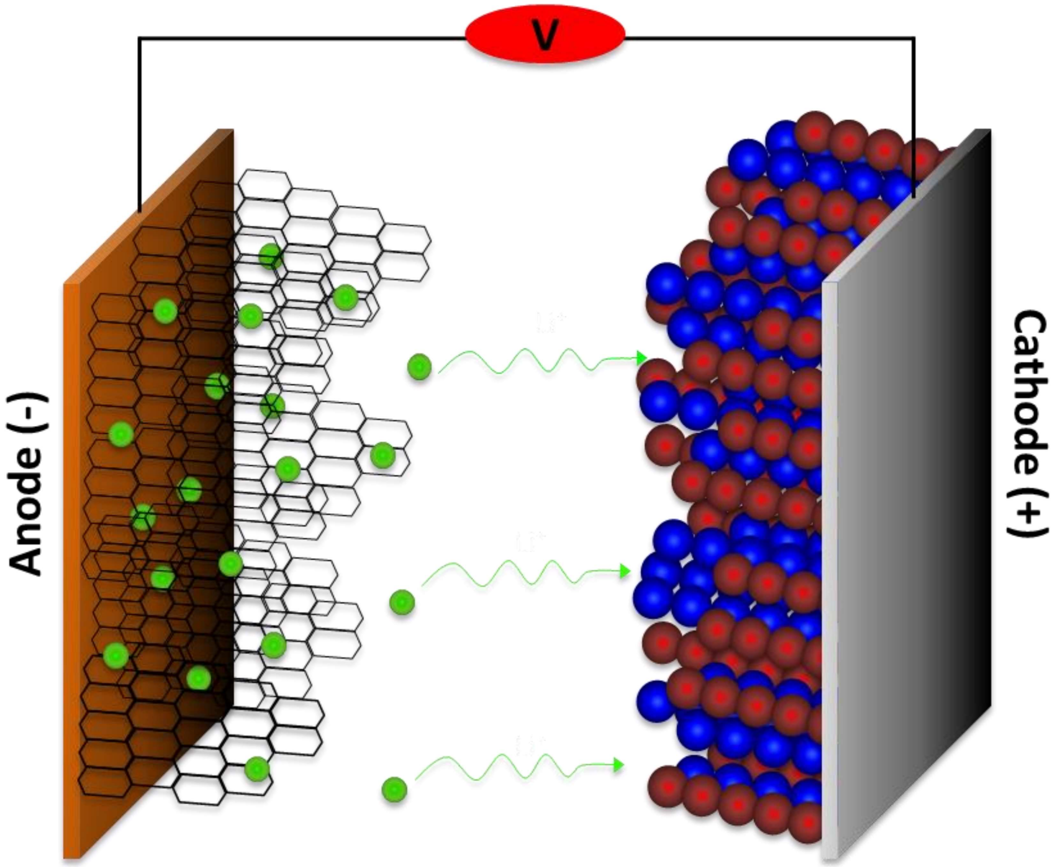
Energy Storage Short Course



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Common Terms

Electrochemical Cell	A device facilitating the generation of electrical energy from chemical reactions or vice versa.
Supercapacitor	A device facilitating the generation of electrical energy from stored charges on/near electrode surfaces. They typically have higher power and higher cycle life, but lower energy and lower charge retention traits than electrochemical cells.
Half-Cell	A full electrochemical cell consists of two half-cells, one for the oxidation reactions (losing electrons to their current collector) and the other for the reduction reactions (gaining electrons from their current collector). A half-cell can also refer to an electrochemical cell in which one electrode is a pure reference electrode, like lithium metal.
Cathode (+)	The positive terminal/electrode/half-cell during use/discharge of a battery. Reduction reactions occur here.
Anode (-)	The negative terminal/electrode/half-cell during use/discharge of a battery. Oxidation reactions occur here.
Battery	A device consisting of one or more electrochemical cells, in which chemical energy is converted into electricity and used as a power source.
Primary Battery	A battery utilizing an irreversible electrochemical reaction and assembled in a fully charged state.
Secondary Battery	A battery utilizing a reversible electrochemical reaction and typically assembled in an uncharged state that requires a specialized formation charge before use.
Formation	An electrochemical process typically involving a few slow charge and discharge cycles, with some associated irreversible losses, that stabilizes secondary batteries for long term use by passivating the electrodes from unwanted and irreversible reactions within their voltage and temperature range of operation.
C-Rate	The current rate during charge/discharge, relative to the overall capacity of the cell, where 1C indicates a current that would fully charge the cell in 1 hour and C/2 would require 2 hours to fully charge.
Cycle Life	The total number of charge/discharge cycles the cell can sustain before its capacity is significantly reduced, with typical standards rated at 80% of the original capacity.
Coulombic Efficiency	Capacity retention for each cycle (discharge capacity divided by the charge capacity).
Energy Efficiency	The difference between Joules in for charge and Joules out for discharge. This is distinct, though related, to coulombic efficiency.
Capacity	The amount of charge a battery or cell is able to store, in Ampere-hours. This relates to the amount of controlled reactions in the system. Depending on cell design, this translates to the maximum amount of energy a given chemistry can store.

Specific Capacity	The capacity relative to the mass of a cell component containing active material. The value most common academically is relative to active material itself, representing the best-cast scenario, but the most commercially relevant value is relative to the overall cell and/or pack weights (Ah/kg)
Power	The amount of work a battery or cell can perform. $P = V * I$
Energy Density	Energy is the amount of time a battery or cell can sustain a given amount of work (Wh). $E = P * t$, which is commonly reported on a Wh/L basis.
Specific Energy	Similar to Energy Density, but in terms of Wh/kg.
Polarization	The degree of charge separation within a cell. Overall charge must be neutral, but as specific charge builds up near an electrode, it acts as a barrier for further charge transport. As power demands increase, polarization increases.
Active Material (AM)	The electrode component(s) responsible for storing energy. Active materials with high voltages vs. Li/Li^+ are cathodes, while those with low voltages vs. Li/Li^+ are anodes.
Intercalation (AM)	An intercalating active material is one that allows reversible insertion of ions between lattice sites. Most traditional Li^+ systems use intercalation mechanisms at both electrodes.
Conversion (AM)	Also called alloying. A conversion active material is one that forms new compounds at specific stoichiometries with the captured Li. This is associated with large structural changes, including up to 300% volume changes, that are a source of significant mechanical limitations. However, this class of active material has roughly an order of magnitude increase in Li absorption capacity.
Conductive Additive	The electrode component(s) responsible for providing electronic conductivity to the matrix containing active material, intimately associated with the binder.
Binder	The electrode component(s) responsible for binding all the electrode components to each other and to the current collector. This is usually a high molecular weight linear chain polymer.
Current Collector	The substrate for each electrode, serving as a mechanical backbone and a conduit for electron transport between the two half-cells of an electrochemical cell. Aluminum is most common for cathodes, copper for anodes.
Electrolyte	The medium through which ions transport between half-cells. Electrolytes are most commonly a combination of solvent(s) and the dissociated ions from a salt, such as 1 M $LiPF_6$ in 3/7 EC/EMC (ethylene carbonate/ethyl methyl carbonate).
SEI	Solid Electrolyte Interphase: A layer of electrolyte decomposition byproducts that grows on the anode surfaces and, when properly formed, facilitates Li^+ transport during charge/discharge, while limiting further SEI growth upon cycling.

Lithium Chemistries (-)

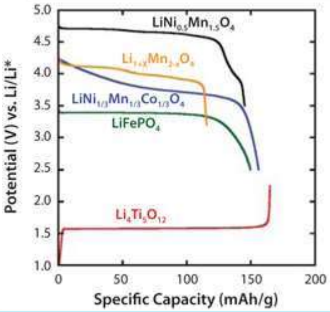
Anodes

Active anode material	Theoretical capacity ($mAh\ g^{-1}$) [Reference]	Advantages	Common issues
Insertion/de-insertion materials			
A. Carbonaceous a. Hard carbons b. CNTS c. Graphene	200-600 [83–85] 1116 [91–94] 780/1116 [45]	➢ Good working potential ➢ Low cost ➢ Good safety	❖ Low coulombic efficiency ❖ High voltage hysteresis ❖ High irreversible capacity
B. Titanium oxides a. $LiTi_4O_5$ b. TiO_2	175 [121] 330 [121]	➢ Extreme safety ➢ Good cycle life ➢ Low cost ➢ High power capability	❖ Very low capacity ❖ Low energy density
Alloy/de-alloy materials			
a. Silicon b. Germanium c. Tin d. Antimony e. Tin oxide f. SiO	4212 [156] 1624 [191,192] 993 [61] 660 [150] 790 [52] 1600 [47]	➢ Higher specific capacities ➢ High energy density ➢ Good safety	❖ Large irreversible capacity ❖ Huge capacity fading ❖ Poor cycling
Conversion materials			
a. Metal oxides(Fe_2O_3, Fe_3O_4, CoO, Co_3O_4, Mn_xO_y, Cu_2O/CuO, NiO, Cr_2O_3, RuO_2, MoO_2/MoO_3 etc.)	500–1200 [51–53, 56]	➢ High capacity ➢ High energy ➢ Low cost ➢ Environmentally compatibility	❖ Low coulombic efficiency ❖ Unstable SEI formation ❖ Large potential hysteresis ❖ Poor cycle life
b. Metal phoshides/sulfides/nitrides (MXy; M = Fe, Mn, Ni, Cu, Co etc. and X = P, S, N)	500–1800 [54–56]	➢ High specific capacity ➢ Low operation potential and Low polarization than counter oxides	❖ Poor capacity retention ❖ Short cycle life ❖ High cost of production

Subrahmanyam Goriparti, Ermanno Miele, Francesco De Angelis, Enzo Di Fabrizio, Remo Proietti Zaccaria, Claudio Capiglia, **Review on recent progress of nanostructured anode materials for Li-ion batteries.** Journal of Power Sources, Volume 257, 2014, 421–443

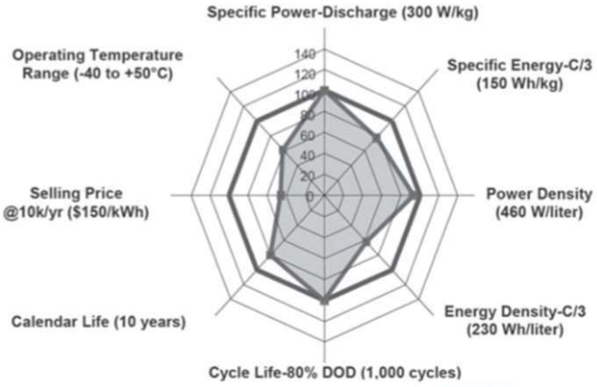
Lithium-Ion Chemistries (+)

Material	Structure	Potential versus Li/Li^+, average V	Specific capacity, mAh/g	Specific energy, Wh/kg
$LiCoO_2$	Layered	3.9	140	546
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	Layered	3.8	180–200	680–760
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC)	Layered	3.8	160–170	610–650
$LiMn_2O_4$ and variants (LMO)	Spinel	4.1	100–120	410–492
$LiFePO_4$ (LFP)	Olivine	3.45	150–170	518–587

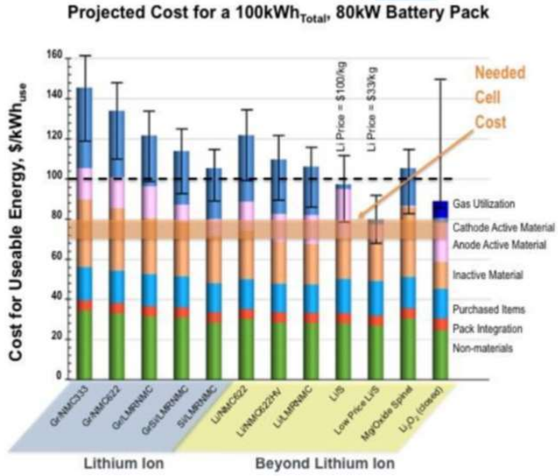


Material	Advantages	Disadvantages
LMO	Low Cost Excellent High Rate Performance High Operating Voltages	Mn Solubility affects Cycle Life Low Capacity
NCA	High Capacity High Voltage Excellent High Rate Performance	High Cost
NMC	High Capacity Higher Operating Voltages Moderate Safety	High Cost
LFP	Low Cost Good High Rate Performance Excellent Safety	Low Operating Voltage Low Capacity

Battery Performance Targets



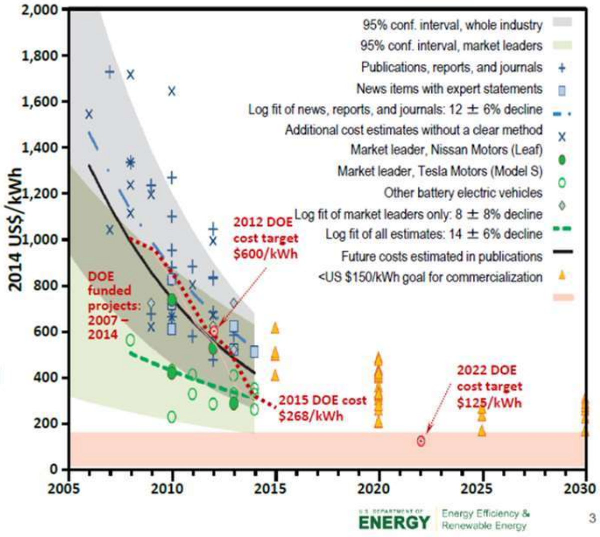
‘Radar’ Performance Chart from June 2016 DOE Roadmap
Specific Energy Targets now at 200+ Wh/kg



Projections Sourced from EESTT Roadmap September 2017

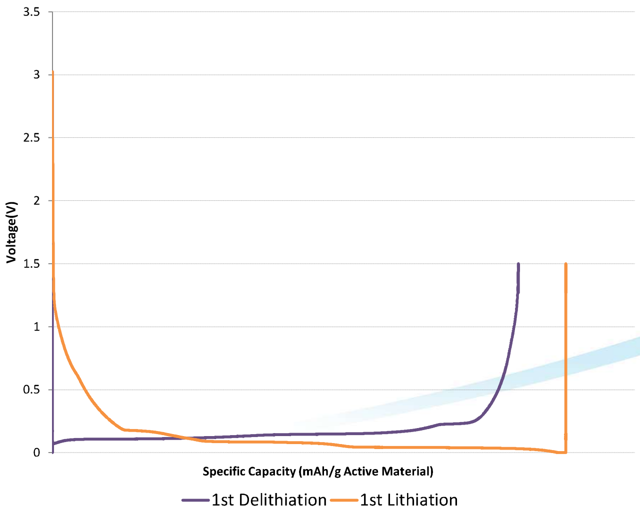
June 2016 DOE Views / Forecast

- EDV 8% annual cost reductions for major manufacturers
- Battery production doubling globally every year since 2010
- Economies of scale leading towards $200/kWh
- Combined with new chemistries, ICE parity could be reached in 10 years



Half Cell Testing – 1^{st} Cycle

Graphite Half Cell 1^{st} Cycle

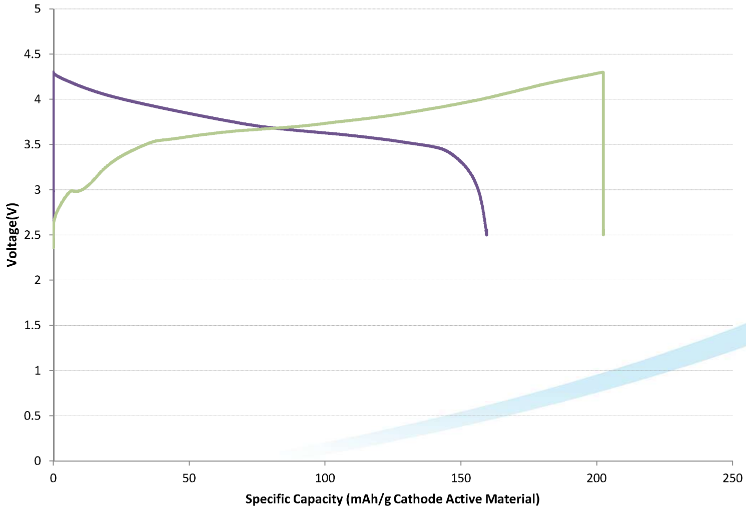


OCV: 3.0 V

Graphite – Lithium Metal Cell

- Expect voltage differential (no lithium in graphite)
  - Positive due to position of Li in the cell
- 1^{st} Lithiation: lithium moving into the graphite anode
- 1^{st} Delithiation: lithium moving out of the graphite
  - Loss in capacity (irreversible loss) due to interaction of Li, solvents, and salts
    - Chemical reaction referred to as SEI formation
    - Adds to cell stability later on
      - Prevents unwanted side reactions and further electrolyte degradation
      - Improved Li^+ insertion kinetics

Full Cell Testing – 1^{st} Cycle

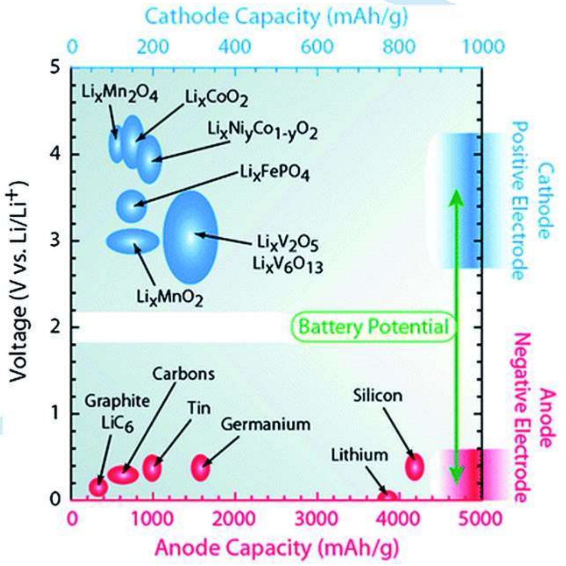


Cathode: LiNiMnCo (NMC)
Anode: Graphite
*Slightly more Anode than Cathode so the cell is Cathode-limited

1^{st} Charge Capacity: 3.2 mAh
(202 mAh/g Cathode Active Material)
1^{st} Discharge Capacity: 2.5 mAh
(159 mAh/g Cathode Active Material)

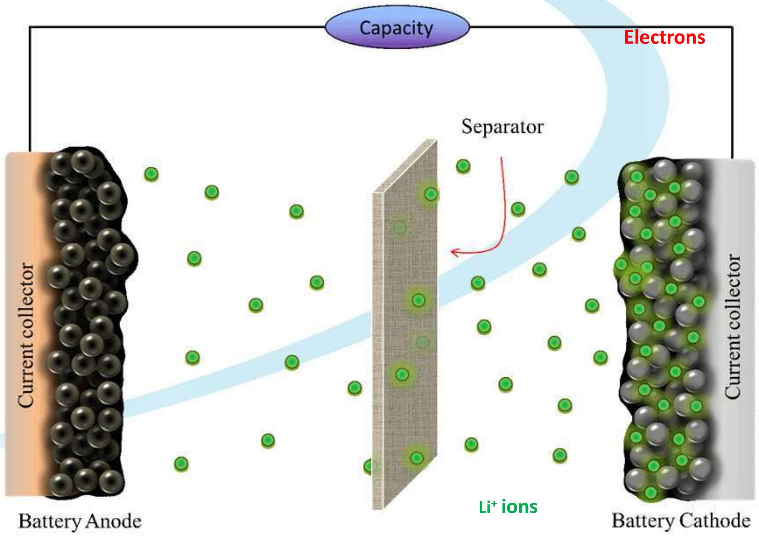
Mechanisms of Operations

- Potential (voltage)
  - The amount of potential energy between the exchange of charge in a reaction
- Charge Transfer (**Li ↔ Li^+ + e^-**)
  - Versions exist at every interface and tend to be the fundamental rate limiting step
- Diffusion
- Intercalation
  - The reversible insertion of Li^+ between the lattice sites of the active materials
  - **$6C + Li^+ + e^- \leftrightarrow LiC_6 \Rightarrow 372$ mAh/g**
- Conversion / Alloying
  - The reversible generation of a new structure incorporating the reactants
  - **$5Si + 22Li^+ + 22e^- \leftrightarrow Li_{22}Si_5 \Rightarrow 4200$ mAh/g**

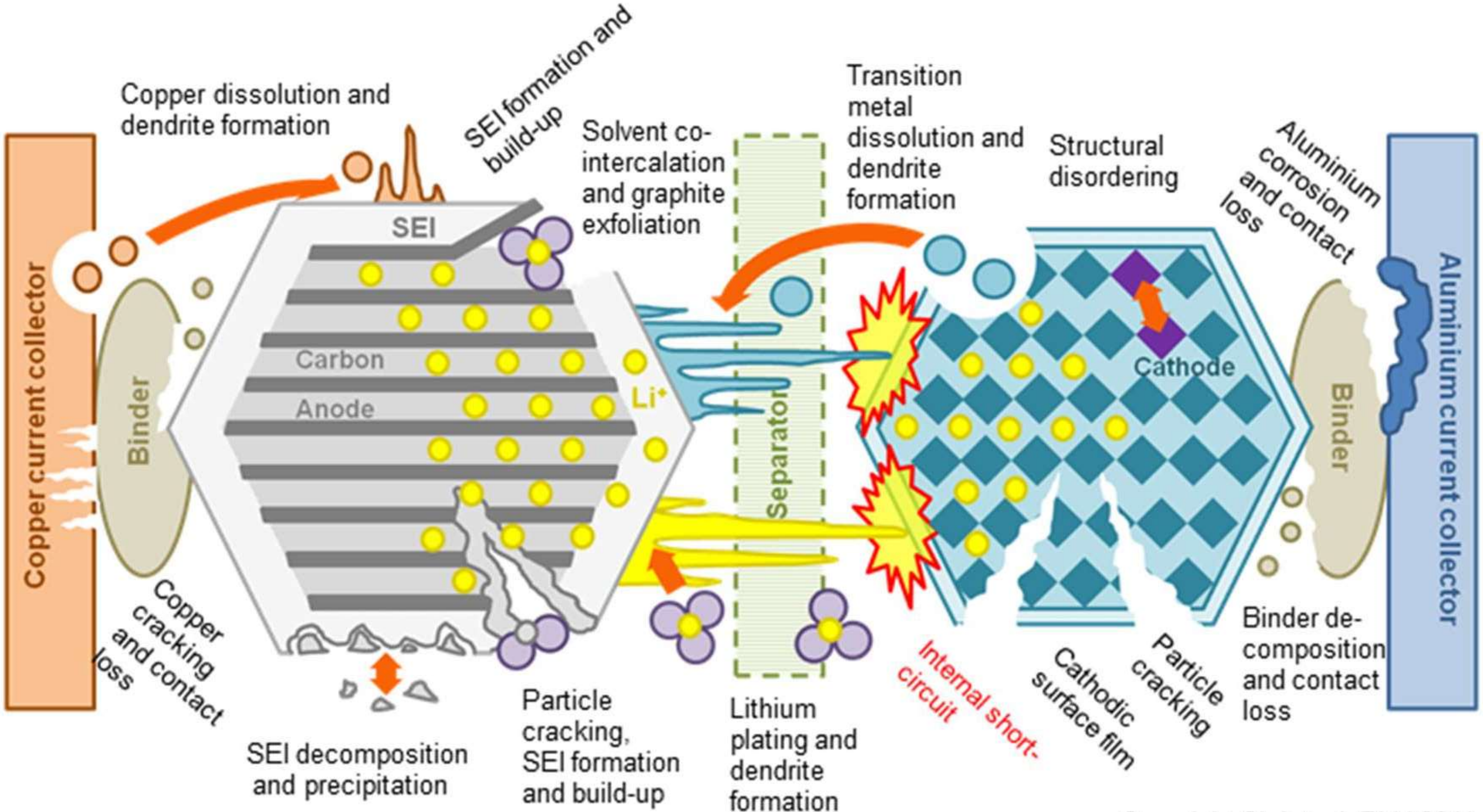


Mechanisms of Operations

- Electron conduction
  - Current collector & circuit
  - Conducting matrix around active material
  - Active material
- Li^+ conduction / charge transfer / polarization
  - Separator
  - Electrolyte
  - Electrode porosity
  - Active material
  - SEI (Solid Electrolyte Interphase)
- Other concerns
  - Volume change due to lithiation
  - Irreversible reactions
  - Coulombic vs. Energy efficiency



Lithium Battery Concerns



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Battery Pack Event-Response Flow

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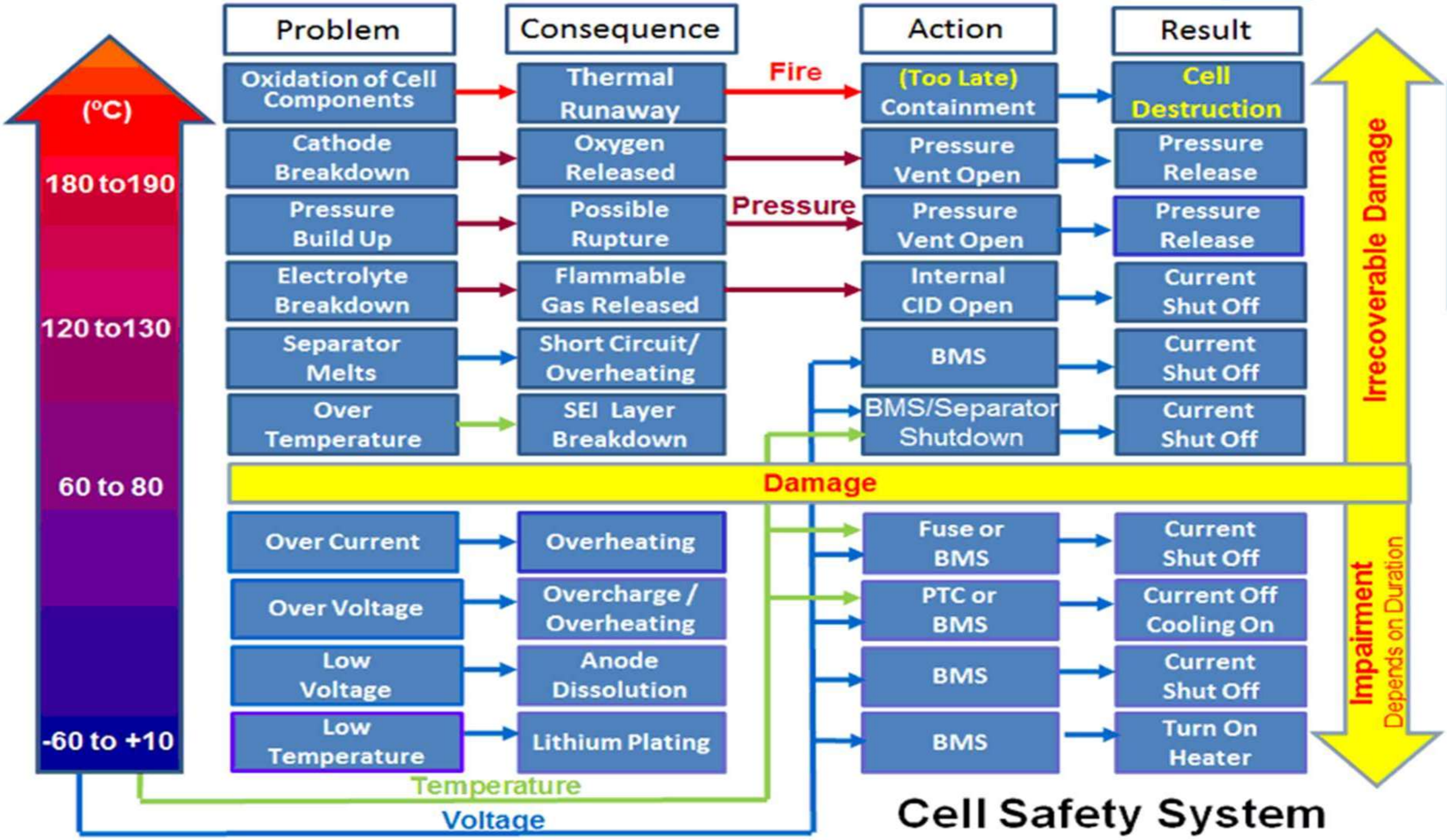

Problem	Consequence	Action	Result
Oxidation of Cell Components	Thermal Runaway	(Too Late) Containment	Cell Destruction
Cathode Breakdown	Oxygen Released	Pressure Vent Open	Pressure Release
Pressure Build Up	Possible Rupture	Pressure Vent Open	Pressure Release
Electrolyte Breakdown	Flammable Gas Released	Internal CID Open	Current Shut Off
Separator Melts	Short Circuit/ Overheating	BMS	Current Shut Off
Over Temperature	SEI Layer Breakdown	BMS/Separator Shutdown	Current Shut Off
Over Current	Overheating	Fuse or BMS	Current Shut Off
Over Voltage	Overcharge / Overheating	PTC or BMS	Current Off Cooling On
Low Voltage	Anode Dissolution	BMS	Current Shut Off
Low Temperature	Lithium Plating	BMS	Turn On Heater

Cell Safety System

Project	BIC Energy Storage Short Course
Description / Notes	Generic Cell Build Example Overview / Description

FUNDAMENTAL ELECTRODE PROPERTIES

Cathode (Positive Electrode)		**Anode (Negative Electrode)**	
Active Material 1	**NMC523 - Targray #**	Active Material 1	**Superior Graphite SLC1520T**
Active Material 2		Active Material 2	
Substrate	**Al**	Substrate	**Cu**
AM 1 wt %	**94**	AM 1 wt %	**92**
AM 2 wt %	**0**	AM 2 wt %	**0**
Conductor 1 wt %	**2.5**	Conductor 1 wt %	**3**
Conductor 2 wt %	**0**	Conductor 2 wt %	**0**
Binder 1 wt %	**3.5**	Binder 1 wt %	**5**
Binder 2 wt %	**0**	Binder 2 wt %	**0**
Electrode Theoreitcal Density g/cm^3	4.44	Electrode Theoretical Density g/cm^3	2.14
AM 1 Initial Capacity (Ah/g)	0.185	AM 1 Initial Capacity (Ah/g)	0.400
AM 1 Reversible Cap. (Ah/g)	0.160	AM 1 Reversible Cap. (Ah/g)	0.355
AM 2 Initial Capacity (Ah/g)		AM 2 Initial Capacity (Ah/g)	
AM 2 Reversible Cap (Ah/g)		AM 2 Reversible Cap (Ah/g)	
Total (1+2) Active Material wt. %	94	Total (1+2) Active Material wt. %	92
AM(1,2) Composite Initial Cap (Ah/g)	0.185	AM(1,2) Composite Initial Cap (Ah/g)	0.400
AM(1,2) Composite Reversible Cap (Ah/g)	0.160	AM(1,2) Composite Reversible Cap (Ah/g)	0.355
Target Weight Loading mg/cm^2	20.0	Target Weight Loading mg/cm^2	10.10
Target Porosity (%)	25	Target Porosity (%)	25
Target Single Side Area Capacity (mAh/cm^2)	3.01	Target Single Side Area Capacity (mAh/cm^2)	3.30
Target SS Cathode Thickness [no foil] (µm)	60	Target SS Anode Thickness [no foil] (µm)	63
Target DS Cathode Thickness [with foil] (µm)	135.21	Target DS Anode Thickness [with foil] (µm)	137.72
Cathode Slurry Lot #		Anode Slurry Lot #	181016-
Actual Weight Loading mg/cm^2		Actual Weight Loading mg/cm^2	
Actual Single Side Area Capacity (mAh/cm^2)		Actual Single Side Area Capacity (mAh/cm^2)	
Actual Porosity (%)		Actual Porosity (%)	
Cathode DS Thickness [with foil] (µm)		Anode DS Thickness [with foil] (µm)	

AREAL N:P
1.10

Cathode Density Calculations

Positive	**Density**	**Wt, g**	**Vol, cm^3**	**Volume%**
AM 1	4.9	94	19.18	**85.11**
AM 2		0		
Cond 1	1.8	2.5	1.39	**6.16**
Cond 2		0		
Binder 1	1.78	3.5	1.97	**8.72**
Binder 2		0		
	Total	100	22.54	100.00

Please note *, volumetric-based electrode design is in more agreement with fundamental functionality than mass-based design*

Anode Density Calculations

Negative	**Density**	**Wt, g**	**Vol, cm^3**	**Volume%**
AM 1	2.18	92	42.20	**90.41**
AM 2		0		
Cond 1	1.8	3	1.67	**3.57**
Cond 2		0		
Binder 1	1.78	5	2.81	**6.02**
Binder 2		0		
	Total	100	46.68	100.00

COIN CELL FABRICATION

Positive Electrode			
Reversible Capacity (Ah)	**0.0053**	**Reversible Capacity (mAh)**	**5.32**
Coated area, cm^2	1.77	Weight AM, g	0.0332
		Irreversible Cap, Ah	0.0008

Negative Electrode			
Reversible Capacity (Ah)	**0.0066**	**Reversible Capacity (mAh)**	6.63
Coated area, cm^2	2.01	Weight AM, g	0.0187
		Irreversible Cap, Ah	0.0008

N/P Ratio:	**1.25**	**--> Note, this N:P counts total area and is less significant than pure areal N:P**

Mixing sheet	Slurry Lot#:	**181016-**	**Project**	BIC Energy Storage Short Course
Date Recipe Created	8/27/2018	(date & run of year,month,day-#)	**Notes**	Students to be broken up into 2 groups, starting with the same 1st step, but deciding their own order of operations from there: (Group 1) Mixes with C65 conductive additive & (Group 2) Mixes with Ketjen Black conductive additve

Slurry Composition

	Material	Weight (g)	Total wt %	Wt % Of Solids	Actual Weight
Active 1:	Superior Graphite	20	35.8	92.00	
Active 2:		0.0000	0.0	0.00	
Carbon diluent 1:	Super C65 OR KB	0.6522	1.2	3.00	
Carbon diluent 2:		0.0000	0.0	0.00	
Binder 1:	10% Kynar HSV900	10.8696	1.9	5.00	
Binder 2:		0.0000	0.0	0	
Other Additive:	Oxalic Acid (sublimes)	0.1087		0.5000	
Initial solvent	NMP (from binder)	9.78			0
Added solvent	**NMP to Add:**	24.22			
total solvent	NMP	34.0022	60.9		0
Dry Room Conditions	total weight (g)	55.9		100.5	0.0
Temp (F) -> Target: 67	solids weight (g)	21.7			0.0
	% solid	**39.00**			#DIV/0!
Dew point (C) -> Target -45	% liquid	60.9			#DIV/0!
	total volume (mL)	43.2			0.0

Order of Operations & Mixing Notes

STEP 1: (a.) Start with 50 ml PP beaker + 10.87g of PVDF-NMP Solution

(b.) Add 24.22g NMP

(c.) Add 0.11g Oxalix Acid

STEP 2: Dissolve / homogenize solution @ 300 RPM with JM-Blade & Overhead Stir

STEP 3:

STEP 4:

STEP 5:

Relevant Standards in Energy Storage

UN 38.3 – Cell level and module level. Required for commercial shipments of Li-Ion chemistry

This is commonly called a self-certification because it is not required that the tests be observed by a regulatory body. It is only necessary, per 49CFR, that documentation of adherence be made available upon request. UN38.3 tests are not performance tests; they are the minimum tests to determine whether a battery can safely be shipped. The tests called out are Altitude Simulation, Thermal Test, Vibration, Shock, External Short Circuit, Impact, Overcharge, Forced Discharge.

UL 1642 – Cell and portable battery level. Safety testing for Li-Ion chemistry

In addition to design reviews and regular manufacturing audits, testing to this standard is required for small batteries and cells to obtain a UL watermark. The tests included in this standard are Short Circuit, Abnormal Charging, Forced Discharge, Crush, Impact, Shock, Vibration, Heating, Temperature Cycling, Low Pressure, and Projectile. Some tests are aligned with UN38.3, but often have stricter requirements.

IEC 62133 – Cell and portable battery level. Safety testing for Li-Ion chemistry

Originally (before 2011) this was Standard was like an international version of UL1642. In fact, if a manufacturer had obtained a UL1642 certification, a certified body could grant certification to this standard. Now to conform to IEC62133, cells and batteries must be tested to the entire standard. The included tests in this standard are Continuous Charge, Case Stress, External Short-Circuit, Free Fall, Thermal Abuse, Crush, Overcharge, Forced Discharge, Mechanical Vibration, Mechanical Shock, Forced Internal Short (country specific), and Internal AC Resistance.

UL 1973 – Stationary, vehicle auxiliary power, and electric rail applications. Safety testing for all chemistry electrochemical batteries

Most often used for stationary grid applications, this standard applies to modules and racks that connect to the grid. Due to multiple fires being caused by thermal runaway of batteries, this standard has been updated to provide more rigorous testing at the cell level. Testing cells to UL1642 above is generally the first step in the process that one follows to certify an entire system, but in the case of UL1973, cells do not have to be UL1642 certified if they are tested to UL1973 Appendix E. The reasoning is that UL1973 Appendix E includes UL1642 testing, as well as several more pointed tests to the grid application.

UL 9540 – Energy Storage System (ESS) level. Safety testing for system level ESS, energy storage technology agnostic.

This is the final step to having a grid-connected ESS certified by UL. All applicable components must be certified to appropriate standards, and the entire system must undergo design review and rigorous testing. It is worth noting that this does not have to be a battery energy storage system. For example, a flywheel energy storage system can be certified to this standard.

UL 2271 – Battery pack level. Safety testing for light electric vehicles

This standard is used to certify “not roadworthy” vehicles. Packs that go into golf carts, electric bikes, etc. are applicable to this standard.

UL 2580 – Battery pack level. Safety testing for electric vehicles

Vehicles that command a large amount of power are applicable to this standard. Fork trucks, Electric Vehicles, etc. fall under this umbrella.