DOW

Energy Materials

Advancing Energy Storage

Lithium Ion Battery Failure Mechanisms

Dee Strand

Dow Research Fellow

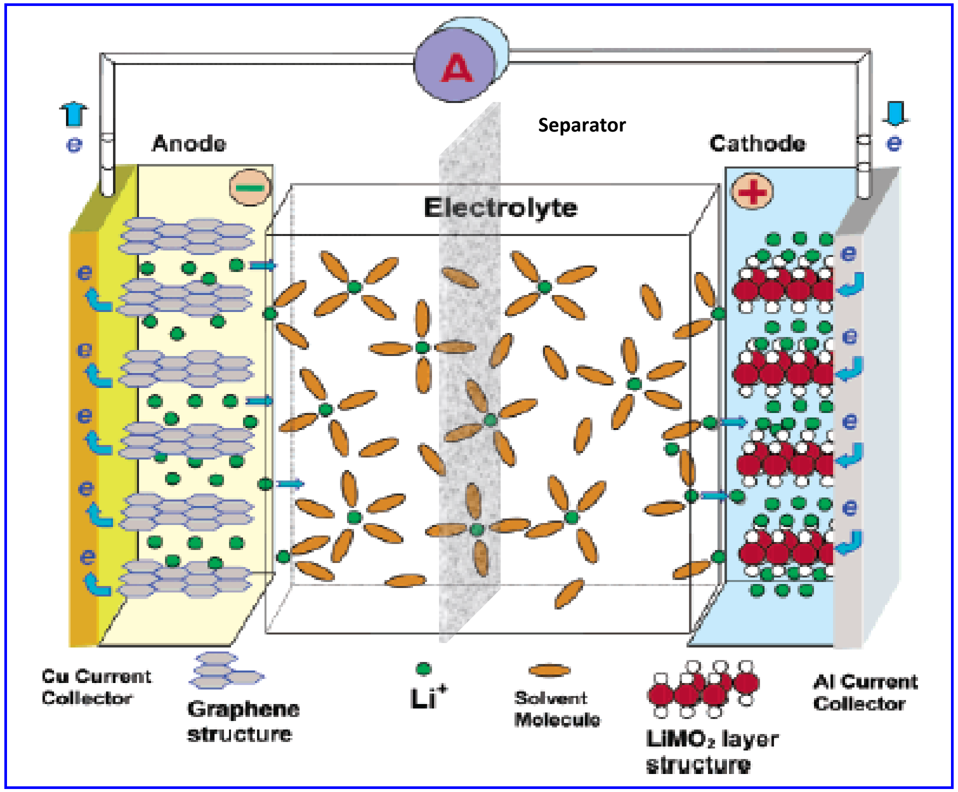
How do LIBs Work?

+1 +3 -4 +4

$$2LiCoO_2 + 6C \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 2Li_{0.5}CoO_2 + LiC_6$$

A passivation layer is required on the anode

- Carbonate electrolytes are not stable at the anode potentials (close to 0 V vs. Li)
- Formed during first cycle or two in situ

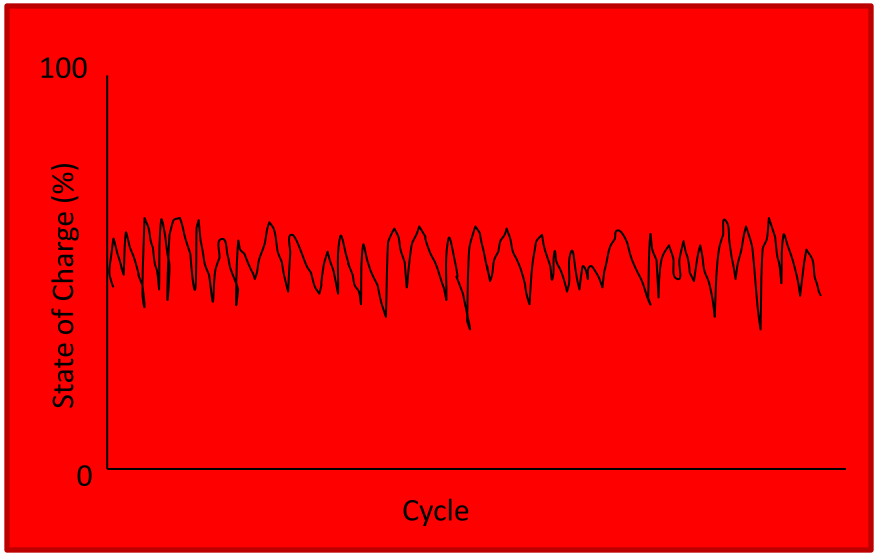


Reprinted with permission from *Chem. Rev.*, **2004**, *104* (10), pp 4303–4418.

Hybrid Electric Vehicles

On market today with NiMH and Lithium Ion Batteries (LIBs)

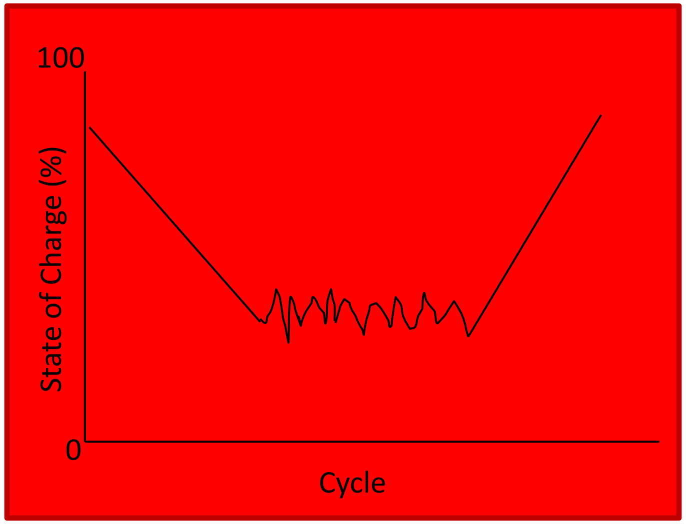
- Extra power in acceleration
- Maintains power during stops
- Recharged during braking



Plug-In Hybrid Electric Vehicles

New to the Market

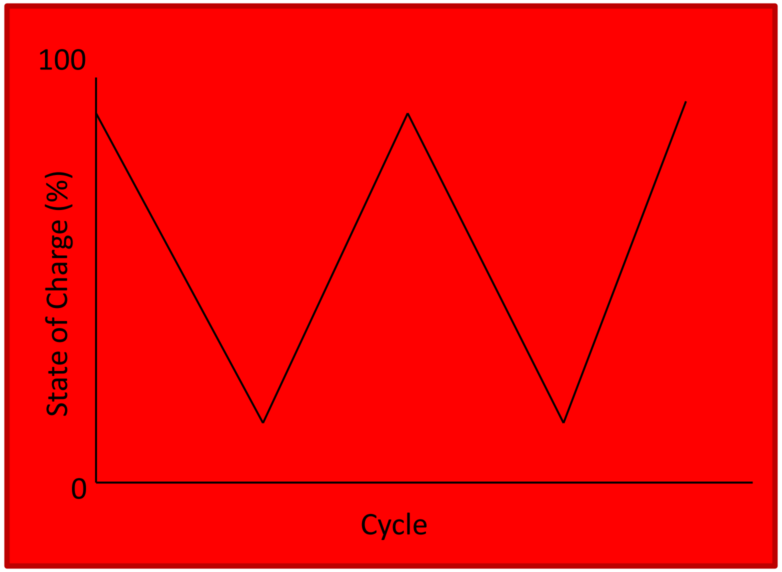
- Defined “all electric” range (40 miles for Chevy Volt)
- “Plugs in” to fully recharge battery
- Electric drive, with gas generator as back-up once batteries are depleted



Electric Vehicles

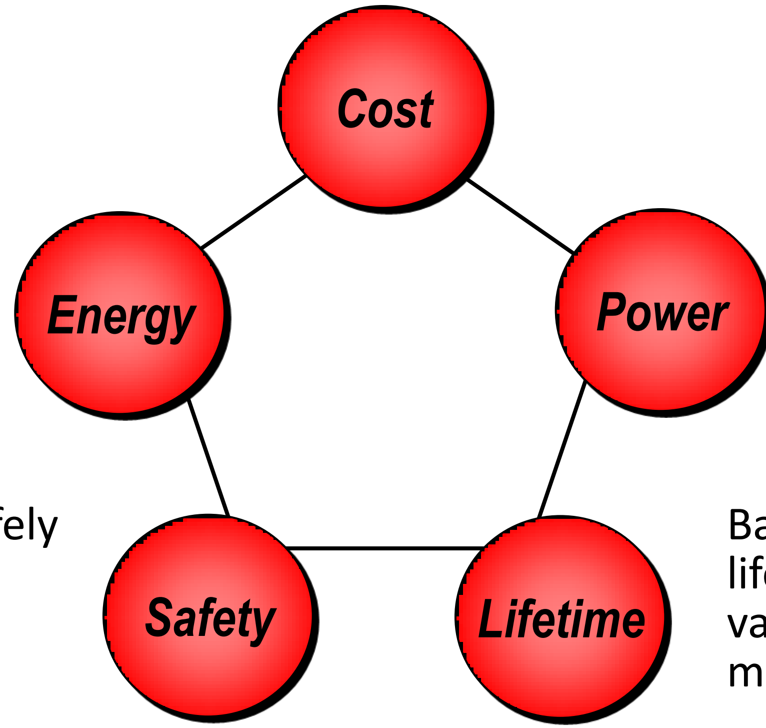
New to the Market

- Powered solely by batteries
- Range defined by battery capacity for particular vehicle (e.g., 200 miles)
- Currently limited by short range
- Technology currently appropriate for “niche” type vehicles/fleets



What Performance is Required?

Needs to bring (P)HEV costs down to “regular” vehicles or at least a short payback time at current fuel prices.



Needs to deliver appropriate range for vehicle – will vary depending on PHEV or EV

Needs to deliver power so driver does not sacrifice performance

Needs to perform safely over the life of the battery and under potential abuse conditions

Battery needs to last the life of the car and resale value needs to be maintained

Energy Definitions

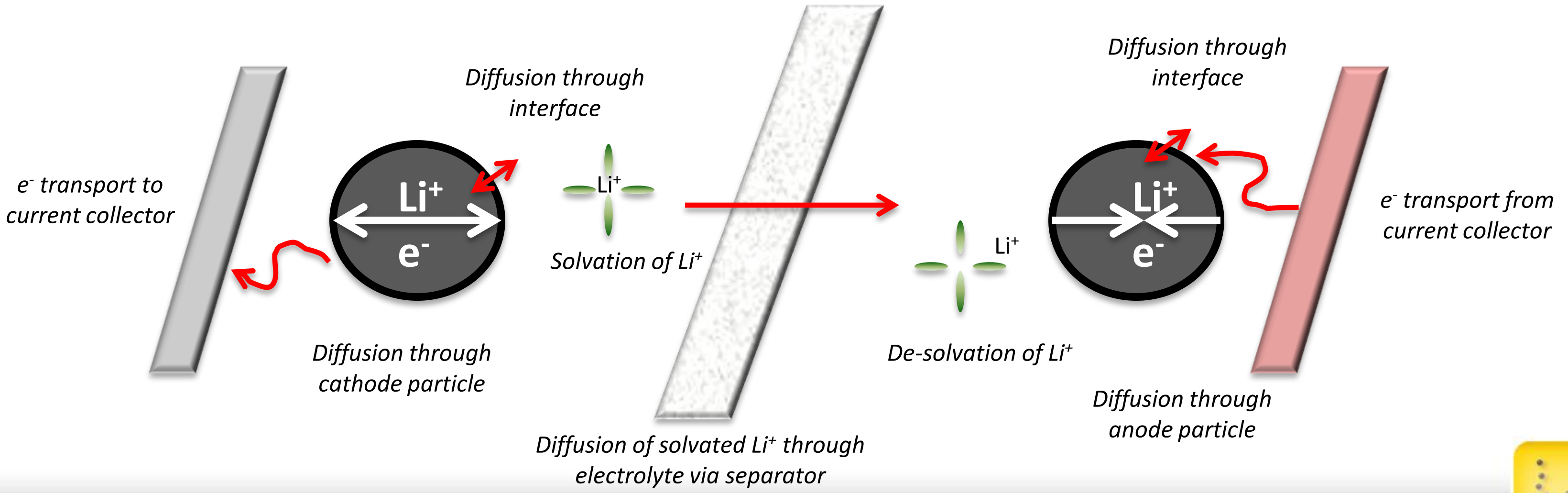
- Current (1 ampere = 1 coulomb/sec)
  - Ampere is the amount of electric charge passing a point per unit time
- Capacity (amp-hours, Ah)
  - Current x time = electric charge
  - Unit of charge
  - 1 amp hour = 3,600 coulombs
- Specific capacity (Ah/g or mAh/g)
  - Amount of charge per unit mass
- Energy (Wh or kWh)
  - Can calculate from Ah (amp hours) – remember this is charge
  - Ah = Wh/voltage **OR** Wh = Ah x "average voltage"
  - Approximate because the voltage is not constant during discharge of a battery

How much charge can I get out of 1 g of cathode material?
How much charge can I store in 1 g of anode material?
What is the discharge voltage of the battery?
How much cathode and anode material can I fit into the battery?

Power Definitions

- Watt – unit of power
  - Power = energy/time
  - 1 watt = 1 Joule/sec
  - 1 watt = 1 V x 1 ampere (one amp of current flows through a potential difference of one volt)

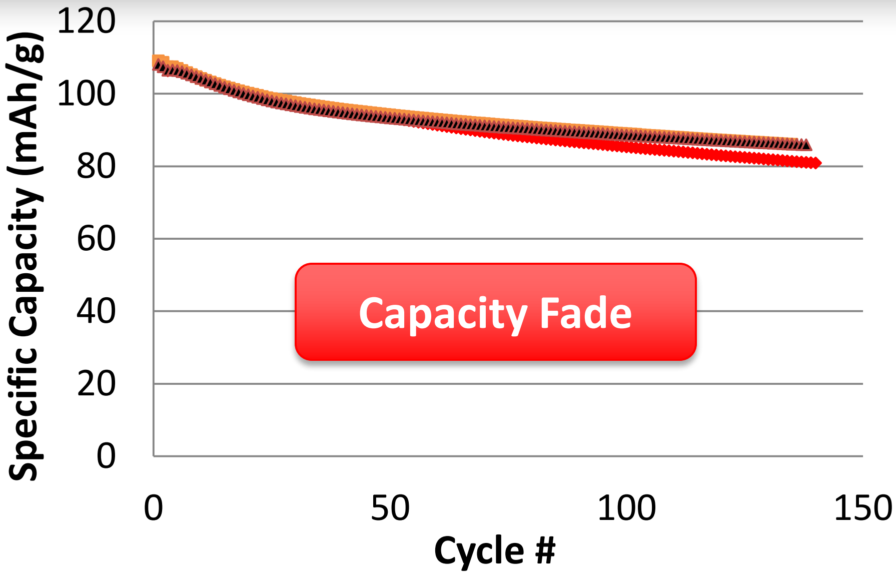
How fast can I move the charge?
Can I move the charge at all?

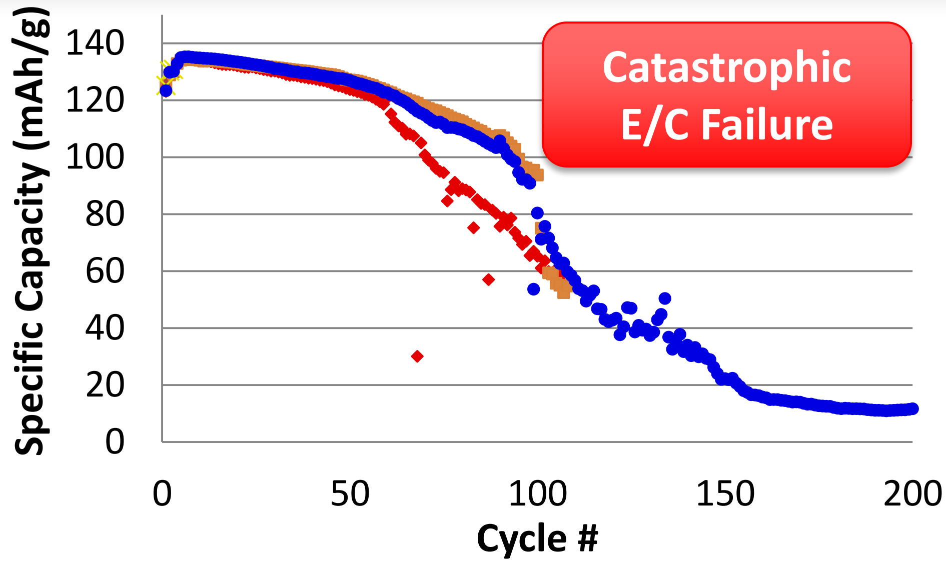


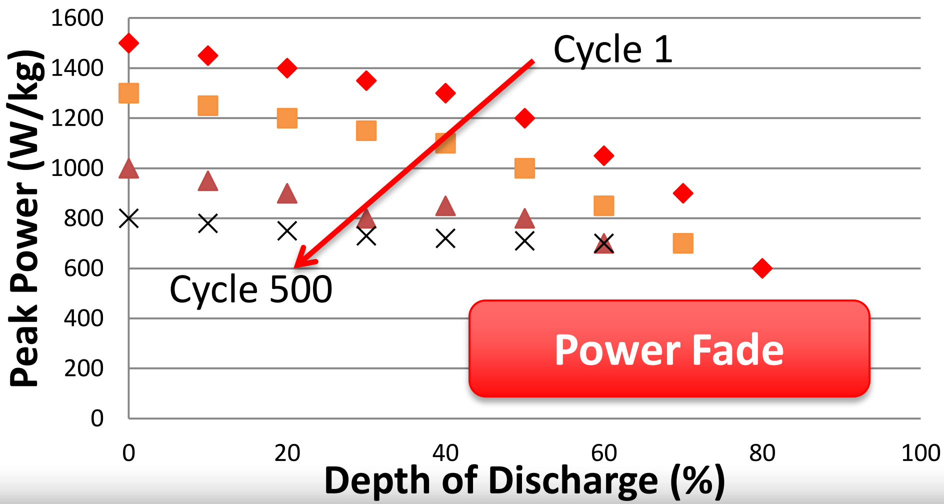
How do LIBs Fail?

- Some general statements
  - There are many failure modes/mechanisms
  - All can occur simultaneously
  - Relative contributions of different failure mechanisms are material dependent and material combination dependent
  - “Reflective” effects often occur
  - Solutions that inhibit one mechanism frequently enhance others
  - Failure can often depend more on how the cell is made than what the material is capable of
  - Some aspects are not well understood in the industry

What Does Failure Look Like?







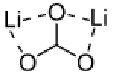
Categories of Failure

- Loss of lithium
- Loss of active material (host)
- Inability to move lithium
- Catastrophic-type failures

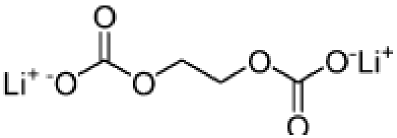
Loss of Lithium

- Anode SEI formation
  - "Necessary" process during the first few cycles
  - Degradation mechanism after that
    - Mechanical instability
    - Thermal instability
    - Catalytic-type decomposition
      - Graphite properties
      - Metals from the cathode
    - Probably more….

Gachot et al., J. Power Sources (2008), 178(1)

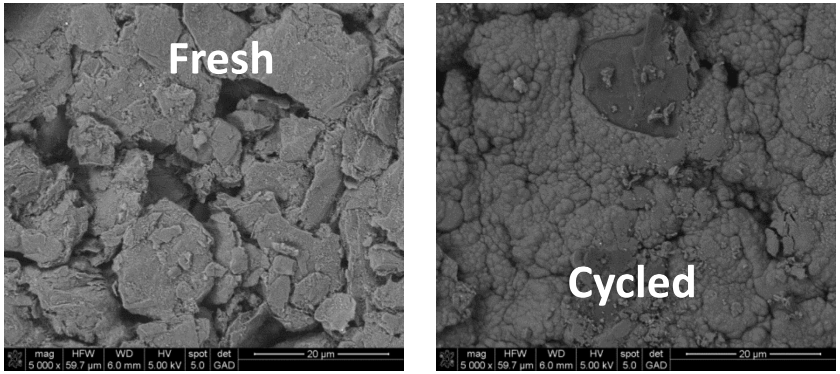


Li_2CO_3



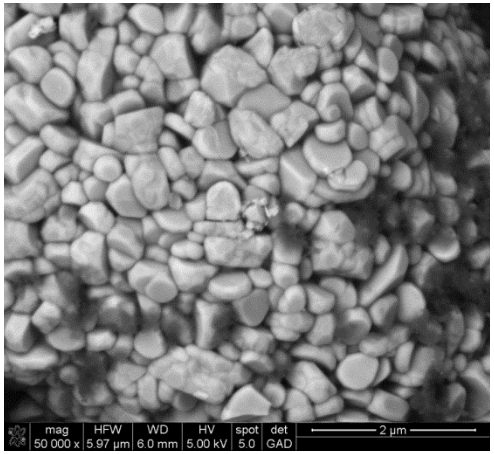
LiF

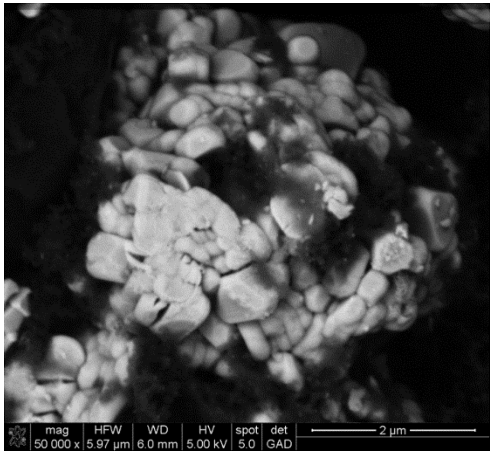
CH_3OLi

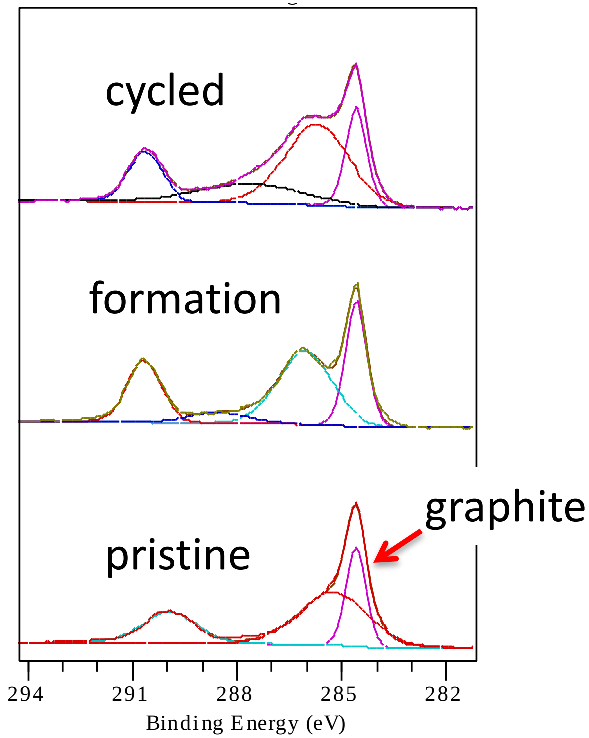


Loss of Lithium

- Cathode SEI formation
  - Much less known about this
  - Very dependent upon cathode voltage and choice of electrolyte





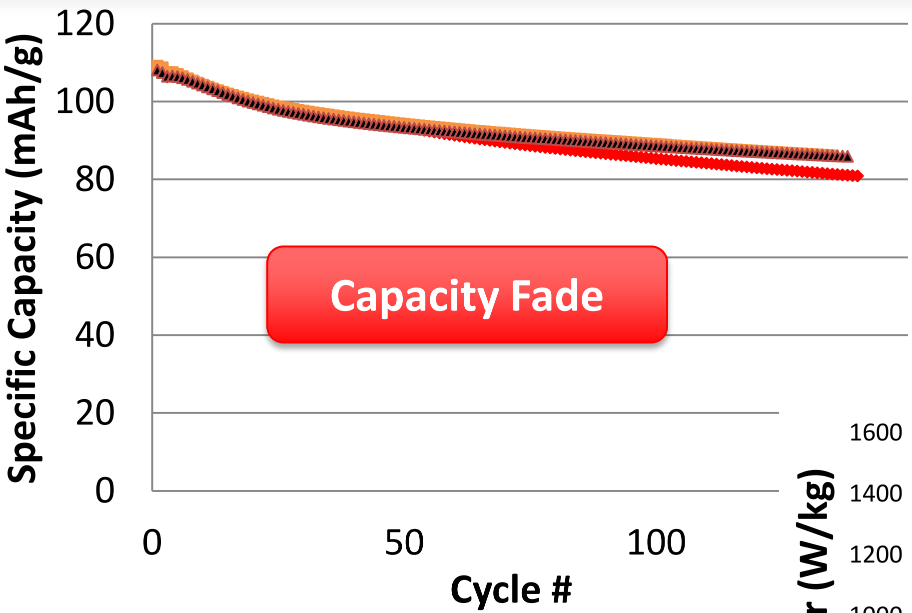


XPS C1S spectra of NMC Cathode

Fresh

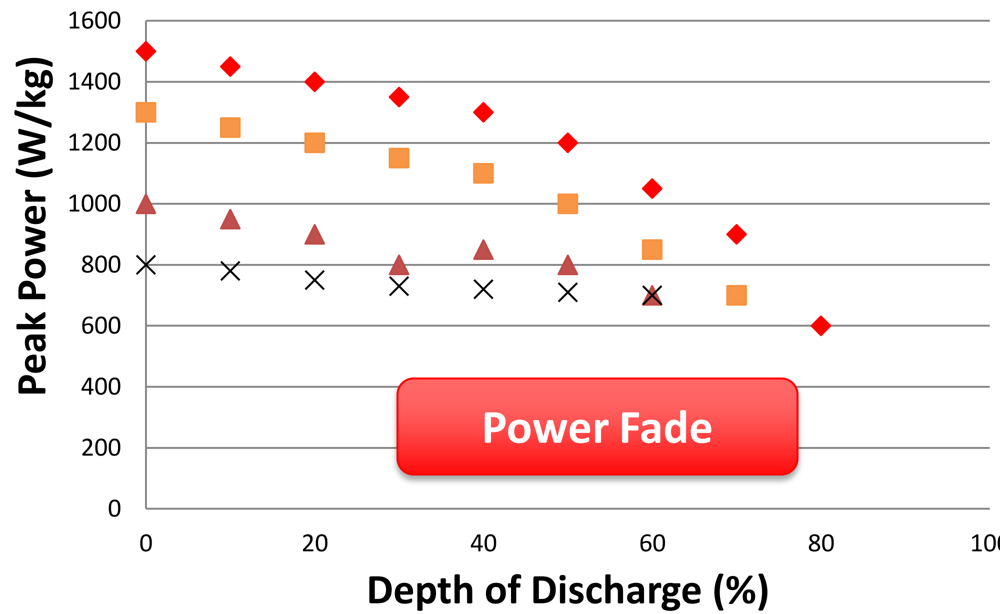
Cycled

Loss of Lithium



Less lithium to move back and forth

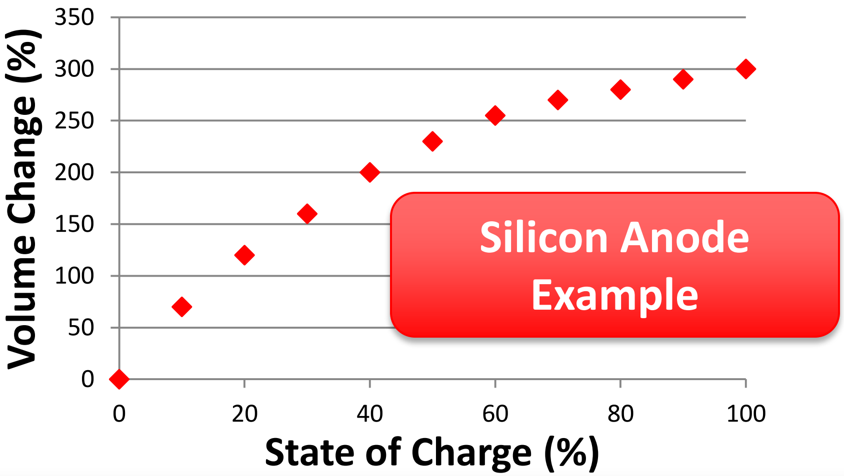
SEI coatings on electrodes slow down movement of lithium

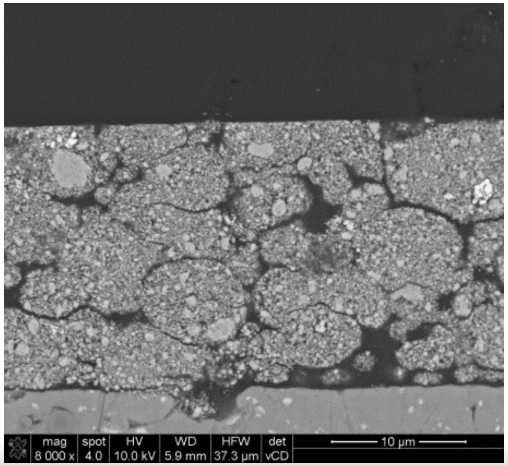


Loss of Active Material

- Electrode adhesion failures
- Particles become "disconnected"
- Particles fracture due to stresses on cycling

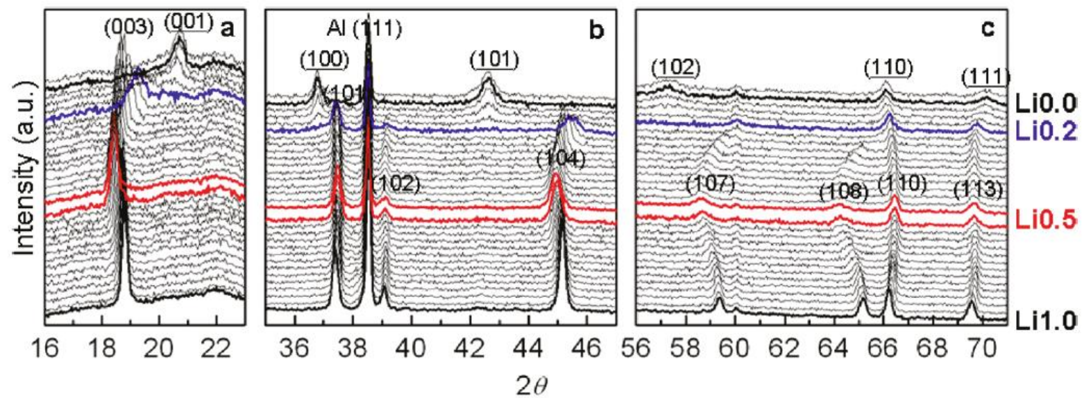
Typical Electrode Composition
- 90-94% active material
- 3-5% conductive additive
- 3-5% polymeric binder



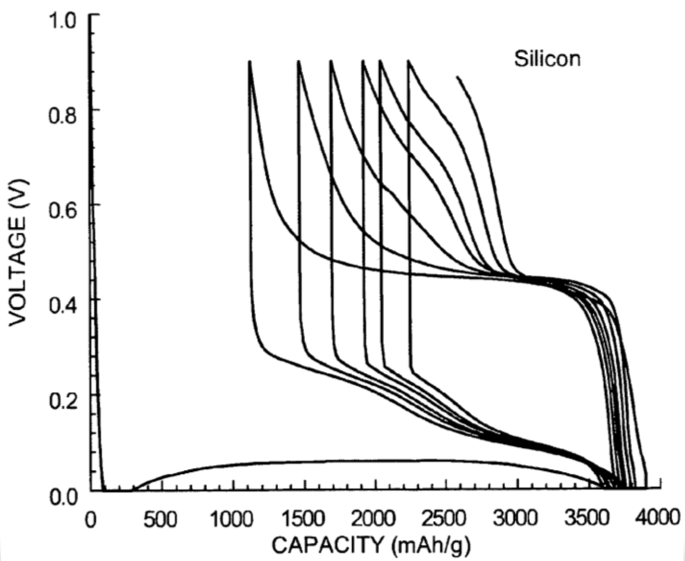


Loss of Active Material

- Cathode phase changes
- Irreversible electrochemistry



Reprinted with permission from *Chem. Mater.*, **2010**, *22* (3), pp 1209–1219. Copyright 2010 American Chemical Society.

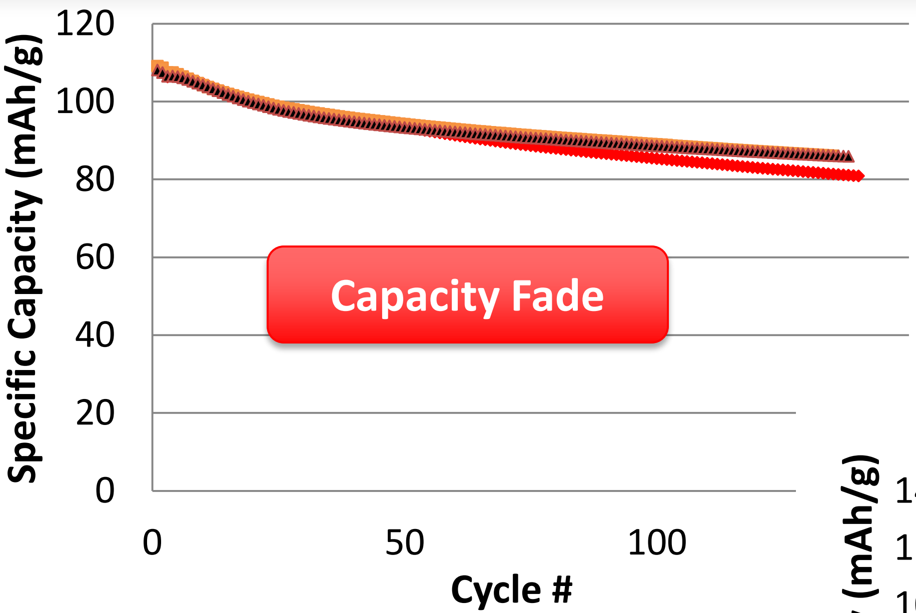


Si + Li goes through a number of phases during lithiation

- Some are not reversible
- Cannot do electrochemistry on that fraction of the material

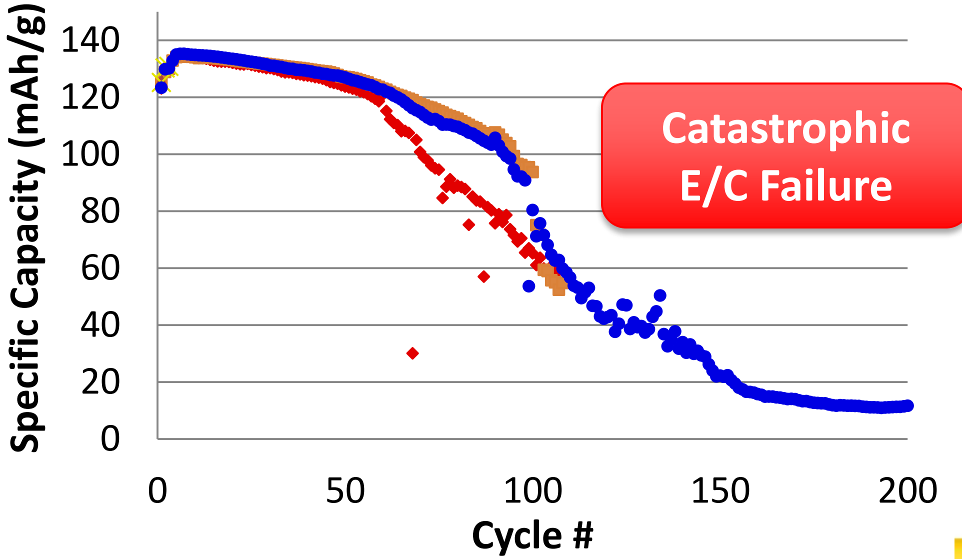
Obrovac, US 2006/0046144A1

Loss of Active Material



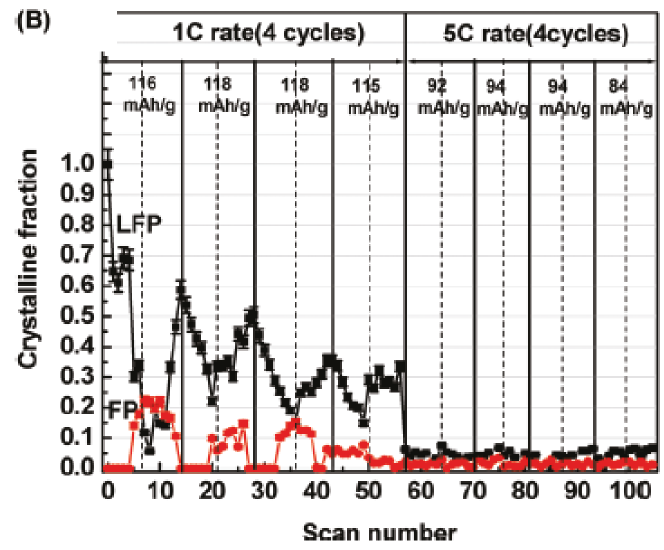
Gradual loss of host due to irreversible changes

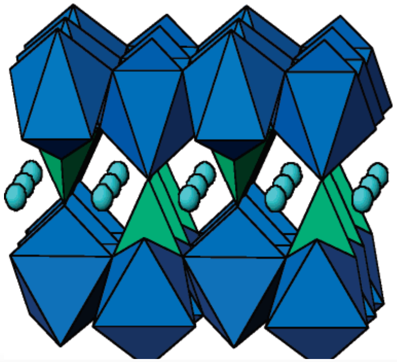
Large amounts of active material lost due to massive structural changes and/or adhesion failure



Inability to Move Charge

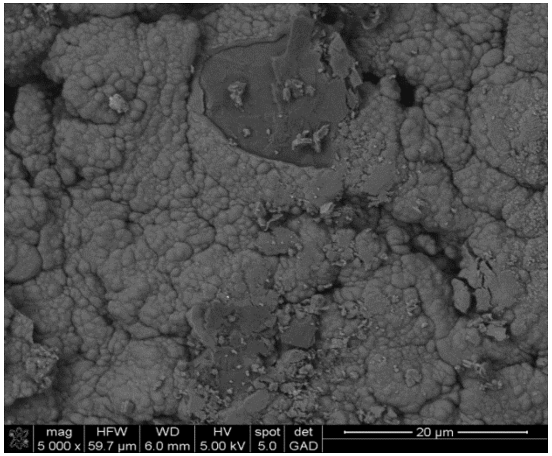
- Cathode structural changes
  - Change lattice parameters
  - Change conductivity
- Blocking of lithium pathways in the cathode
  - Movement of transition metals into Li^+ channels





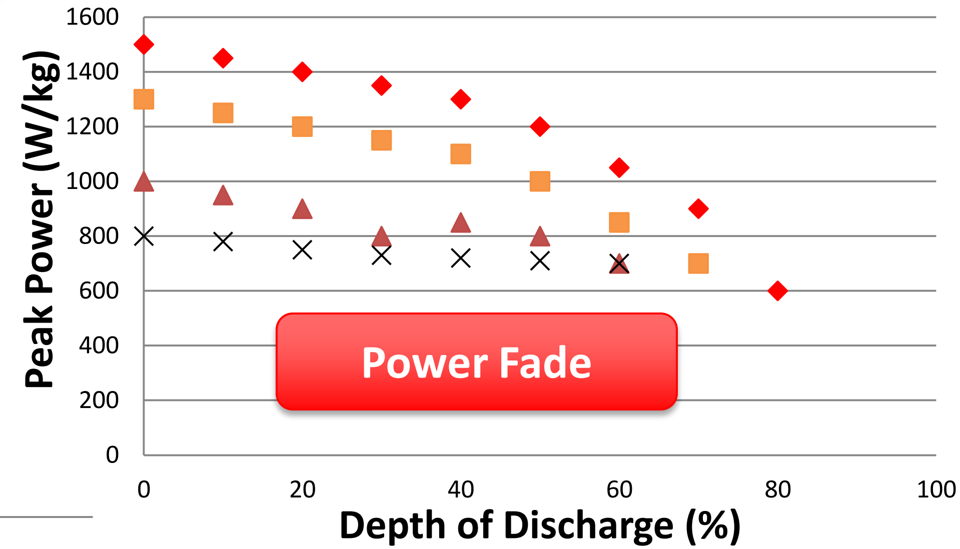
Inability to Move Charge

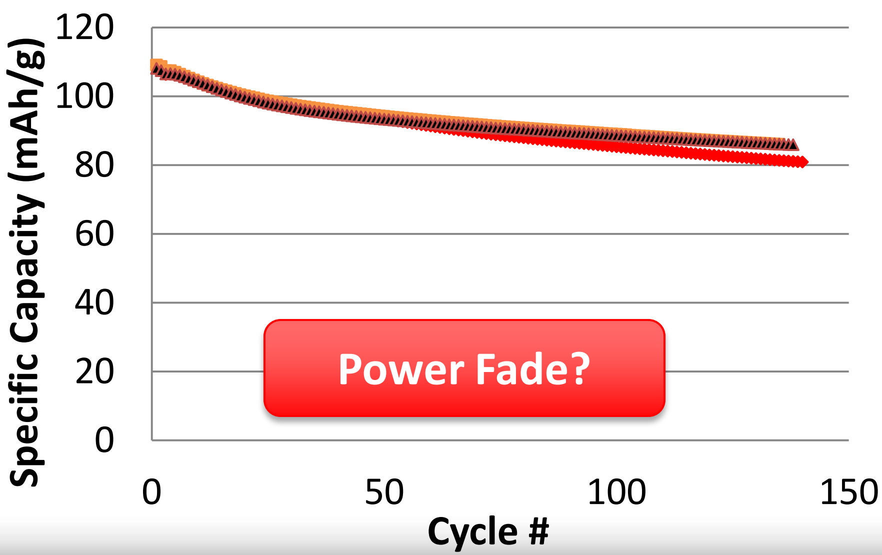
- Barriers to movement of lithium into/out of electrodes
  - Thick SEI layers
  - Poorly conductive SEI layers
- Loss of electrolyte to form gases
  - Cell gets “dry” areas
- HF effects



Inability to Move Charge

SEI coatings on electrodes slow down movement of lithium





Apparent loss of capacity when measured at a specific rate

Catastrophic Failures

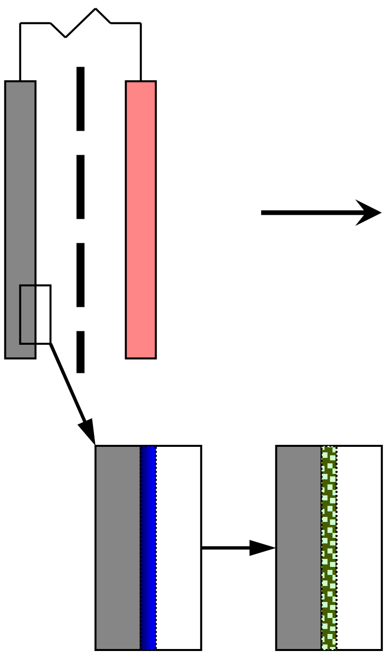
- Shorting
- Separator failure
- Electrolyte shortage
- Abuse situations

Catastrophic Failures

~80°C

Passivating (SEI) layer on anode begins to break down

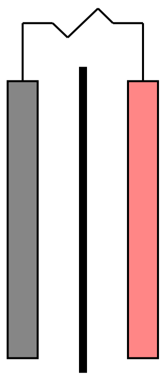
Exothermic reaction begins between anode & electrolyte



~135°C

Heating continues, separator pores close (shut-down)

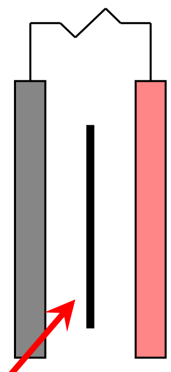
Exothermic reaction at anode continues



~150-180°C

Separator loses mechanical integrity & shrinks

Massive, catastrophic internal short develops causing rapid heating



~180-250°C

Highly exothermic reactions between cathode & electrolyte

Rapid temperature & pressure increase

Battery vents hot, flammable mist

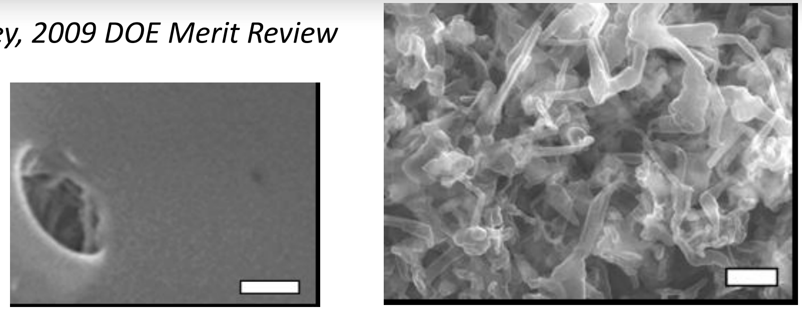
Separator
Poor dimensional stability

Electrolyte
Flammability

Catastrophic Failures

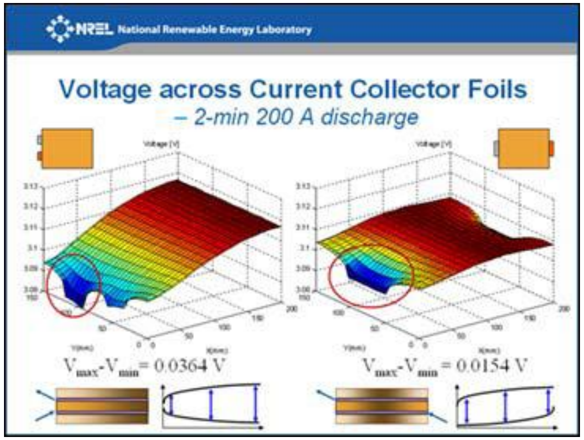
Lithium Dendrites

Vaughey, 2009 DOE Merit Review



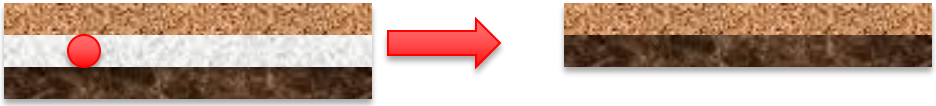
Local Hot Spots

Nonuniform SOC



Pesaran, 2009 DOE Merit Review

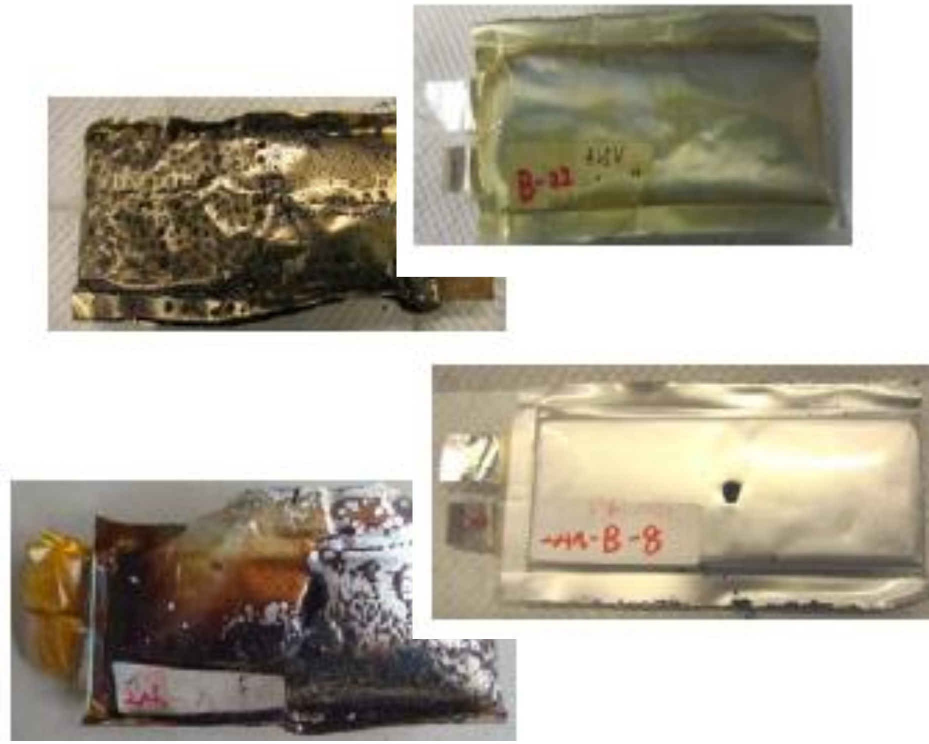
Separator Puncture



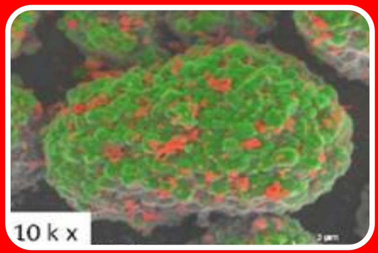
Catastrophic Failures

Abuse

- Thermal
- Puncture
- Crush
- Overcharge

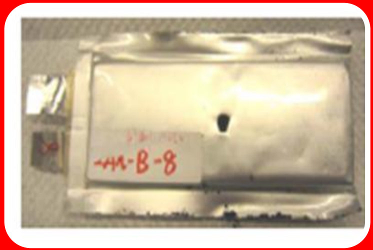


How to Improve Durability?



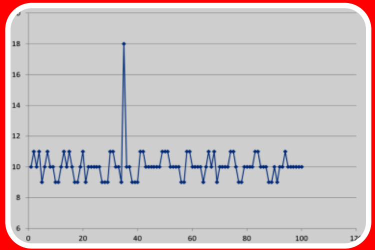
Improved Materials

- Nonflammable electrolyte
- Nonreactive electrolyte
- Structurally stable cathode materials
- Modified active material surfaces
- Thermally stable SEI layers
- Thermally stable separators



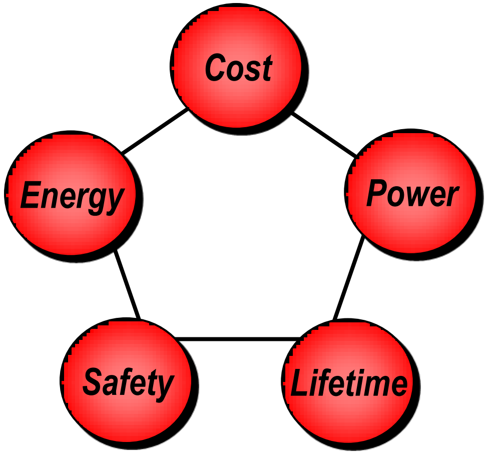
Improved Cell Design

- Proper anode/cathode balancing
- Better thermal management
- Robust packaging
- Lower impedance



Manufacturing Quality

- Defect-free separators
- Elimination of metal particulates
- Electrolyte purity
- Electrode alignment



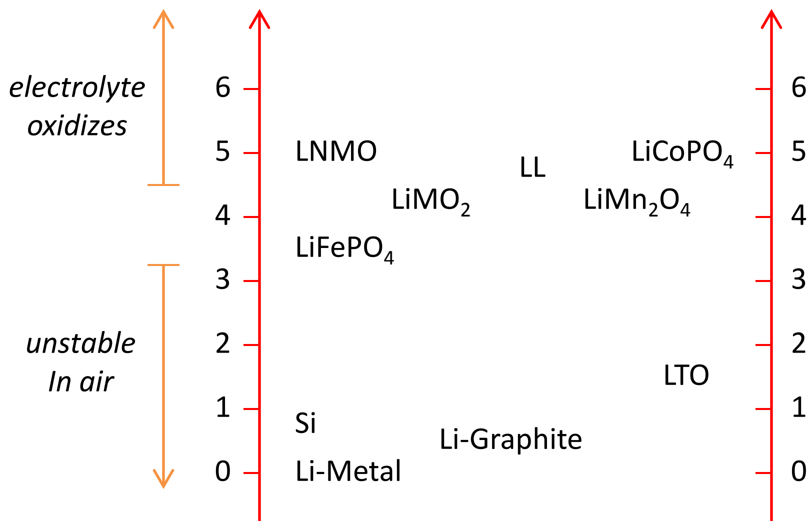
Summary

- There are many failure modes/mechanisms in LIBs
- All can occur simultaneously
- It is difficult to address one mechanism without affecting another
- Improvements in materials, cell design, and manufacturing are necessary

THANK YOU!

Material Choices

Operating Voltages



	Chemistry	Specific Capacity (mAh/g)
LNMO	$LiNi_{0.5}Mn_{1.5}O_4$	140
LL	$x Li_2MnO_3$-$(1-x)LiMO_2$	>200
$LiMO_2$	$LiCoO_2$, Ni, Mn, Al substituted	150
LMO	$LiMn_2O_4$	140
$LiMPO_4$	Fe, Mn, Co	160
LTO	$Li_4Ti_5O_{12}$	140
Li-graphite	LiC_6	370
Si	Li_xSi	>2000

Material density also matters!!!

Today's LIB Materials

All mechanisms can occur depending on many factors (other components, how the cell is built and operated, etc.). I am listing only the most prevalent concerns.

	Loss of Lithium	Loss of Active Material	Inability to Move Charge	Catastrophic Failure
$LiCoO_2$	x	x		X
$LiNi_xMn_yCo_{1-x-y}O_2$	x	x		x
$LiNi_xCo_yAl_{1-x-y}O_2$	x	x		x
$LiMn_2O_4$	X	X	X	
$LiFePO_4$				
Graphite	X		X	X
LTO				

Tomorrow's Materials

	Loss of Lithium	Loss of Active Material	Inability to Move Charge	Catastrophic Failure
$LiNi_{0.5}Mn_{1.5}O_4$	X	x	X	
$x Li_2MnO_3$-$(1-x)$$LiMO_2$	x	X	X	x
$LiMPO_4$ (M = Mn, Co)	X	x	X	
Silicon-Based	X	X	X	