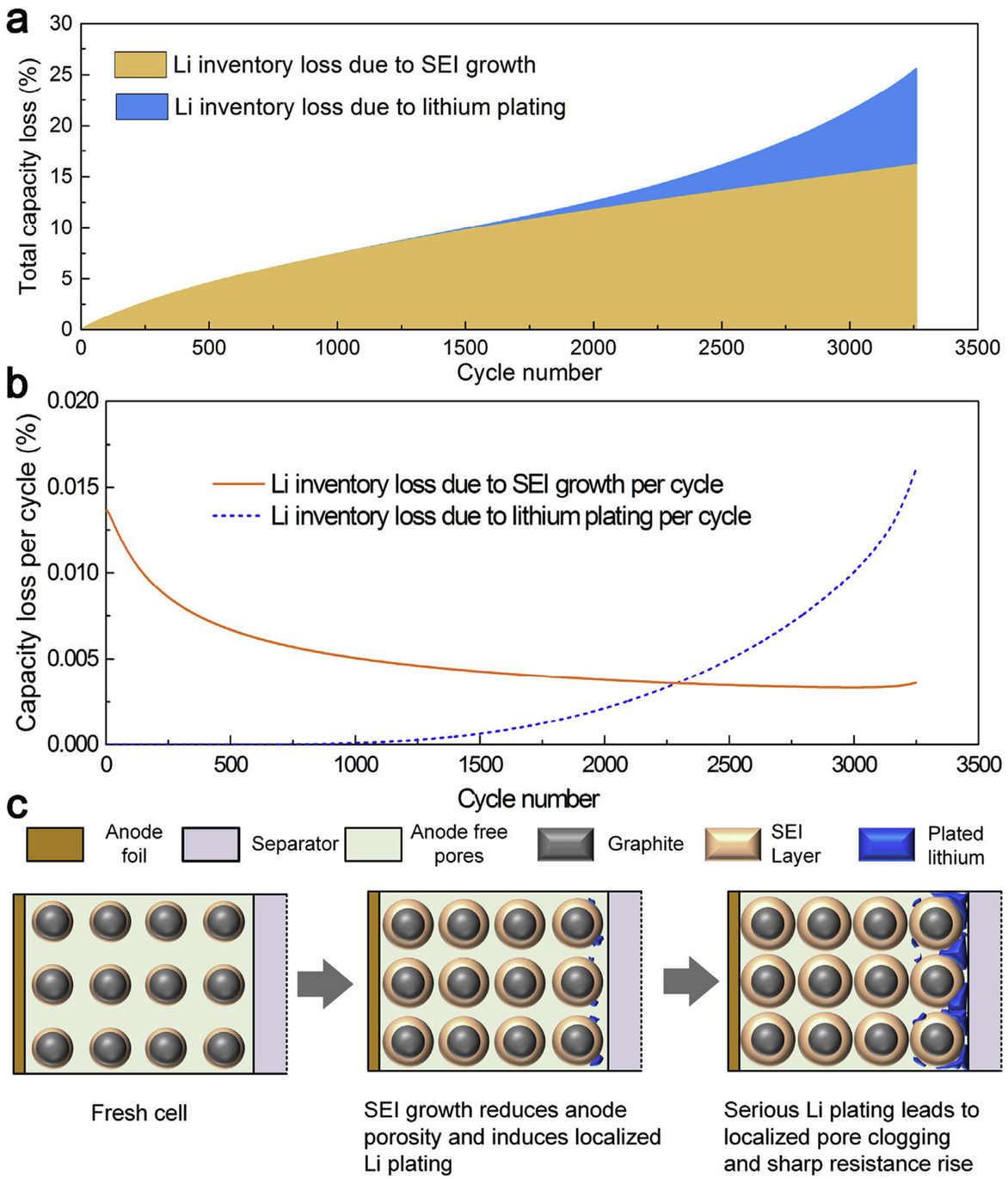
- Anseán et al. extensively studied *rate-independent* plating in aged cells
- Lithium plating will occur if the graphite electrode loses capacity (LAM_{deNE}) but incoming lithium flux is high
- Hidden + snowball trajectories
- Need to measure LAM_{deNE} (bulk echem signals)



Anseán et al., *Journal of Power Sources* (2017)

1. Lithium plating

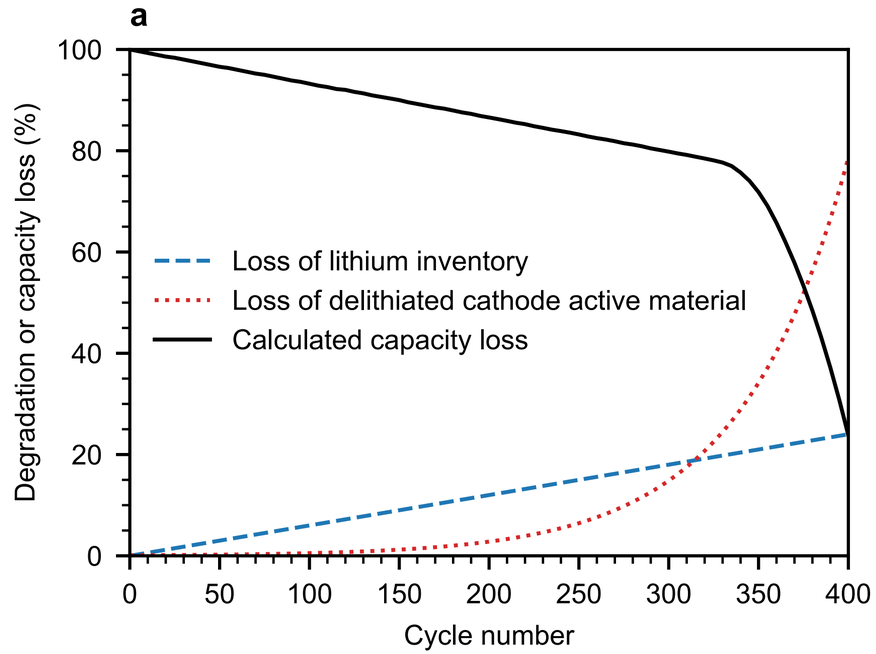
- Yang et al. studied *rate-dependent* plating in aged cells
- SEI growth > porosity decrease > plating
- Threshold + snowball trajectories
- Need to track local porosity (hard!)

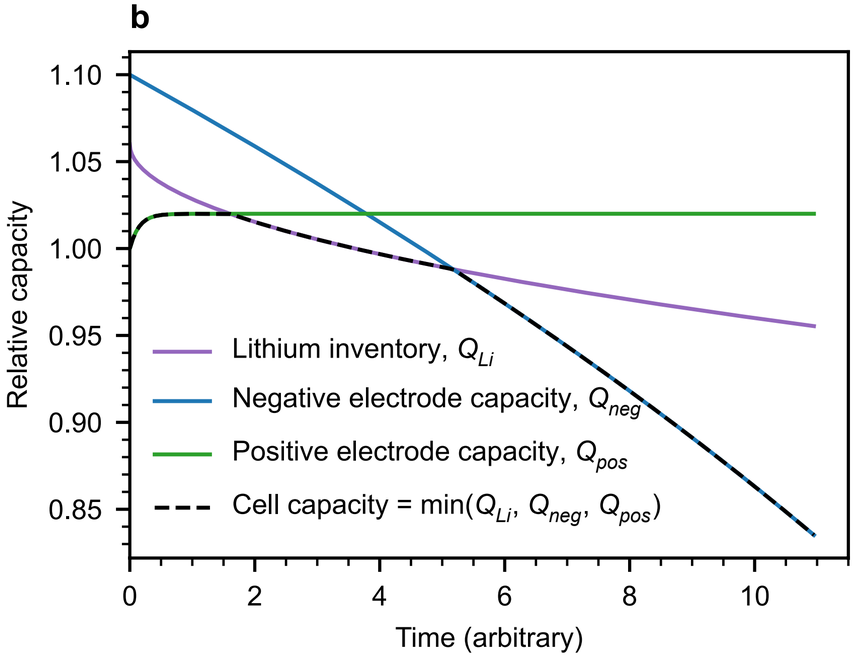


Yang et al. *Journal of Power Sources* (2017)

2. Electrode saturation

- Electrode saturation occurs when an electrode cannot accommodate the incoming lithium flux
- If neg electrode sites < lithium inventory, plating occurs
- Hidden trajectory
- Need to track lithium and active material inventories (bulk echem signals)

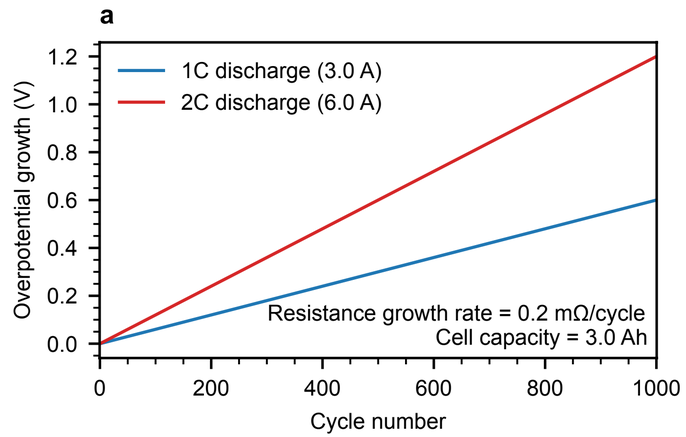


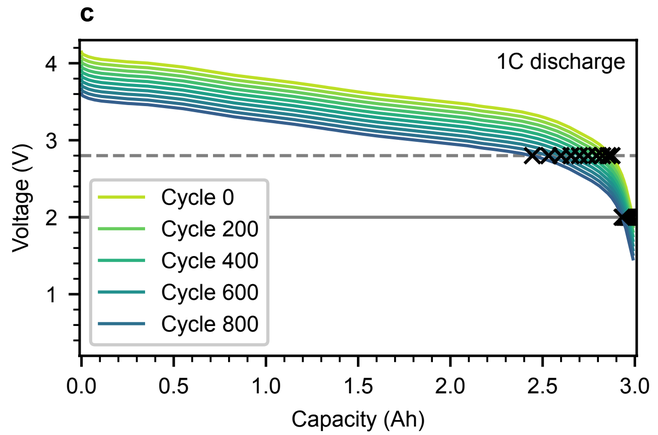


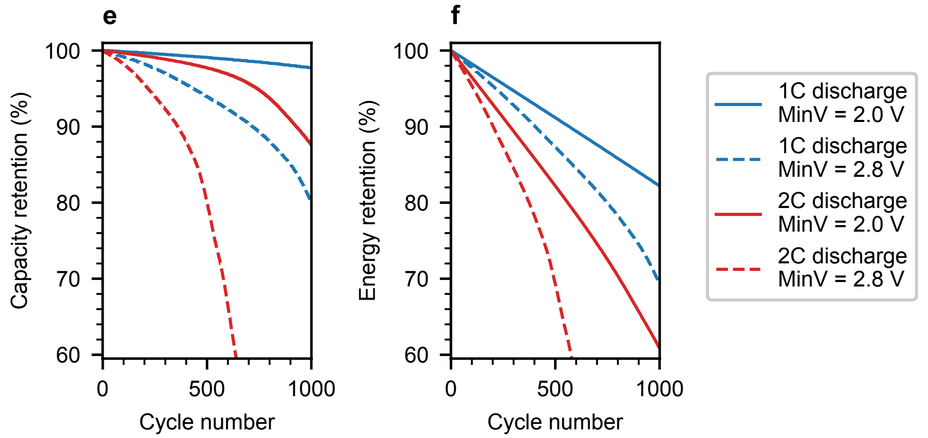
Dubarry et al. *Journal of Power Sources* (2012)
Smith et al. *American Control Conference* (2017)

3. Resistance growth

- Linear resistance growth can lead to nonlinear capacity loss
- Voltage-capacity curves are nonlinear, so high MinV or high discharge rates can lead to low discharge capacities
- Threshold trajectory
- Need to track resistance growth (bulk echem signals)



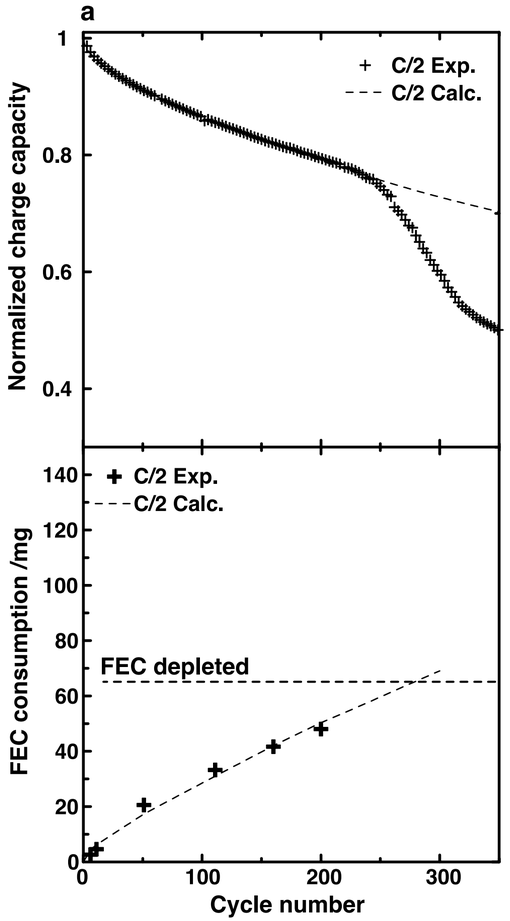


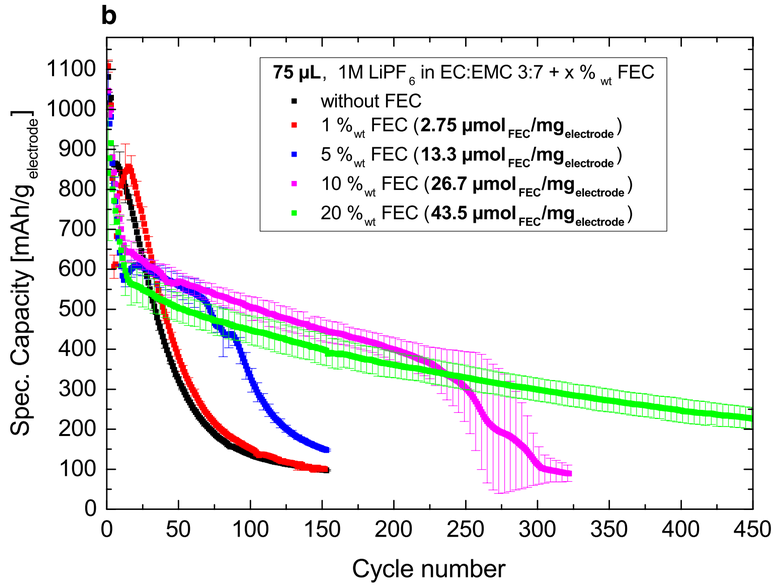


Ma et al. *Journal of the Electrochemical Society* (2019)

4. Electrolyte/additive depletion

- Knees can occur if electrolyte or additives are depleted (globally or locally)
- Si + FEC additives susceptible
- Threshold trajectory
- Need to track remaining electrolyte/additive amounts (ultrasound ok, additives hard!)

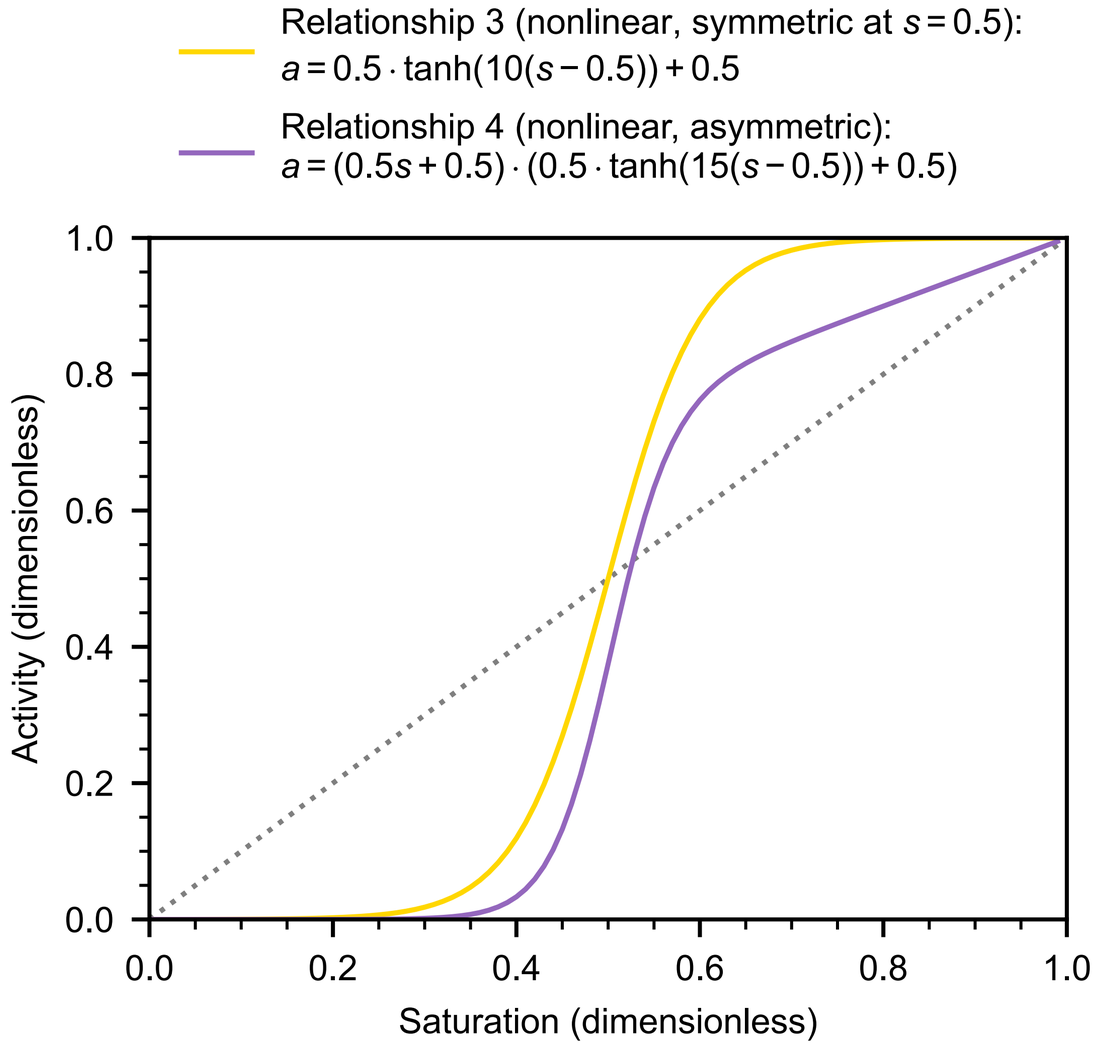




Petibon et al., *Journal of the Electrochemical Society* (2016)
Jung et al., *Journal of the Electrochemical Society* (2016)

5. Percolation-induced knees

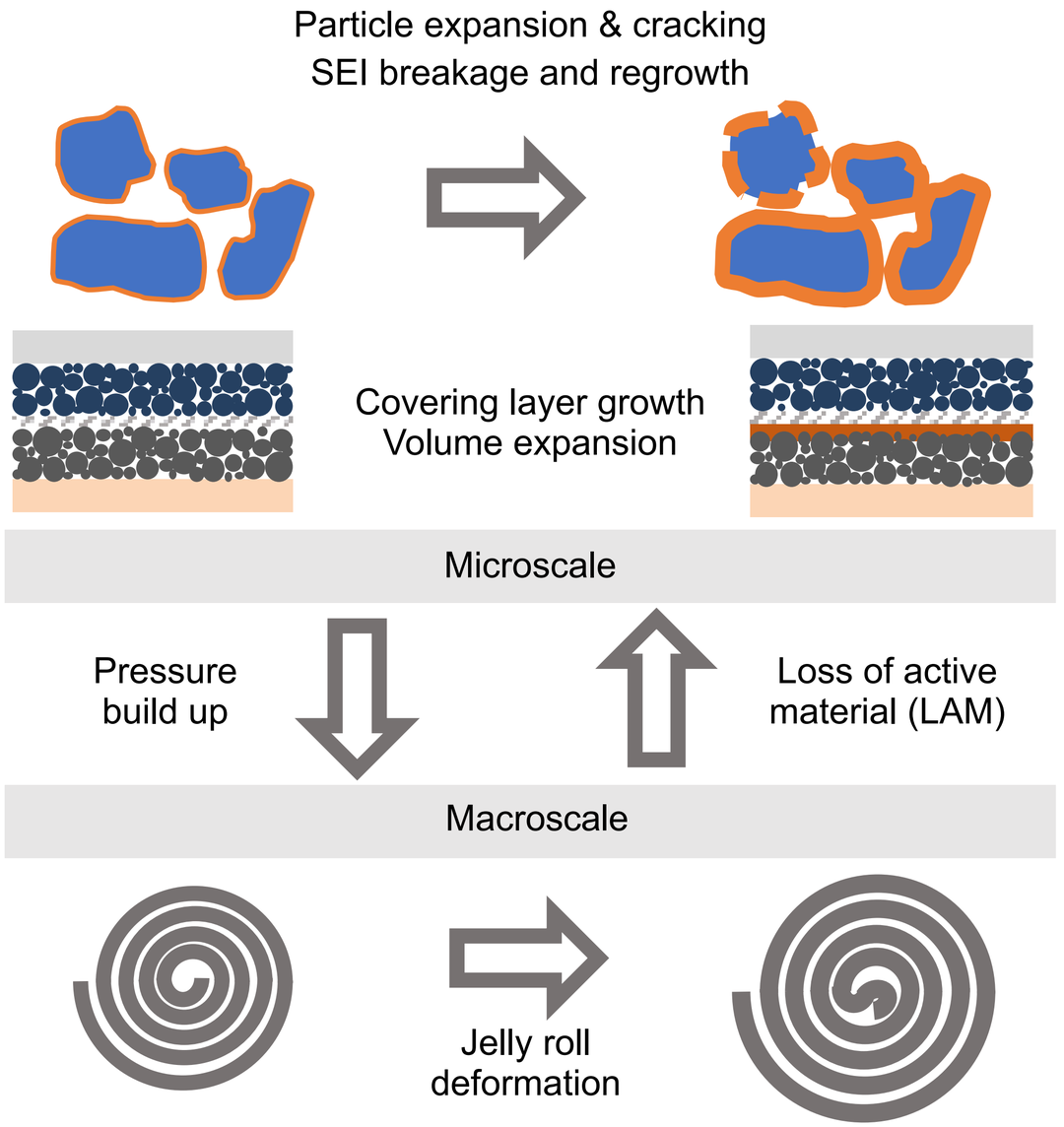
- Speculative, but loss of active material can occur rapidly if the electrode particle network can be described by percolation theory
- Threshold trajectory
- Need to track electrode active sites and critical value (challenging)



Kupper et al., *Journal of the Electrochemical Society* (2018)

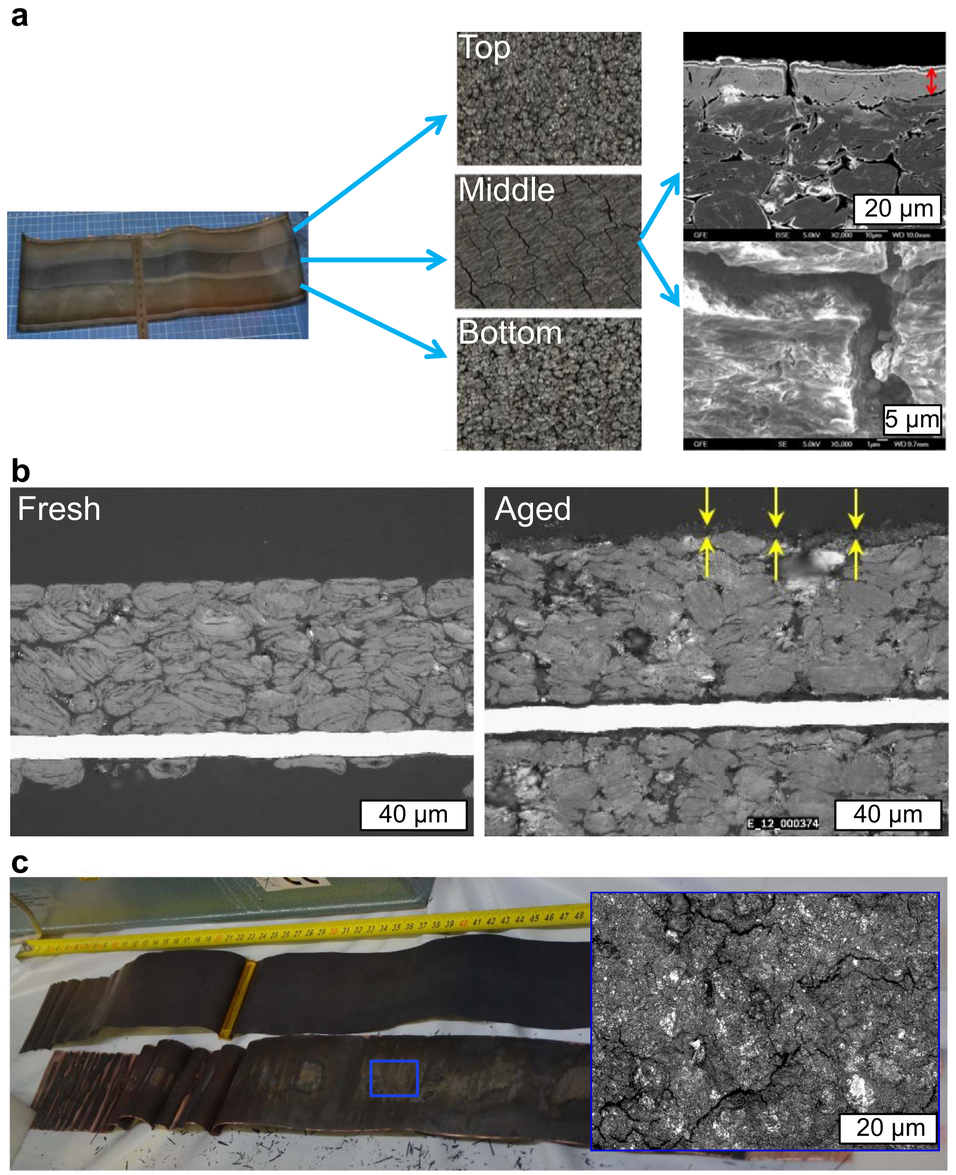
6. Mechanically-induced knees

- Catch-all for mechanical
- Snowball or threshold trajectory
- Need to measure cell performance on many length scales



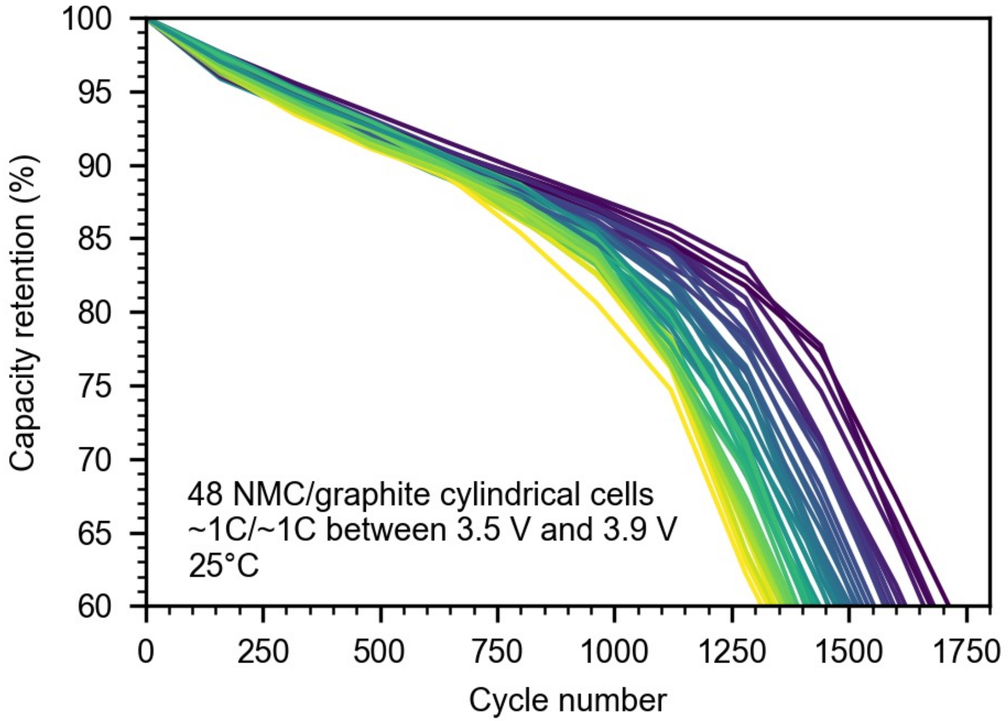
6. Mechanically-induced knees

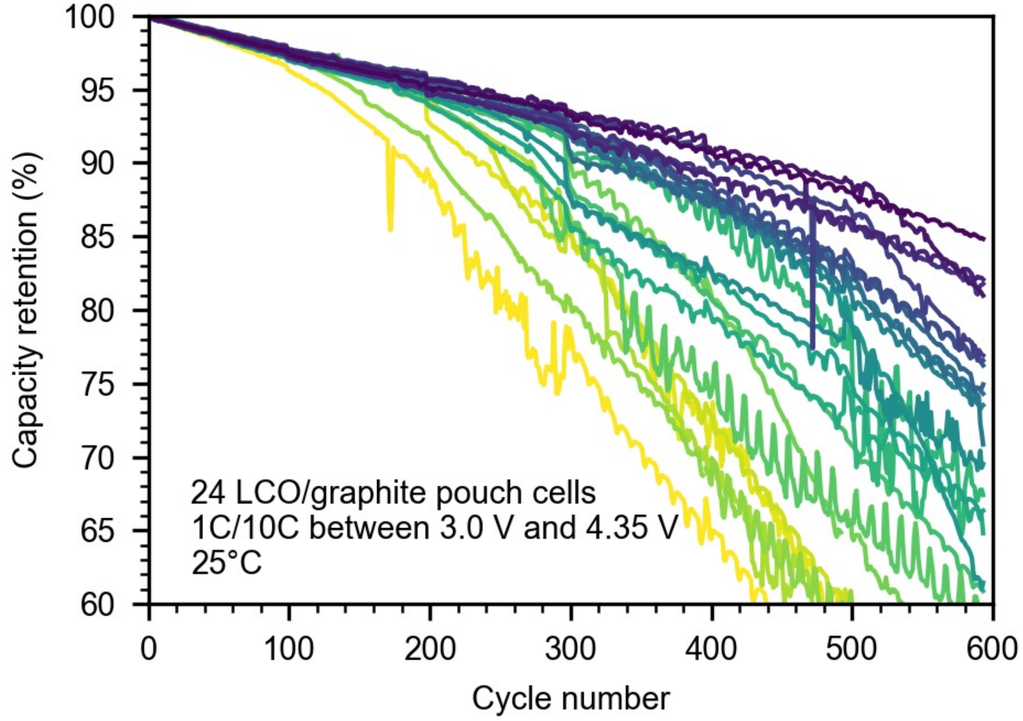
- Microns-thick "**covering layers**" commonly reported in literature reports with knees
- May be lithium plating, often side reaction byproducts (but too thick to be SEI?)
- Worth further investigation



Lewerenz et al., *Journal of Power Sources* (2017)
Stiaszny et al., *Journal of Power Sources* (2014)
Willenberg et al., *Journal of the Electrochemical Society* (2020)

Interactions and heterogeneity and variability, oh my…



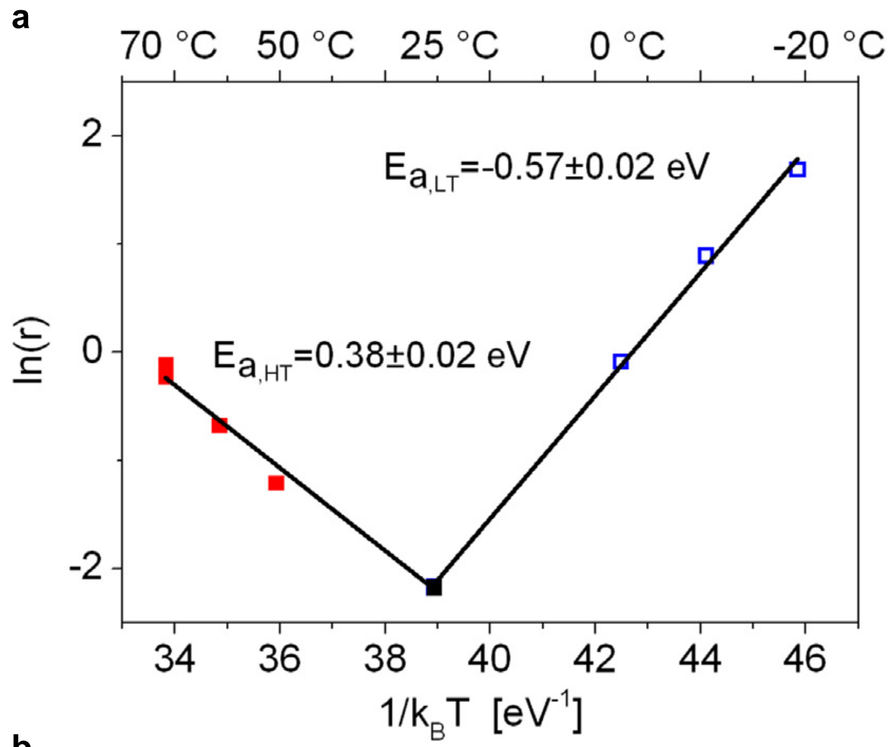


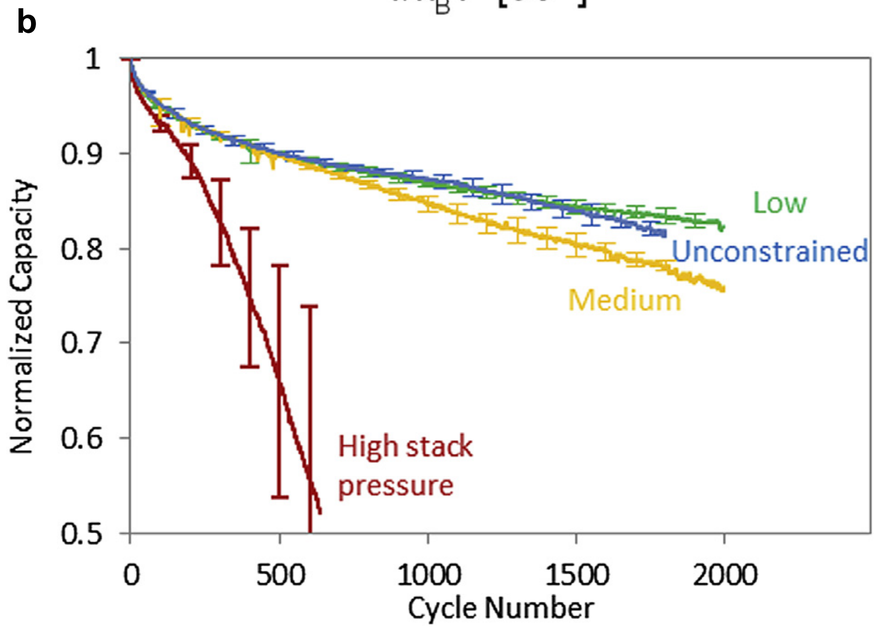
Knees can get a lot more complicated…

Baumhofer et al., *Journal of Power Sources* (2014)
Harris et al., *Journal of Power Sources* (2017)

Knee sensitivities

- Cell design:
  - Electrodes, n:p ratio, electrolytes, formation…
- Usage conditions:
  - Fast charge, high DOD: Bad
  - Temperature, pressure: “Sweet spots”
  - Discharge rate, rests: Mixed

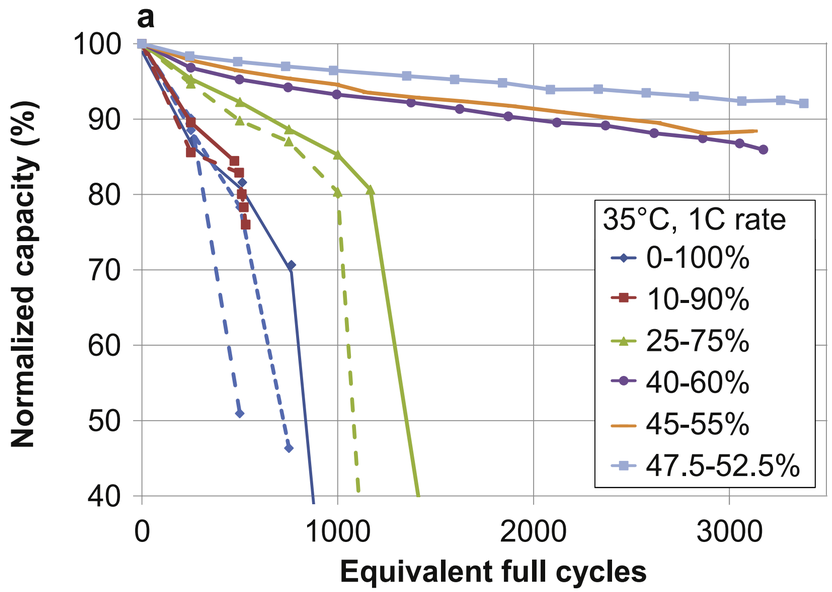


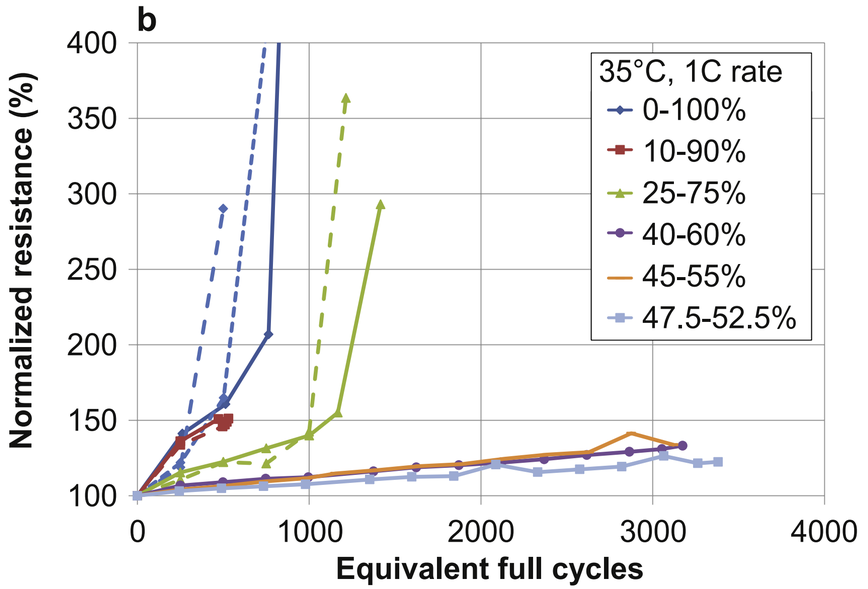


Waldmann et al., *Journal of Power Sources* (2014)
Cannarella et al., *Journal of Power Sources* (2014)

Capacity knees and resistance elbows

- Capacity knees and resistance elbows often appear concurrently in literature
- Correlation is not causation…
  - Resistance will increase if the same current is passed to a lower-capacity cell
- May be useful for detection if one measurement is easier than the other





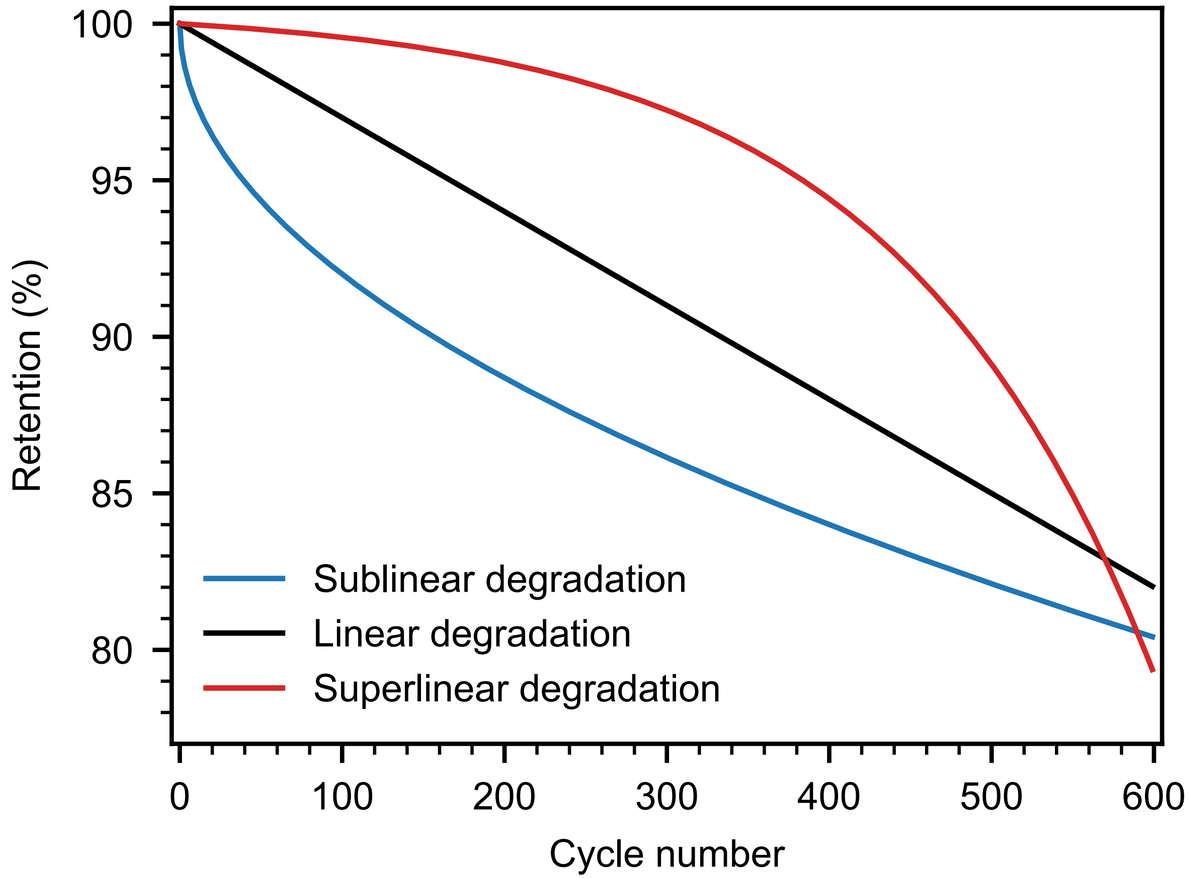
Ecker et al., *Journal of Power Sources* (2014)

Modeling and prediction

- Tracking bulk echem properties: Straightforward
  - Low rate diagnostic cycles often help
- Tracking local porosity, remaining additive amounts: Hard
  - Often requires *ex situ* methods
- Extrapolating snowballs, knowing thresholds, etc.: Hard
- Interactions, heterogeneity, variability: Hard
- Gotta track ‘em all to be confident

Conclusions

- Knees are complex!
- Physical understanding is super useful
- More public data will be great
- Sensitive characterization probes are high value
- Excited for a variety of modeling/prediction approaches (physics-driven to data-driven)



Thanks!

Peter M. Attia, Alexander Bills, Ferran Brosa Planella, Philipp Dechent Gonçalo dos Reis, Matthieu Dubarry, Paul Gasper, Richard Gilchrist, Samuel Greenbank, David Howey, Ouyang Liu, Edwin Khoo, Yuliya Preger, Abhishek Soni, Shashank Sripad, Anna G. Stefanopoulou, and Valentin Sulzer

Preprint coming soon!

Contact me at
- peter.m.attia@gmail.com for questions about this work
- pattia@tesla.com for opportunities at Tesla

P. M. Attia et al., *in preparation*