



Battery Design LLC

Overview of the
Life of Li-Ion Batteries
Robert Spotnitz

Tuesday May 13, 2008

LLIBTA 2008 – Tampa, FL



Overview

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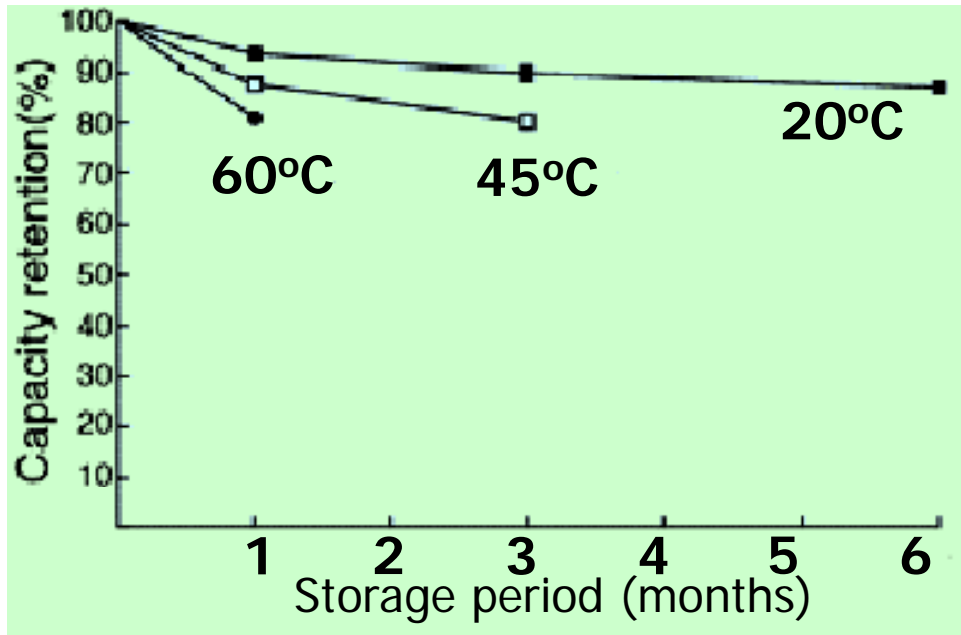
- The Importance of Battery Life
- Life Models
 - Loss of Cyclable Lithium
 - Li Loss through SEI Growth
 - Site Loss Model
 - Impedance Growth
- Conclusions



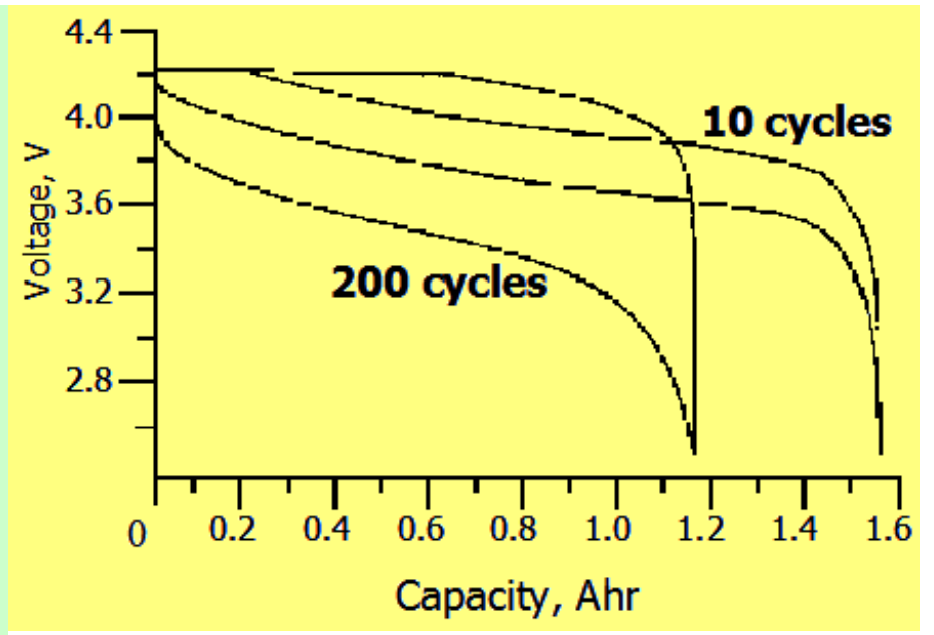
Battery Life - Determined by the decrease in power/capacity that occurs over time.

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Calendar Life – loss on standing

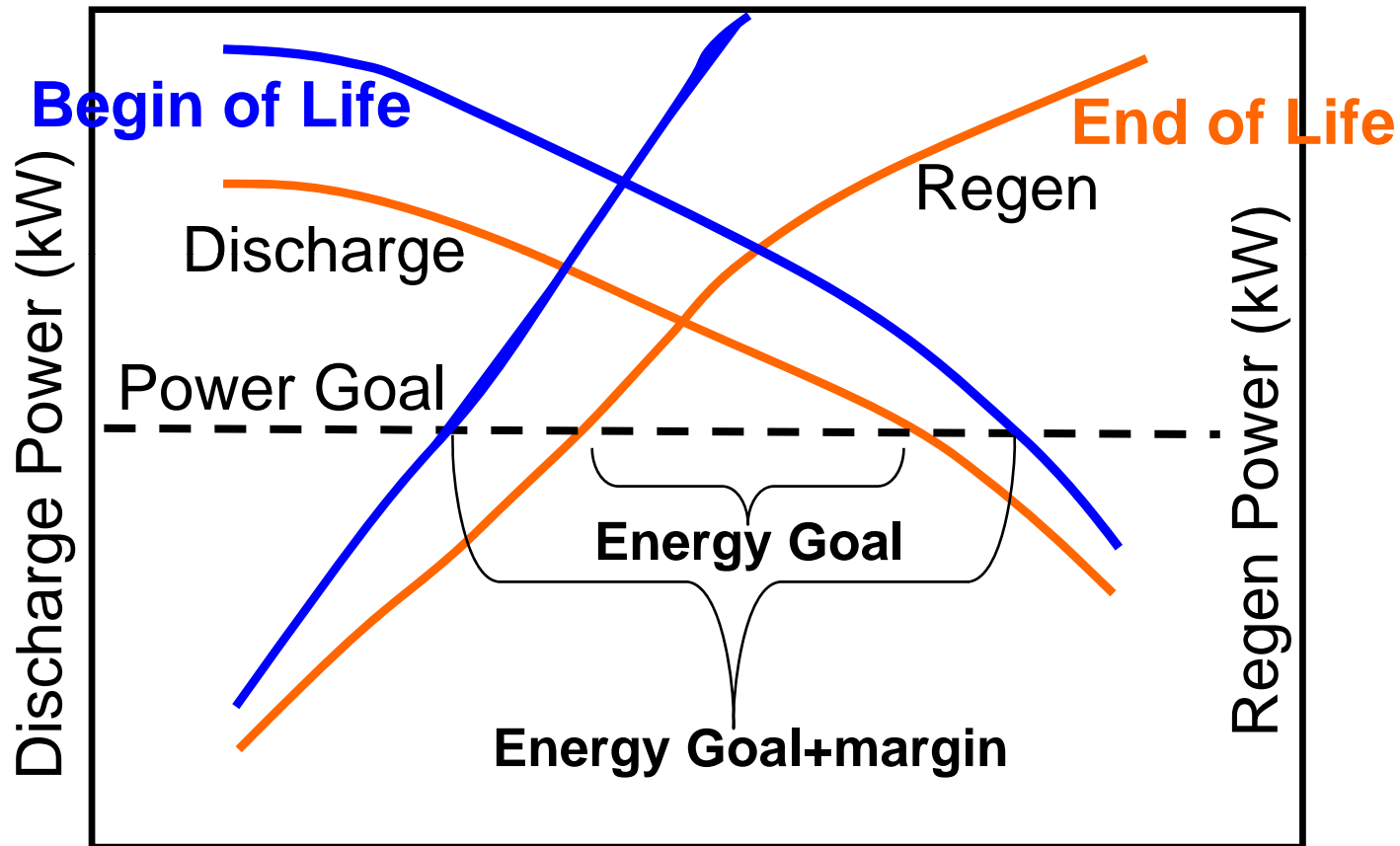


Cycle Life – loss during charge/discharge cycles





Goal: 10-15 Year Battery Life

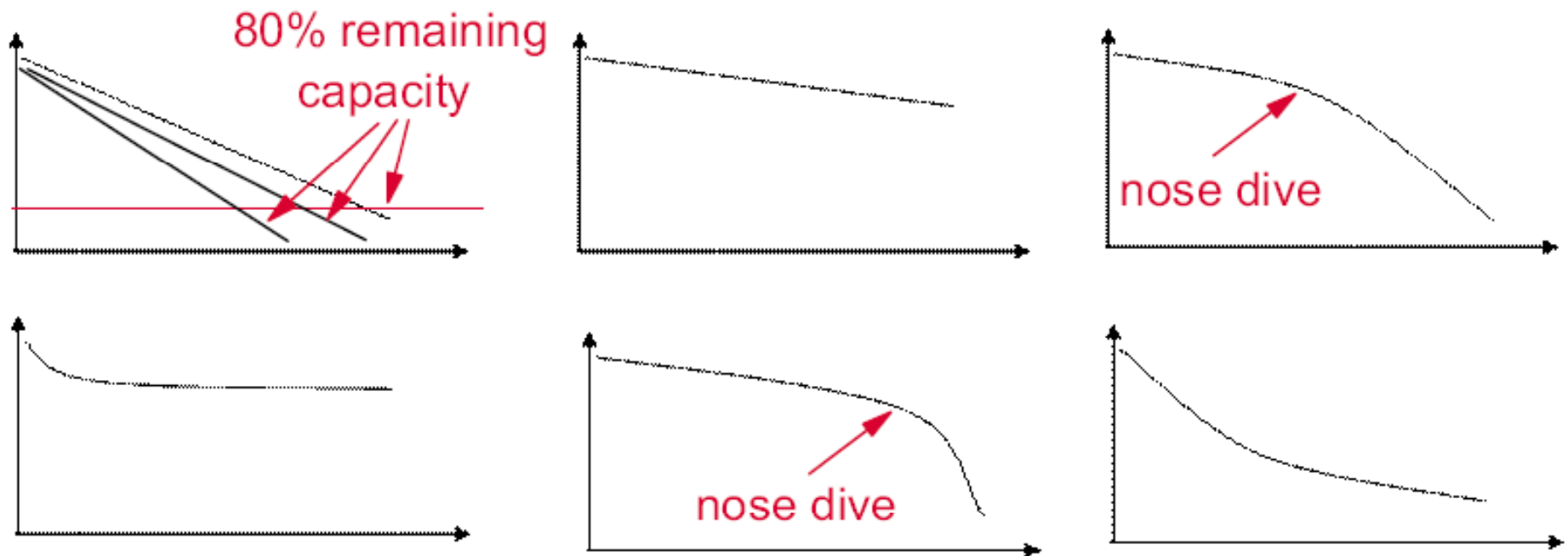


Net Energy Removed (at C/1 discharge rate)



Possible Types of Fading Curves in Cycle Life Testing

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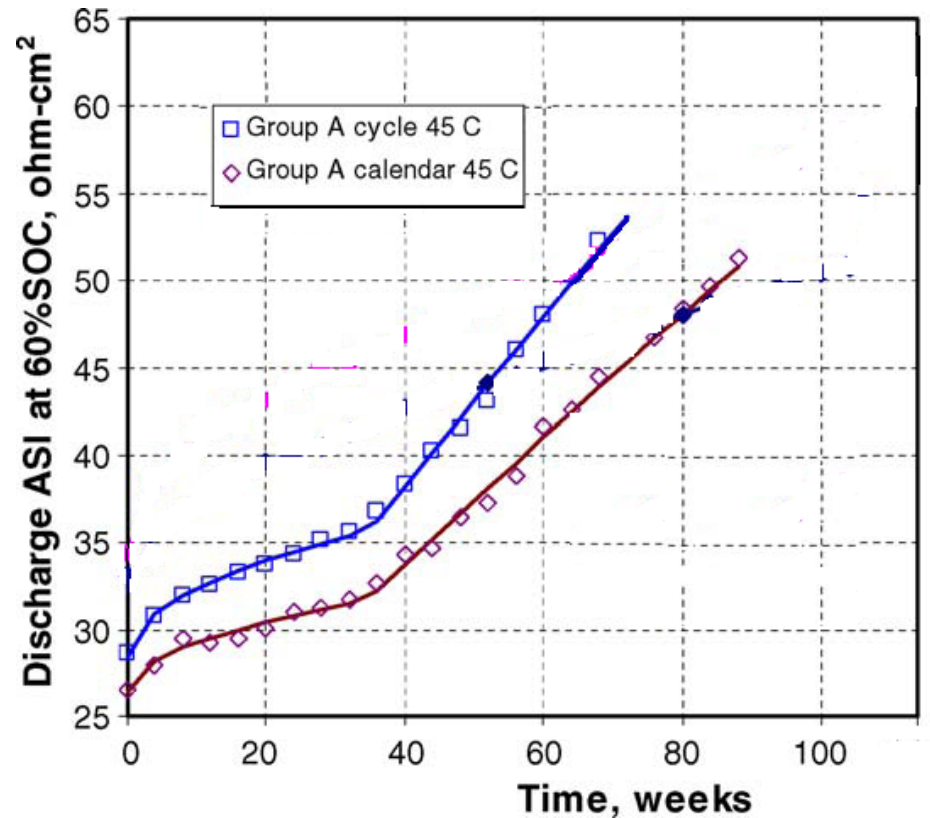
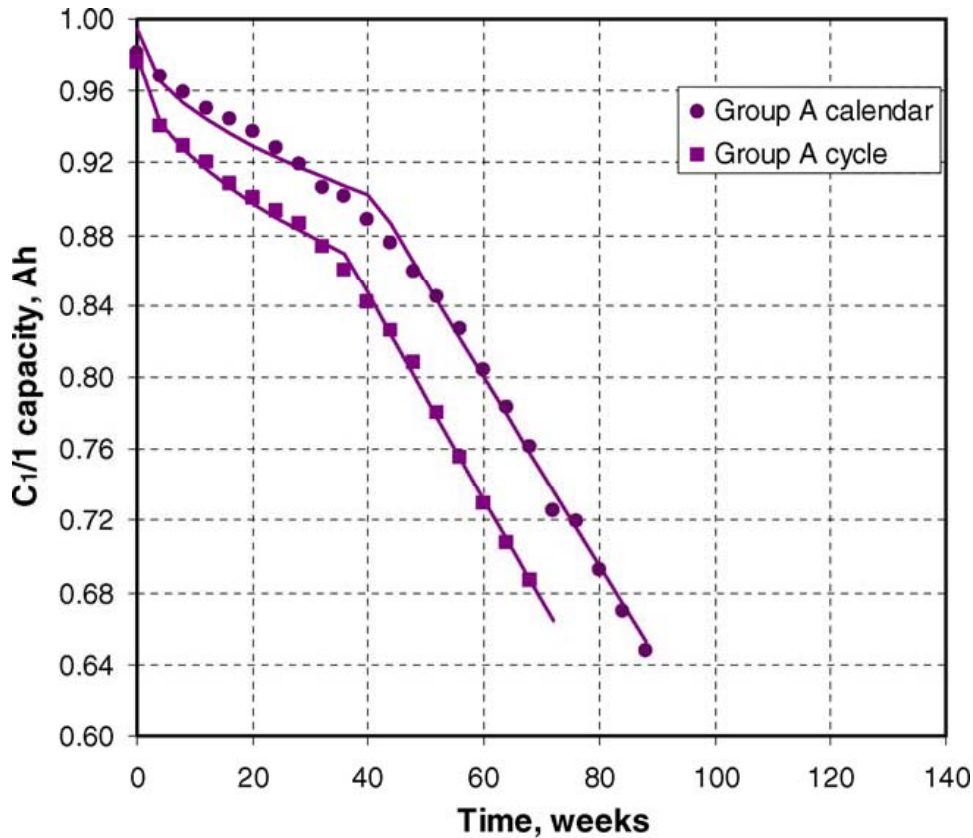


Frank J. Wang, The 25th Intl. Battery Seminar & Exhibit, March 17-20, 2008



ATD Gen 2 Cell Behaviour

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I. Bloom et al. *J. Power Src.* 155 (2006) 415.



Life Modeling

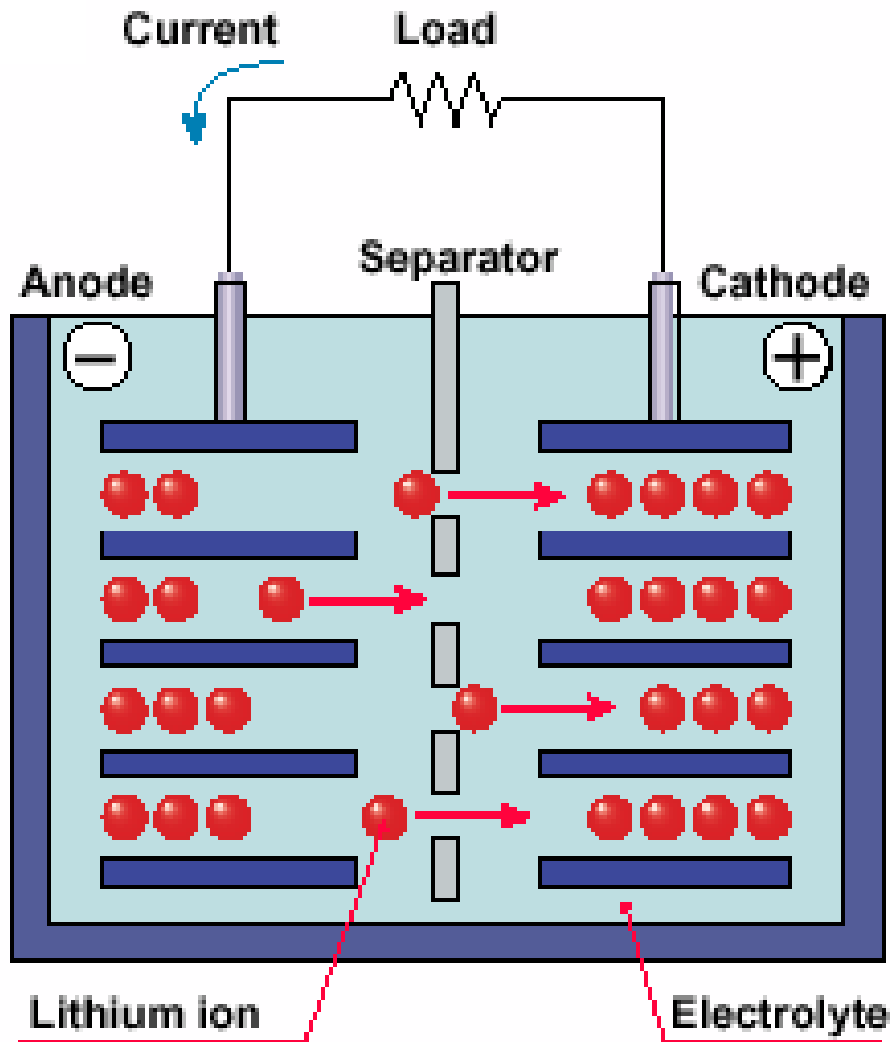
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- Want to account for impedance growth and capacity loss due to calendar time and cycling
- Current state of the art relies upon extrapolation of experimental results
- Simple functional forms are preferred



Key Aspects of Lithium-Ion Cells

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- 1) Insertion compounds that provide sites for lithium
- 2) Amount of cyclable lithium



Approach

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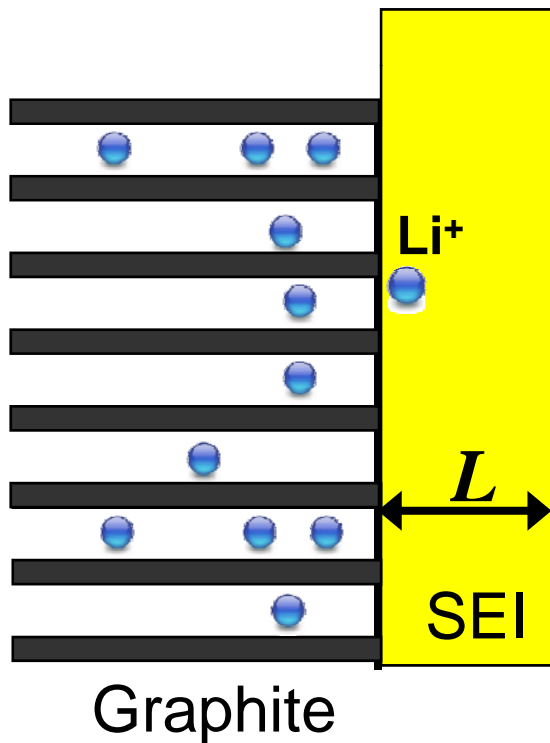
- Model loss of cyclable lithium and/or sites using simple differential equations that can be readily solved
 - Life simulation is possible in reasonable time (minutes to hours)
 - Arbitrary test conditions (rates, depth of discharge, etc.)
- Models available in Battery Design Studio[®] for user-friendly interface



Solid Electrolyte Interface (SEI) Electron Tunneling Model

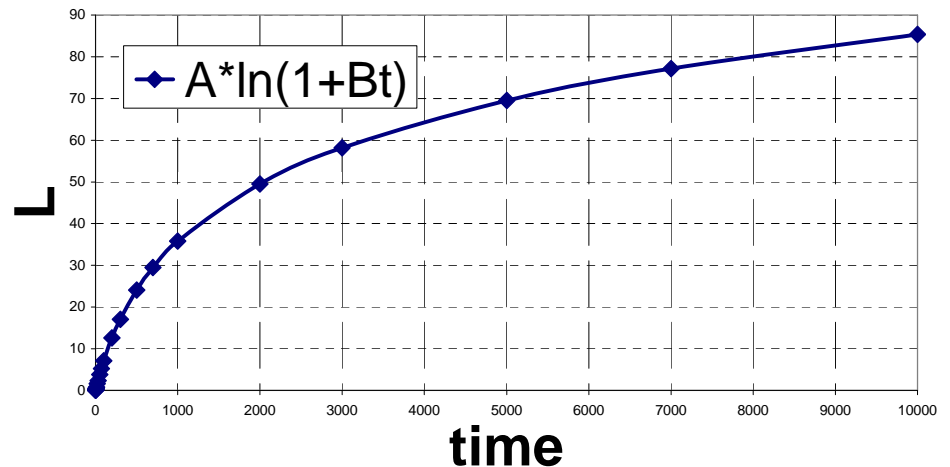
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SEI allows transport of lithium but inhibits electron transfer.
Formation of SEI results in loss of cyclable lithium.



Rate of SEI formation

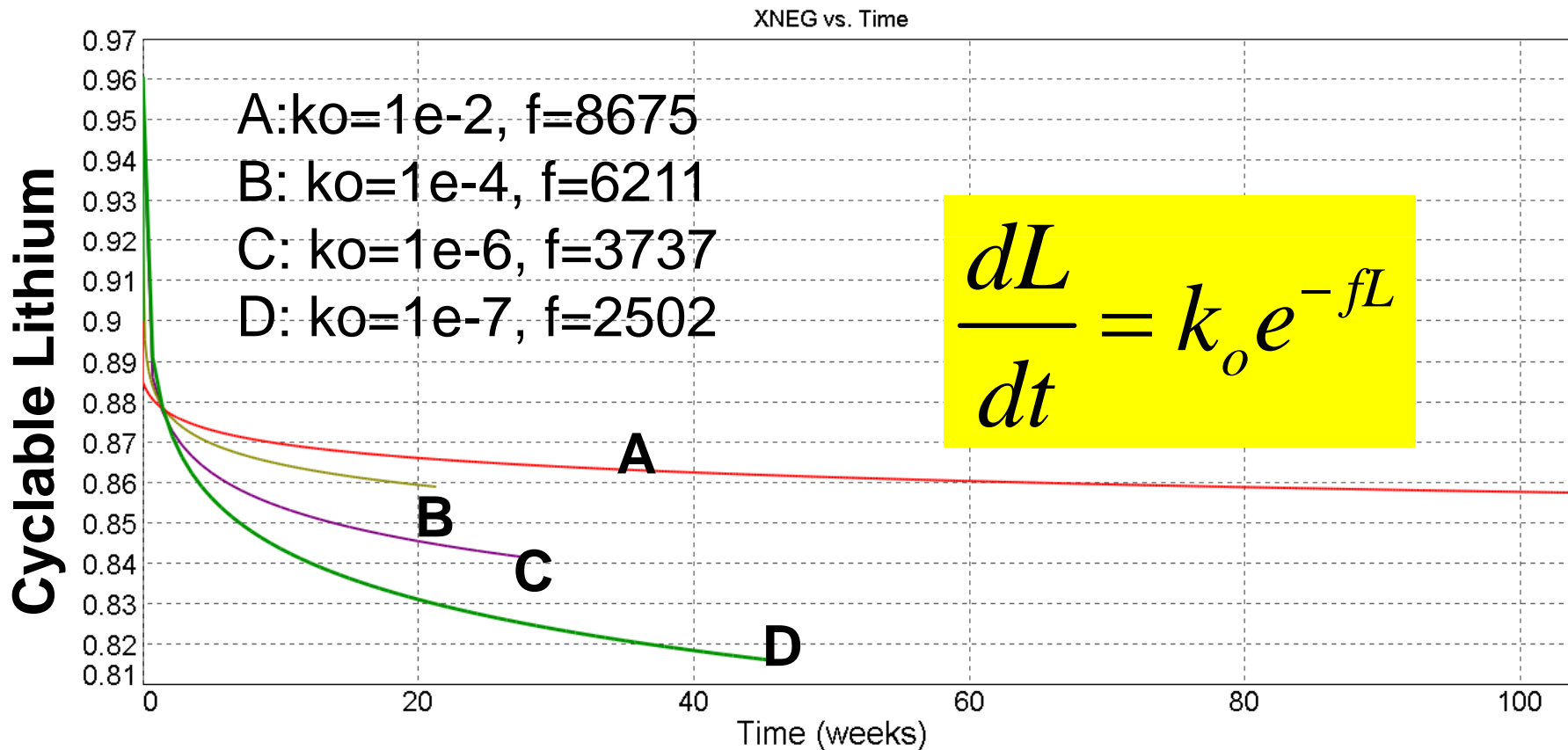
$$\frac{dL}{dt} = k_0 e^{-fL}$$





Electron Tunneling Model

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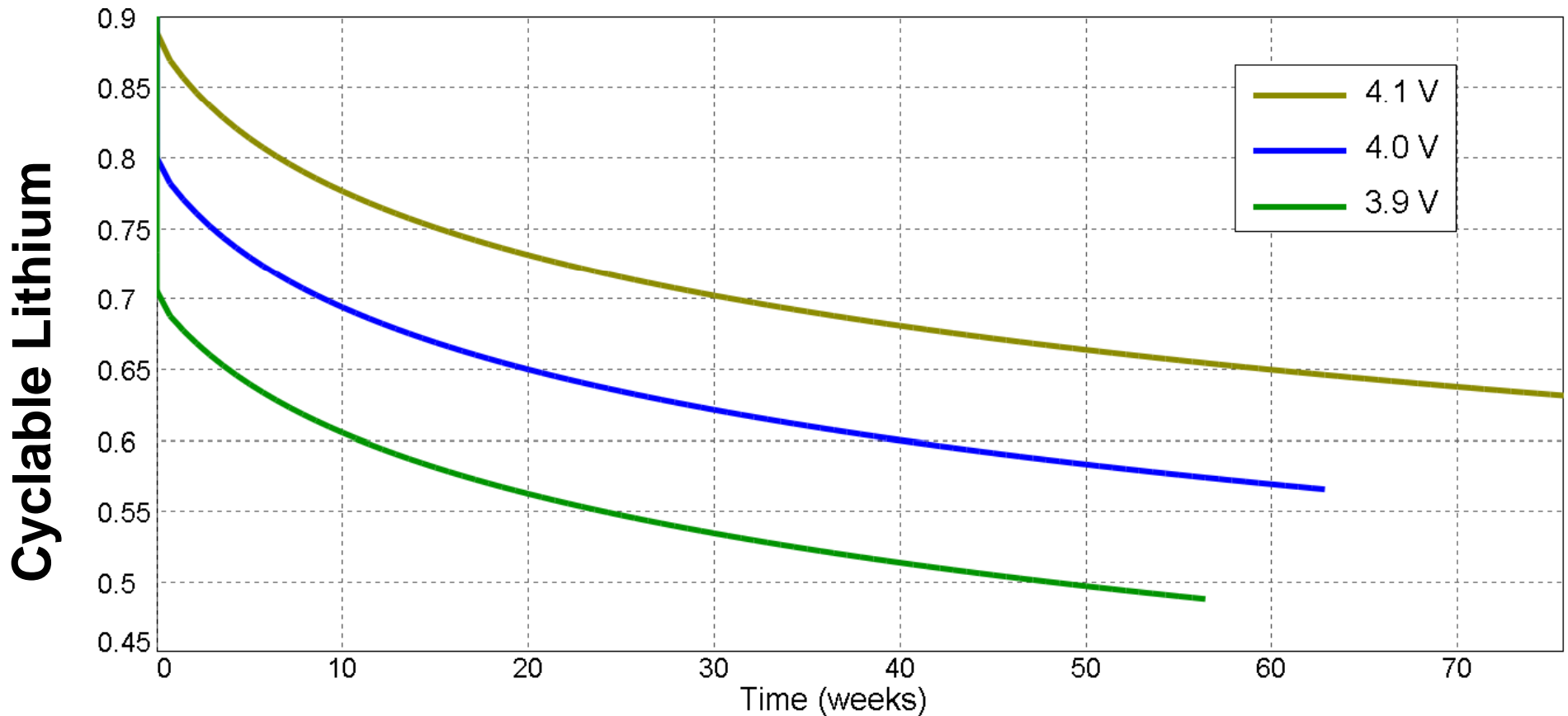


EquilFade-9-1
EquilFade-9-3
EquilFade-9-5
EquilFade-9-6



Electron Tunneling Model Simulated Calendar Life Test

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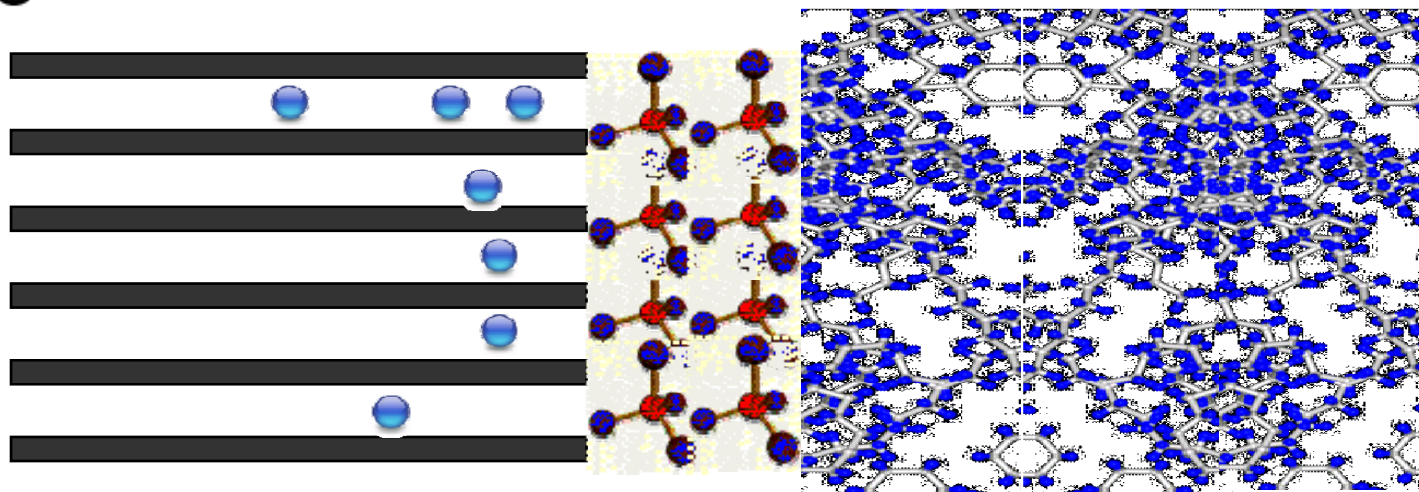
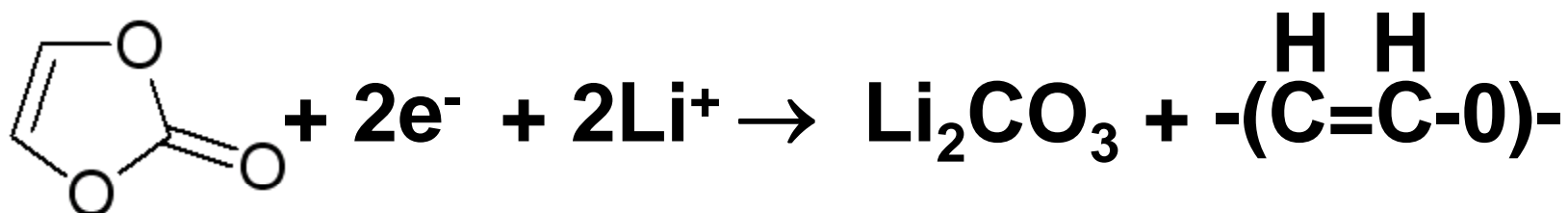
Tunneling model does not predict an effect of voltage on capacity fade.



Schematic of SEI at Graphite

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Vinylene carbonate



Crystalline solid ion conductor

Polymeric film



Acid Generation at Positive

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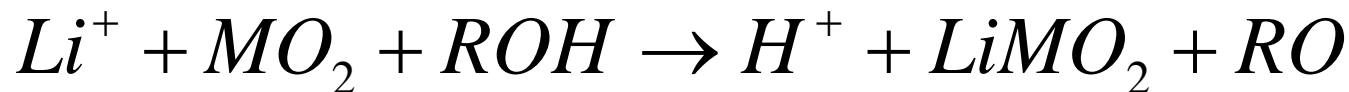
$$i_{Li^+} = Fk_p \exp \left[\frac{F(\phi_1 - \phi_2 - \phi_{eq} - i\rho_f L_p)}{RT} \right]$$



$$i_{H^+} = Fk_{H^+} \exp \left[\frac{F(\phi_1 - \phi_2 - \phi_{eq,H^+} - i\rho_f L_p)}{RT} \right]$$

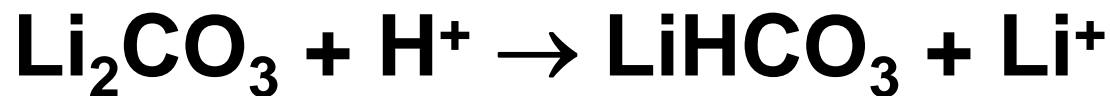
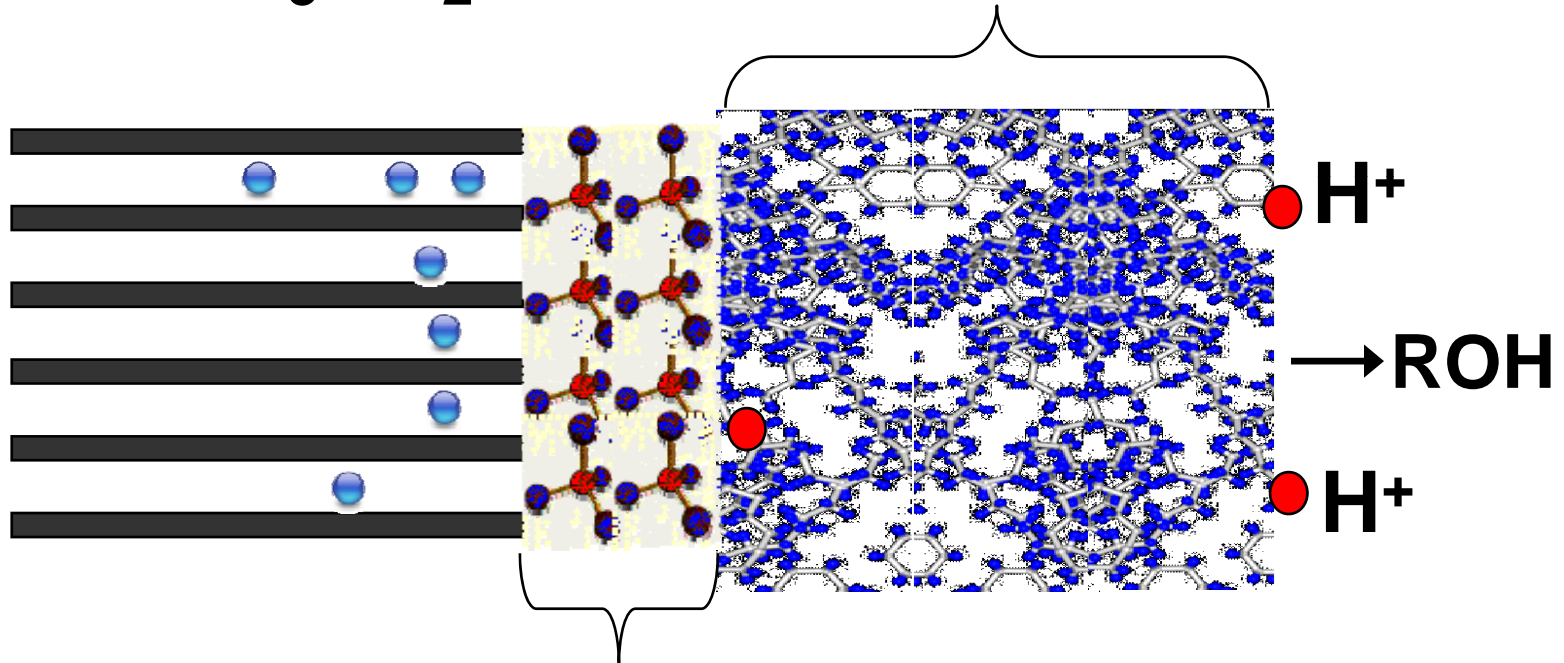
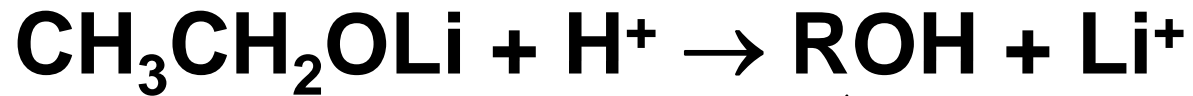
LiMO₂

Net Reaction





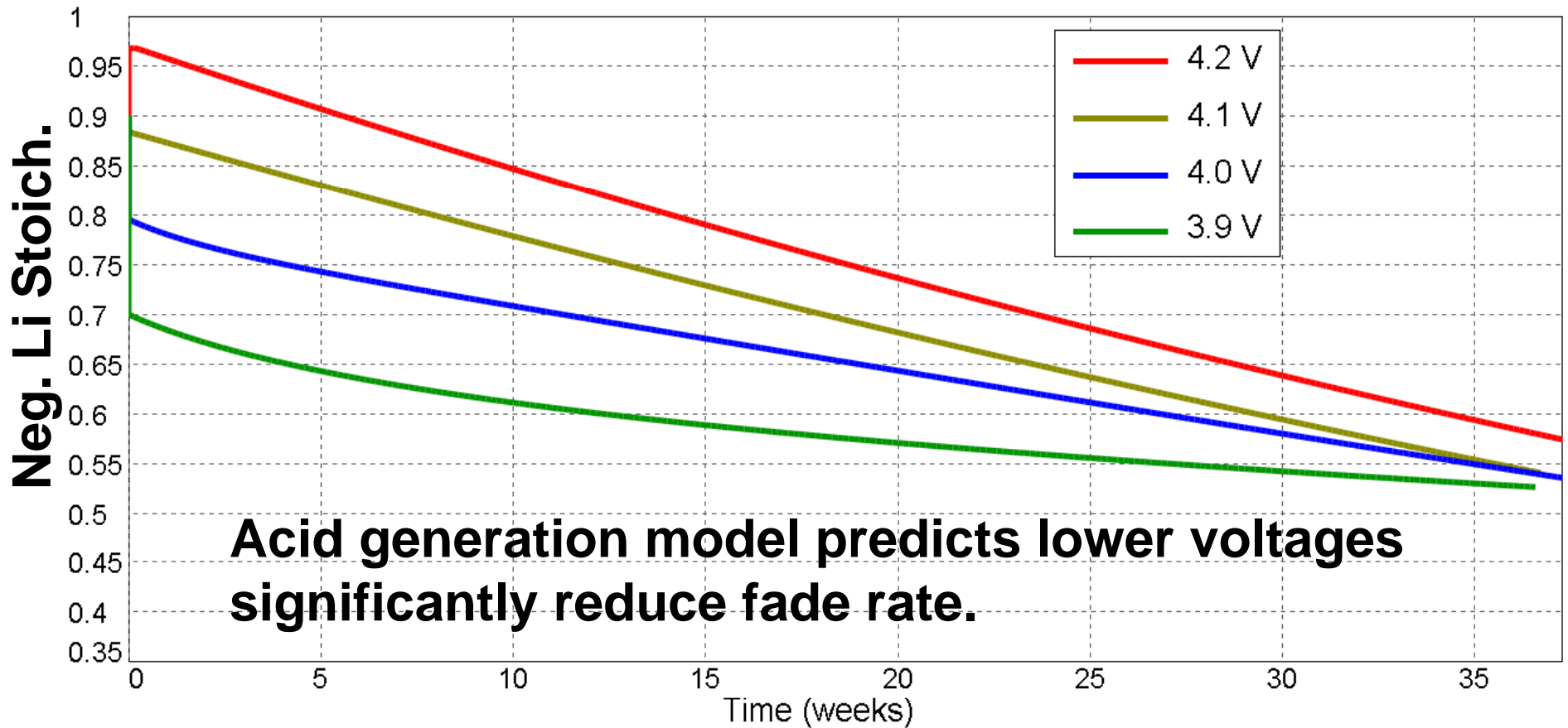
Acid attack of SEI





Electron Tunneling with Acid Generation Model

Simulated Calendar Life Test

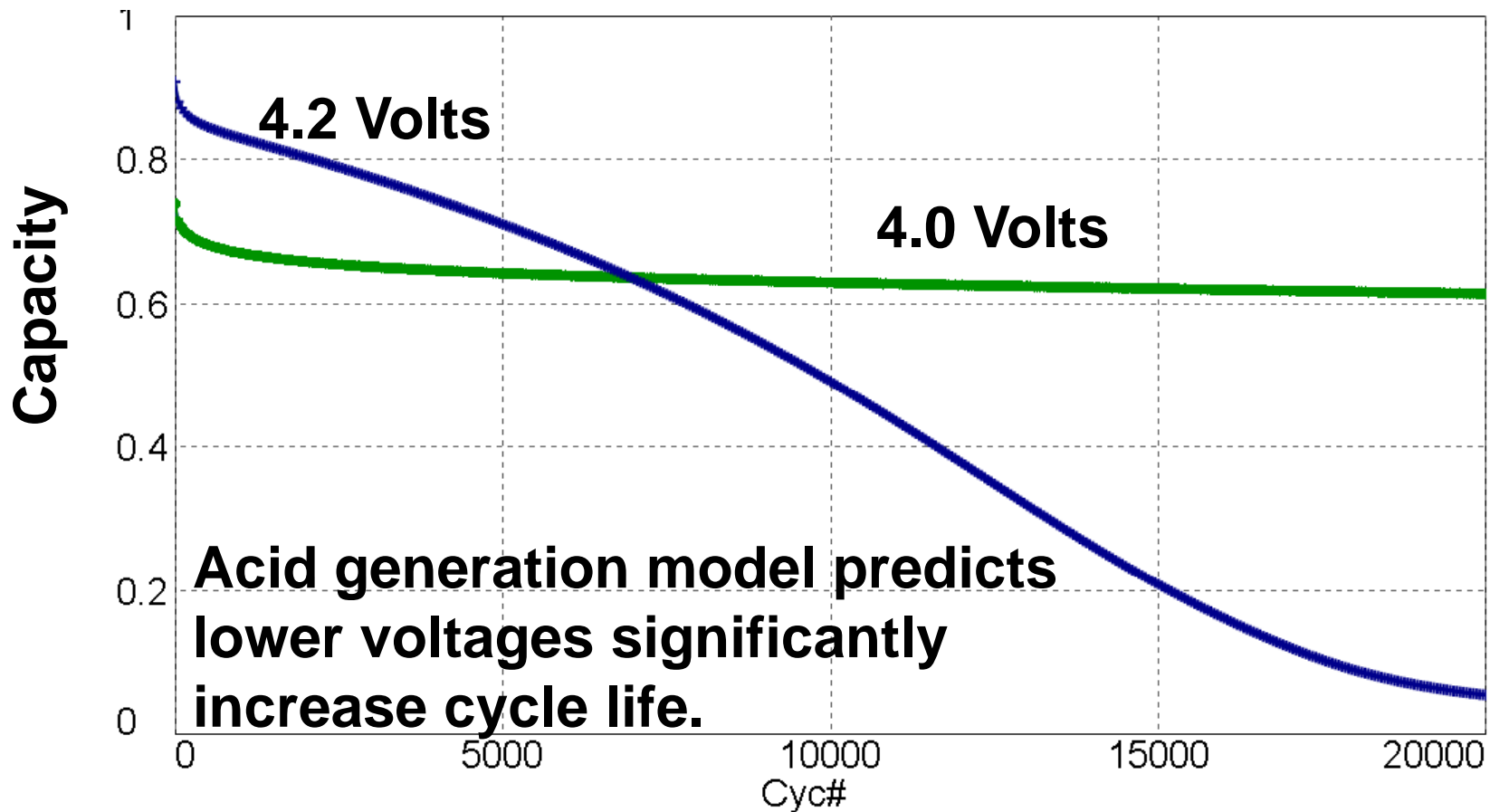




Electron Tunneling with Acid Generation Model

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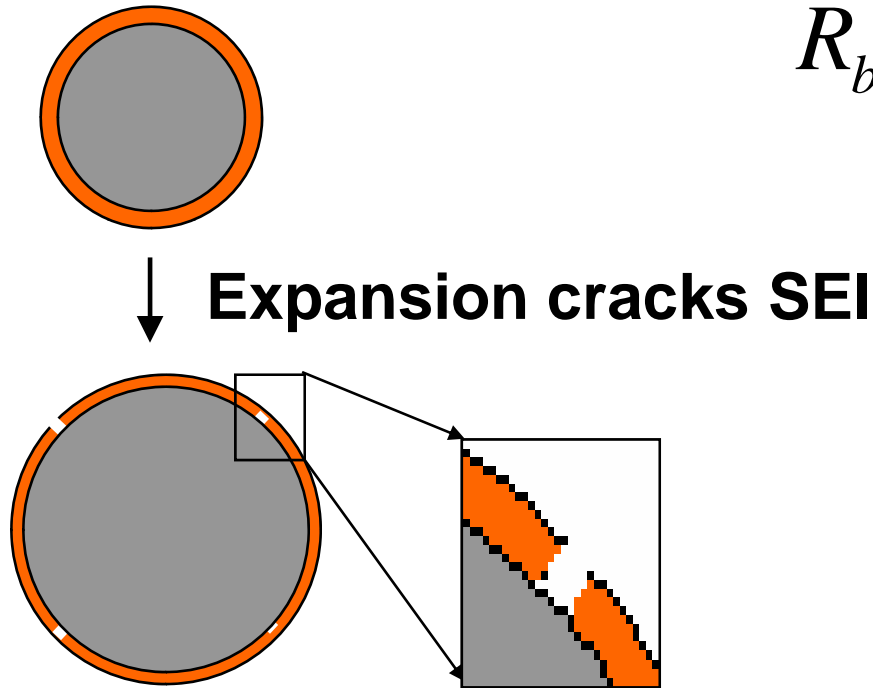
Simulated Cycle Life Test





Particle Expansion/Contraction Damages SEI

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$$R_{break} = k_I N_{sei} \left(\frac{I}{Q} \right)^p |x - x_o|$$

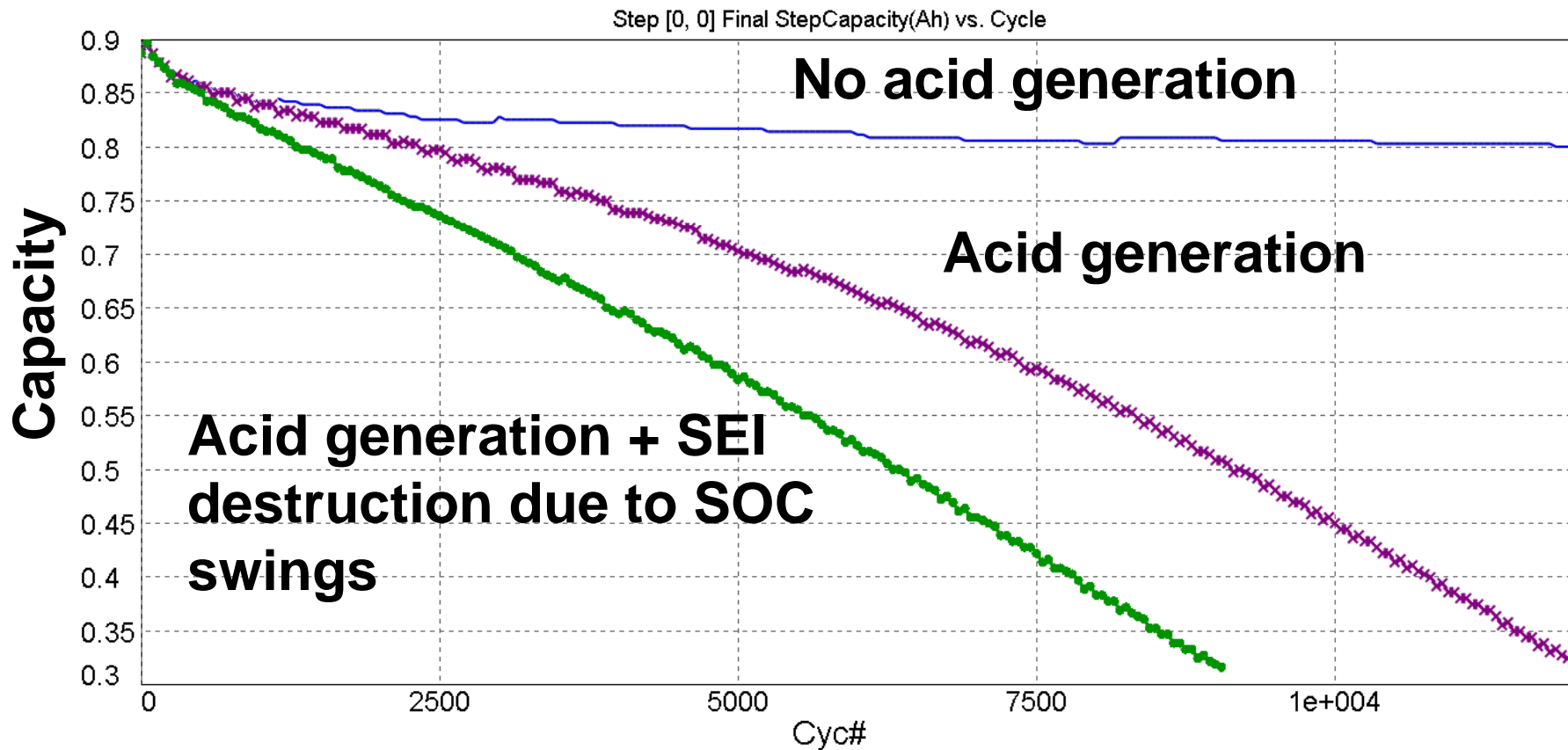
x_o is value at stoichiometry at last time current changed sign

Equation predicts capacity loss increases with charge/discharge current and magnitude of SOC swing



Simulated Cycle Life Acid Generation Models

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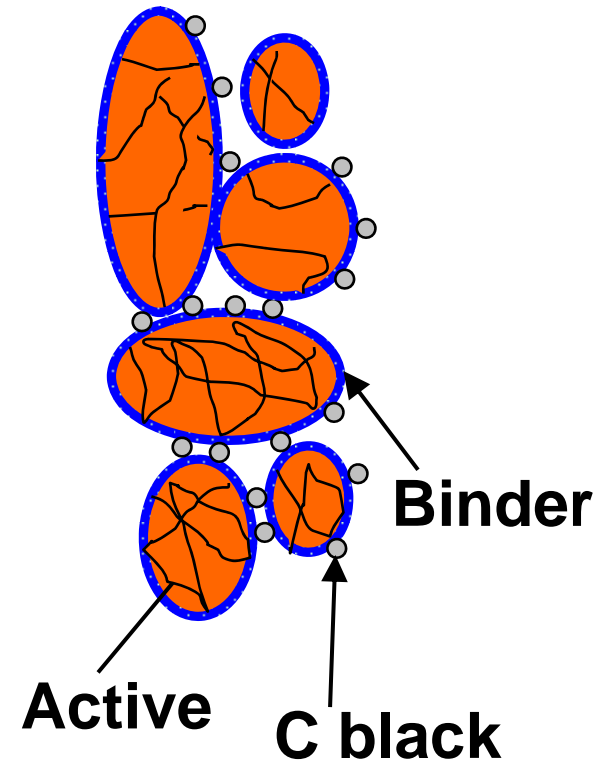




Possible Mechanisms for Site Loss

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- Electrical isolation of particles due to
 - Expansion of positive, recovery from compression or cycling
 - Break-up of agglomerates
 - Resistive film formation on surface
- Change in surface chemistry
 - Phase change to insulating or material with low Li diffusivity
 - Composition change, perhaps due to acidic impurities

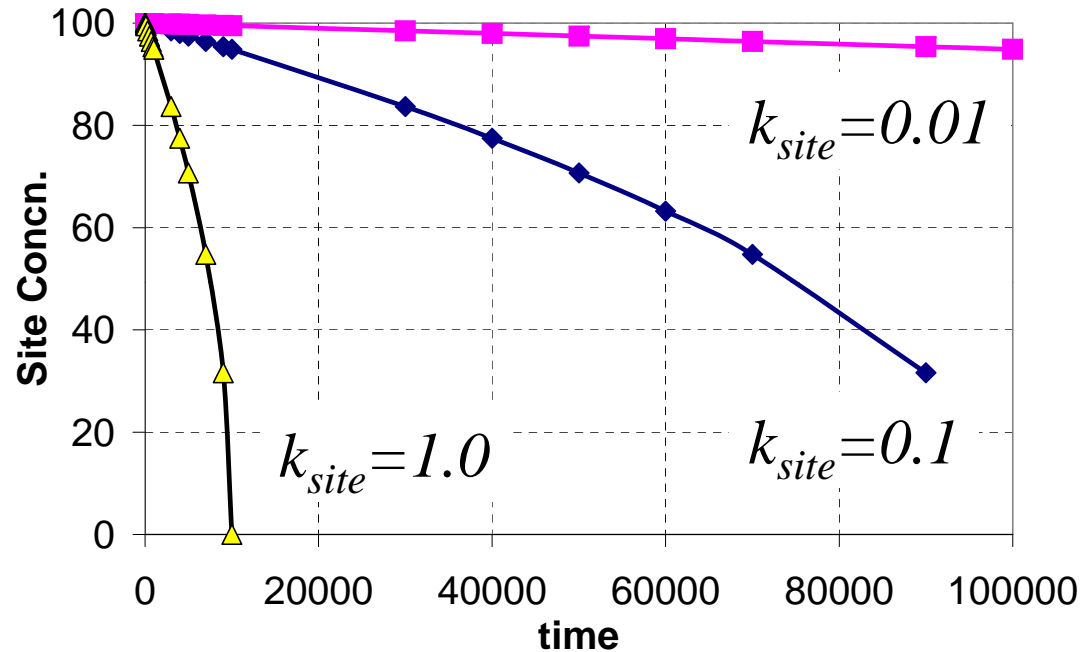




Site Loss Model

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$$\frac{dQ_{site}}{dt} = \frac{-k_{site}}{Q_{site}^{p_{site}}}$$



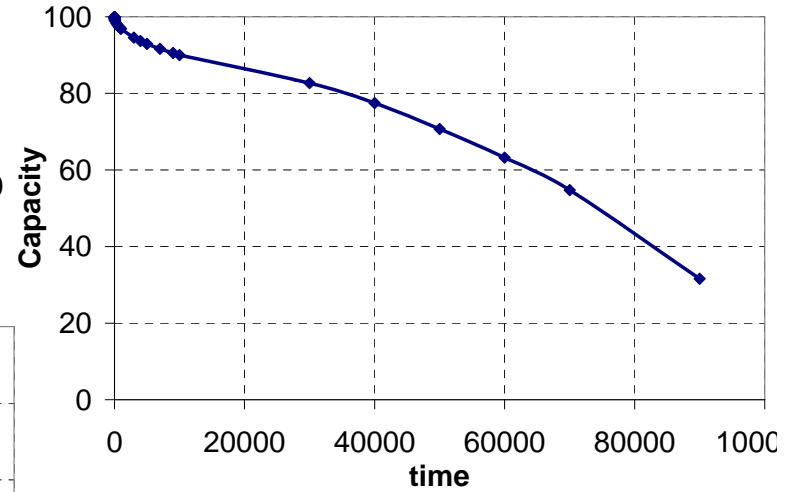
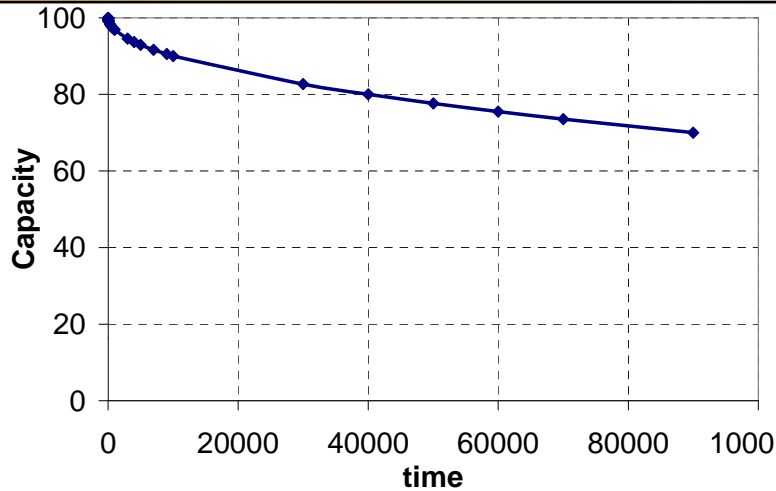
Expect site loss to accelerate as lose sites, since remaining sites are exercised more vigorously and have fewer neighbors to contact.



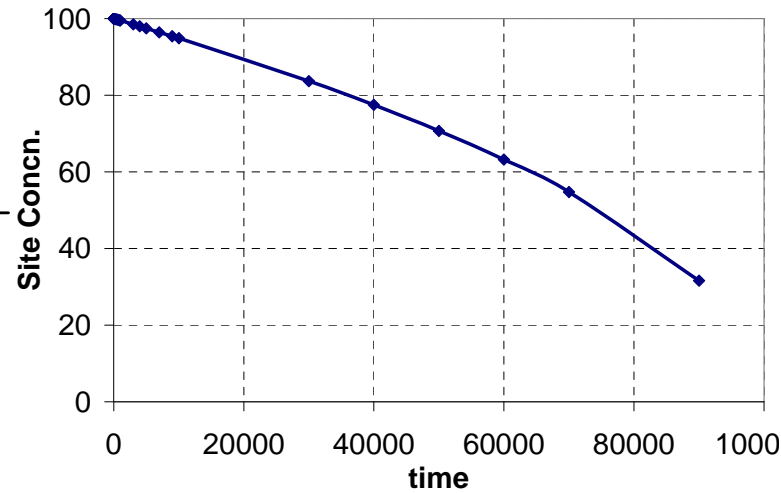
Site Loss + SEI Growth Models

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$$\frac{dQ_{sei}}{dt} = \frac{k_{sei}}{Q_{sei}}$$



$$\frac{dQ_{site}}{dt} = \frac{-k_{site}}{Q_{site}^{p_{site}}}$$

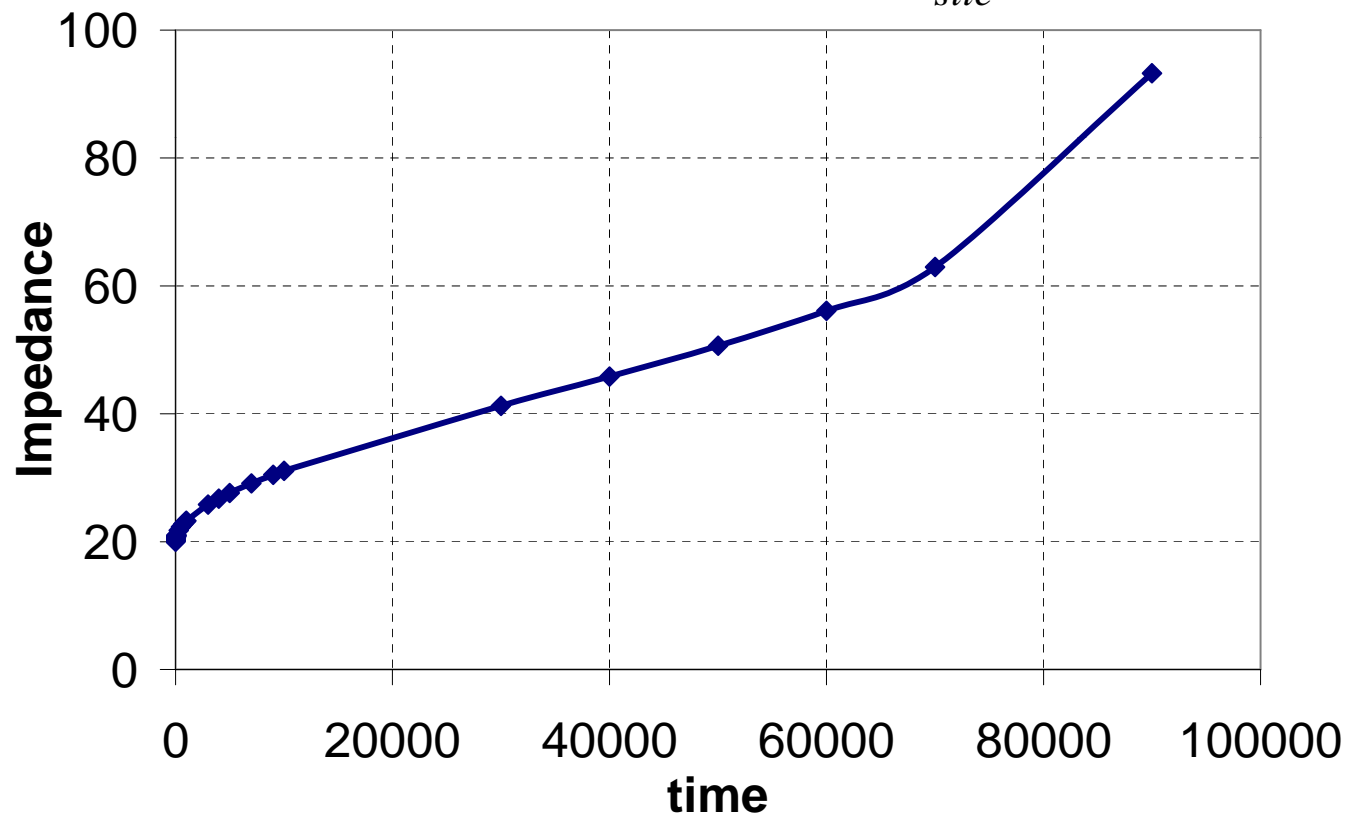




Site Loss + SEI Growth Models Impedance Growth

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$$R_{cell} = R_o + r_{sei} N_{sei} + \frac{r_{site}}{Q_{site}}$$





Summary

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- Defining feature of lithium-ion cells are the lithium sites and the amount of lithium available for cycling, which are determined by electrode loadings, irreversible capacity loss on formation, and equilibrium curves.
- The most common shapes for capacity fade curves can be rationalized by simple models for lithium and site loss.



Constant Ah Throughput

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- Cell passes fixed amount of Ah (Ah_{life}) before reaching end of life

