Li and Li-ion Batteries Basics, Safety, Future

North American Hazardous Materials Management Association

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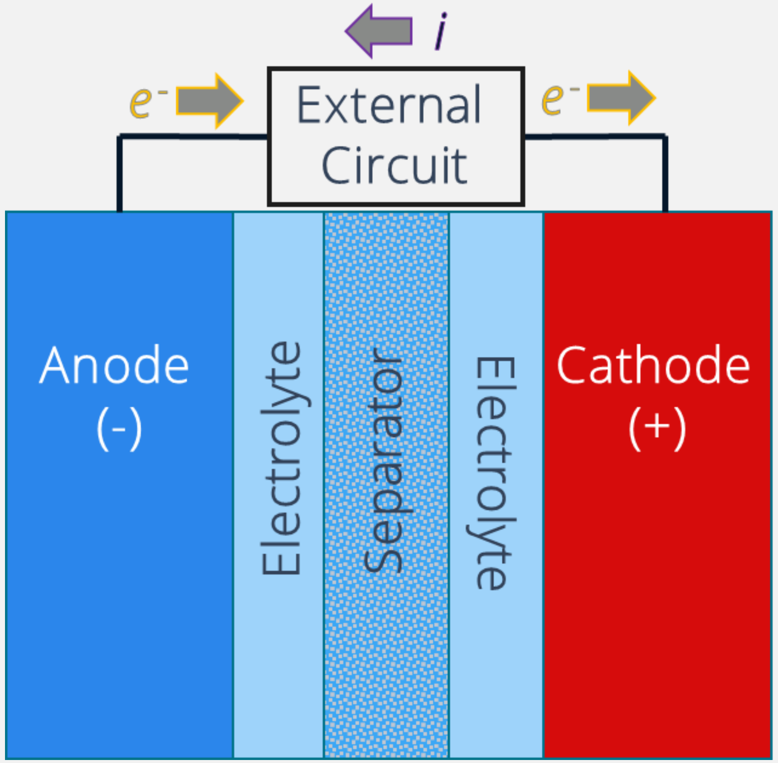
Power Sources R&D

Nov 30th 2022

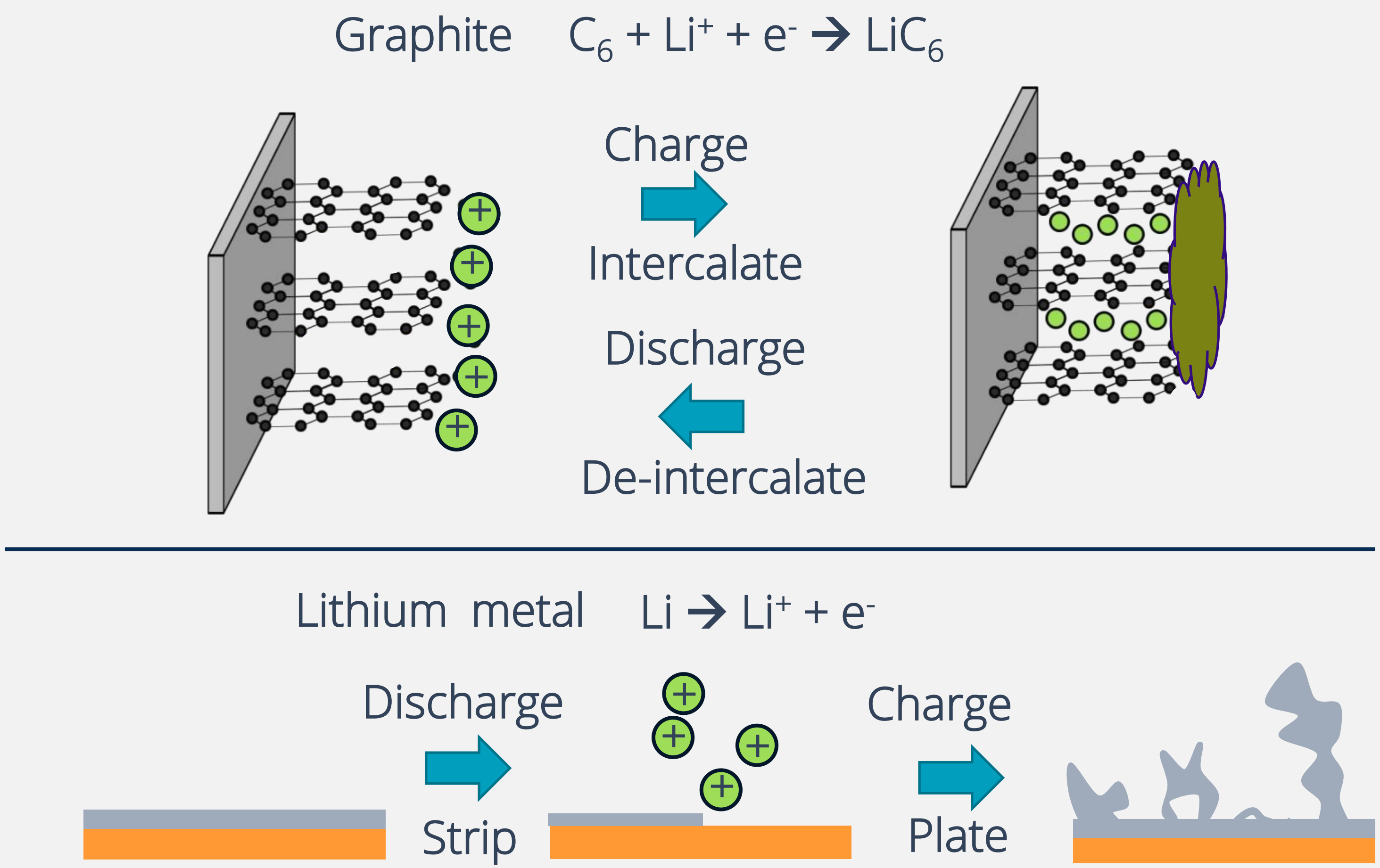
Li-ion vs Li

Knowing the identity of the anode will tell if the battery is Li vs Li-ion



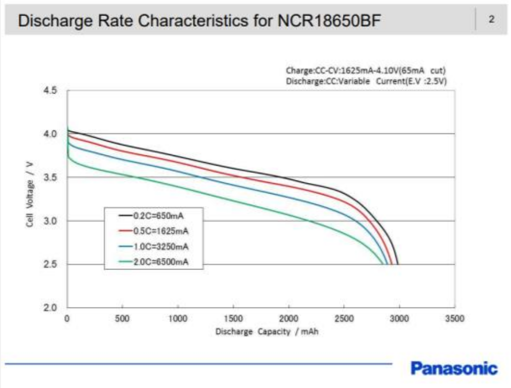
Current → **large = fast ; small = slow**

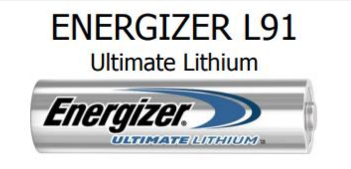
Voltage → **large = more force ; small less force**

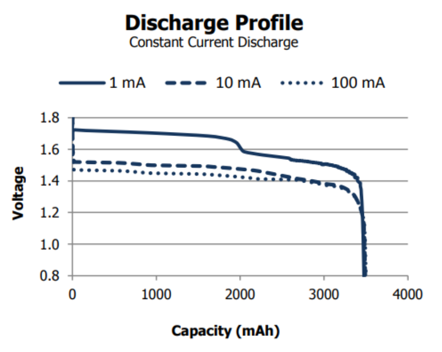


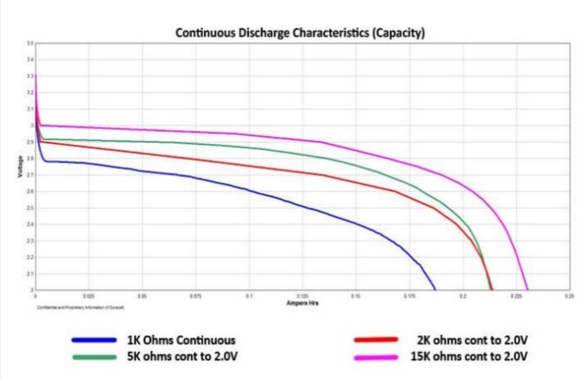
Li-ion vs Li

Knowing the identity rechargeability of a battery can inform if cell is Li vs Li-ion (some limited exceptions)







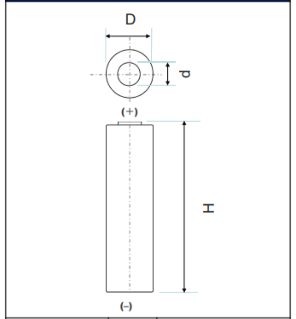


Specifications

Rated capacity[1]		3200mAh	2835mAh
Capacity[2]	Minimum	3250mAh	2875mAh
	Typical	3350mAh	2965mAh
Nominal voltage		3.6V	
Charging	Method	CC-CV	
	Voltage	4.20V	4.10V
	Current	Std. 0.5CA	
Weight (max.) Without tube		46.5g	
Temperature	Charge	10 to +45° C	
	Discharge	-20 to +60° C	
	Storage	-20 to +50° C	
Energy density[3]	Volumetric	677 Wh/l	600 Wh/l
	Gravimetric	248 Wh/kg	219 Wh/kg

[1] At 20° C [2] At 25° C
[3] Energy density is calculated using bare cell dimensions (without tube).

Dimensions



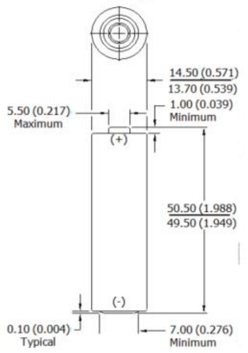
Without tube	H	Max. 65.10mm
	D	Max. 18.24mm
	d	Max. 6.6mm

When designing a pack, refer to the cell's mechanical drawing for precise dimensions.

Panasonic

ENERGIZER L91
Ultimate Lithium

Industry Standard Dimensions
mm (inches)

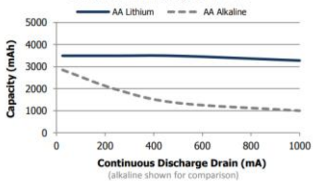


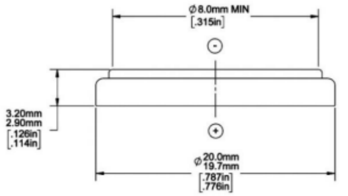
Specifications AA

Classification: "Cylindrical Primary Lithium"
Chemical System: Lithium/Iron Disulfide (Li/FeS_2)
Designation: ANSI 15-LF, IEC-FR14505 (FR6)
Nominal Voltage: 1.5 Volts
Sizing Compatibility: E91 NH15 1215
Storage Temp: -40°C to 60°C (-40°F to 140°F)
Operating Temp: -40°C to 60°C (-40°F to 140°F)*
Typical Volume: 8.0 cubic centimeters (0.49 cubic inch)
Max Discharge: (single battery only) 2.5 amps continuous; 4.0 amps pulse (2 sec on / 8 sec off)
Typical IR: 120 to 240 milliohms (depending on method)
Shelf Life: 20 years at 21°C
More Details: On-Line Catalog-Application Manual (Li/FeS_2)
Shipping: Please refer to PSDS Document
Certifications:

*All data shown tested at 21°C unless otherwise stated.

Milliamp-Hours Capacity
Constant Current Discharge to 0.8 Volts





Electrical characteristics

- Nominal capacity (15kOhm Cont. 2.0V cut-off) 225 mAh
- Open circuit voltage (at + 20 °C) 3.0 V
- Standard Continuous Discharge Current 0.2 mA
- Maximum Continuous Discharge Current 3 mA
- Maximum Pulse Discharge Current at 1 sec 10 mA
- Nominal Energy 657 mWh
- AC Impedance @ 1kHz 20 Ohm

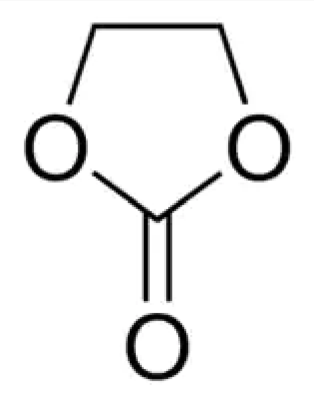
Batteries are Inherently Dangerous (like any energy storage)

Combustion reaction

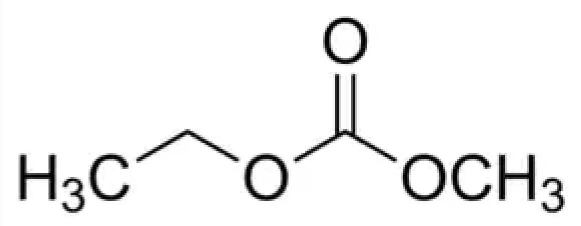
$$C_xH_y + O_2 \rightarrow (y/2)H_2O + (x)CO_2$$

Common Li-ion battery solvents are volatile and flammable

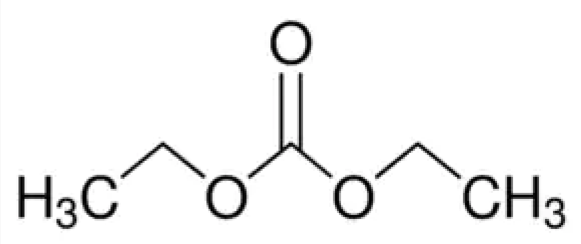
Ethylene carbonate



Ethyl methyl carbonate



Diethyl carbonate



Common Li/Li-ion battery cathode materials

- Lithium Iron Phosphate (LFP)
  $LiFePO_4$
- Lithium Nickel Manganese Cobalt Oxide (NMC)
  $LiNi_{0.5}Mn_{0.3}Co_{0.2}$
- Lithium Cobalt Oxide (LCO)
  $LiCoO_2$
- Lithium Manganese Oxide (LMO)
  $LiMn_2O_4$ or $LiMn_2O$

Fuel + oxidant , all you need is an ignition source to start a fire

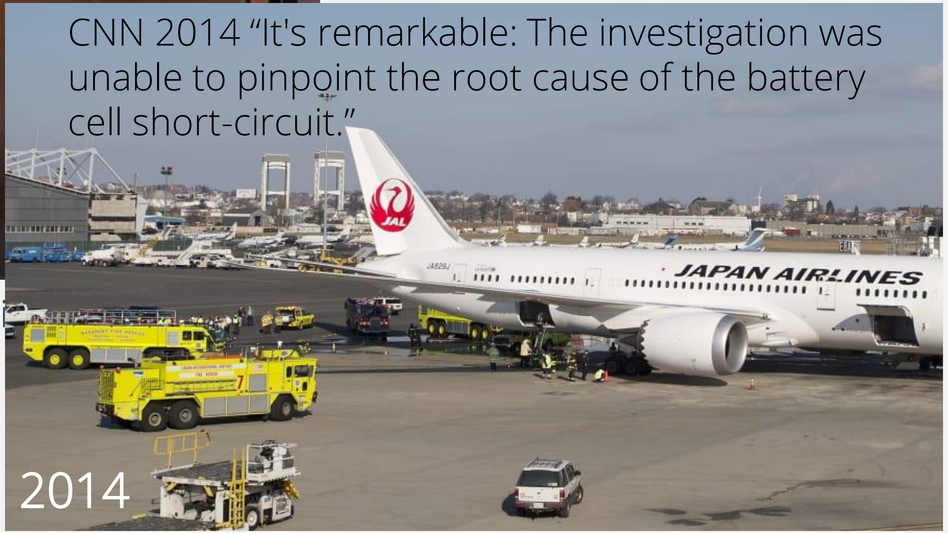
Batteries are Inherently Dangerous (like any energy storage)

NBC news

Fire Department of New York/AFP/Getty Images

Miller T. 247 News Bulletin. 2022 Apri

Photograph: Reuters



CNN 2014 “It's remarkable: The investigation was unable to pinpoint the root cause of the battery cell short-circuit.”

Safety

Moving electrons generates heat. Moving electrons too quickly can have unintended consequences.

The Issues

- Energetic thermal runaway
  - Anode and cathode decomposition reactions
- Electrolyte flammability
  - Low flashpoint electrolyte solvents
  - Vent gas management
  - Fuel-air deflagrations
  - Wide flammability range of decomposition products
- Thermal stability of materials
  - Separators, electrolyte salts, active materials
- Failure propagation from cell-to-cell
  - Single point failures that spread throughout an entire battery system

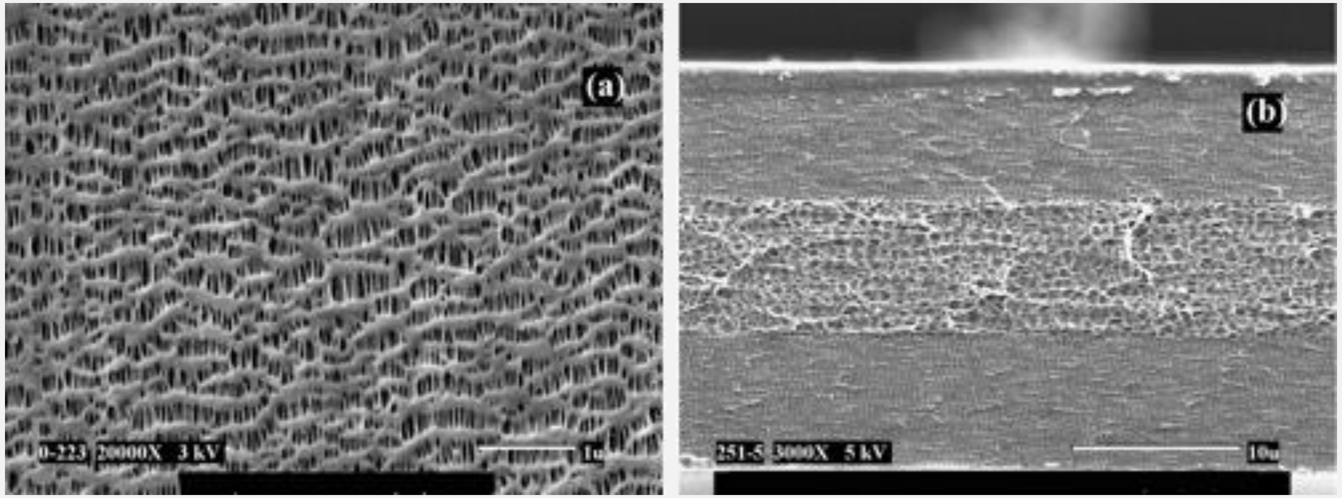
Need to understand

- Battery failure mechanisms
- Fundamentals causes of failure
- Impact of failure:
  - Heat release
  - Gas emission
  - Pressure generation
  - Burn time
  - Waste generation
- Direct comparisons with like battery chemistries/sizes
- Information to help aid in safer batteries:
  - Materials choice
  - Design
  - Engineering controls

Safety in a Cell

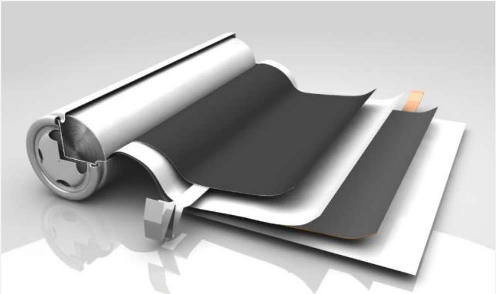
Shutdown separator, a common addition to cells but not a magic bullet

Trilayer polypropylene/polyethylene/prolypropylene (PP/PE/PP)

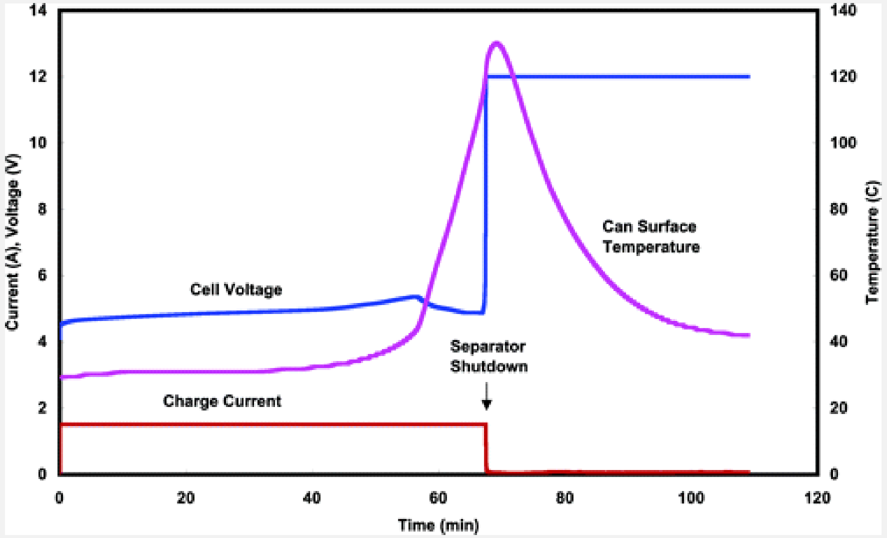


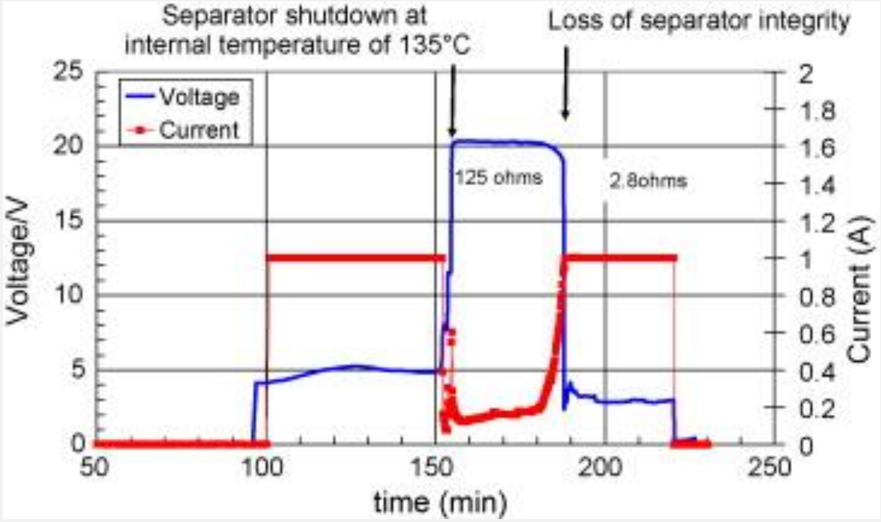
At PE's melting point of 130 °C separator insulates electrodes

Cell



Battery



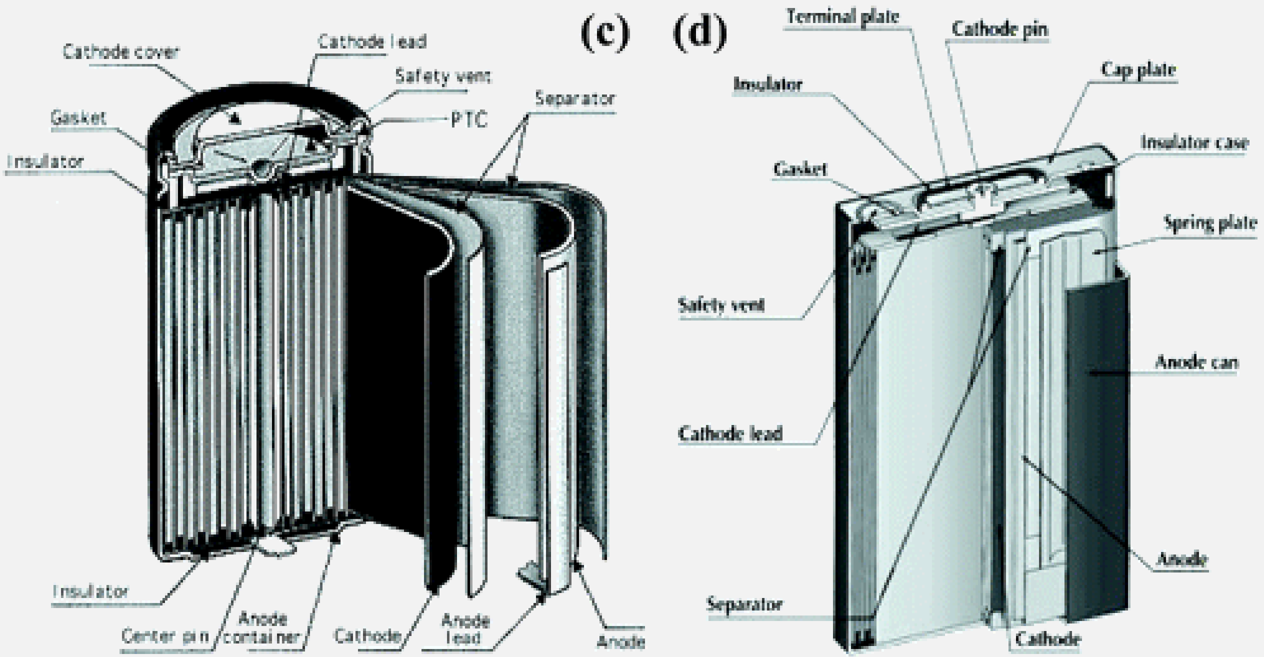


Chem. Rev. 2004, 104, 10, 4419-4462

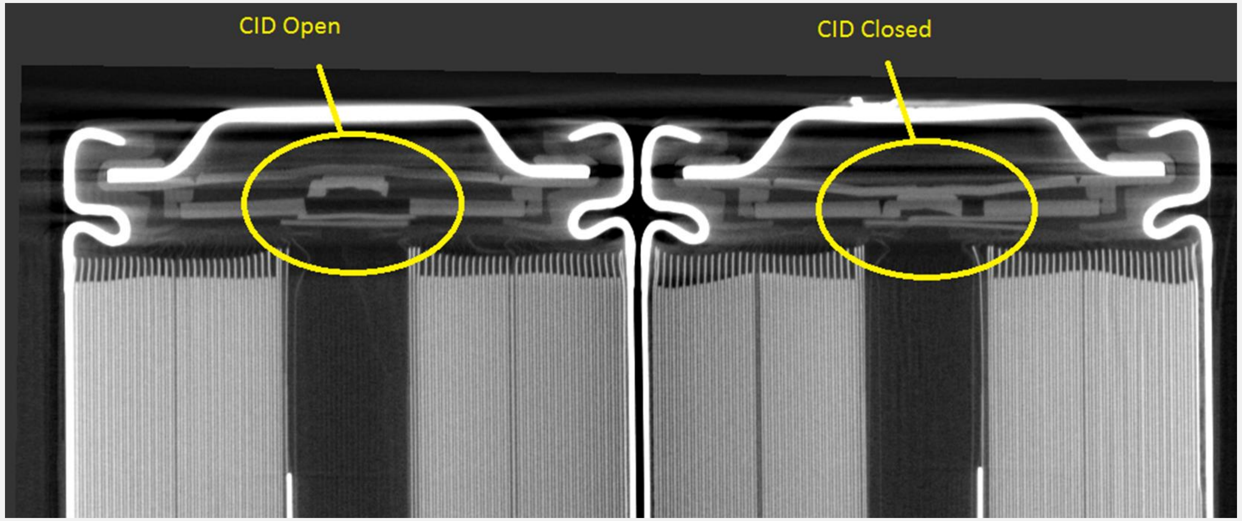
Journal of Power Sources 174 (2007) 579–583

Safety in a Cell

Gaskets, CIDs, vents



Current Interrupt Device (CID)



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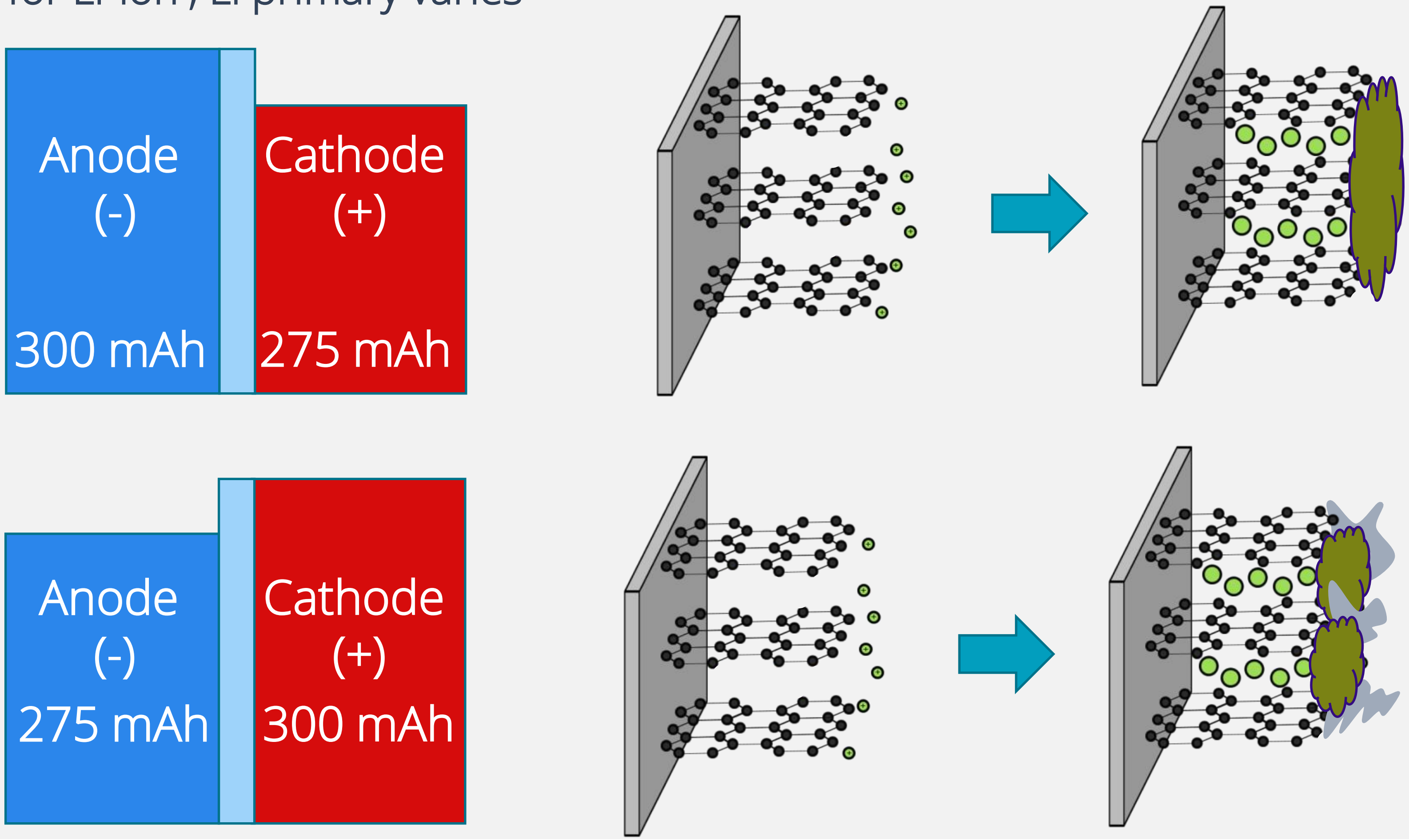
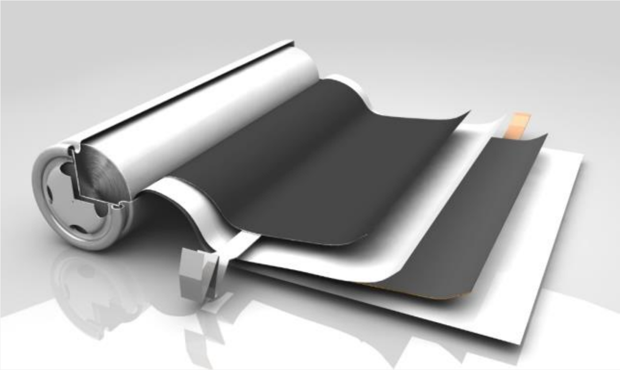
Safety in a Cell

Balancing capacity of anode and cathode essential for performance and safety

N/P > 1 typical for Li-ion , Li primary varies

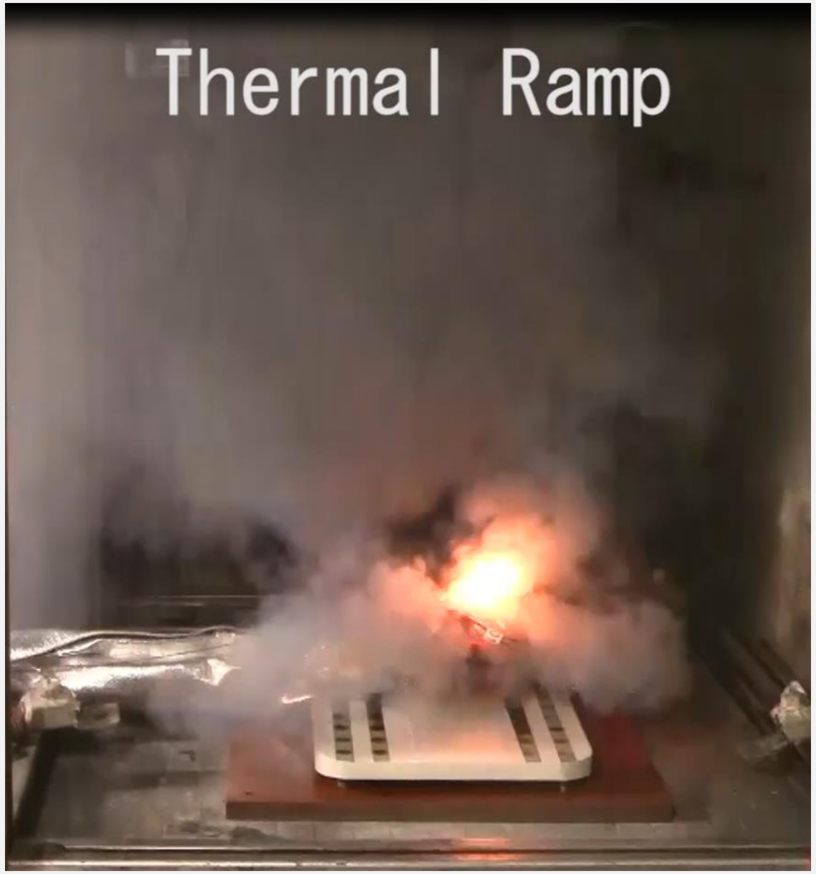


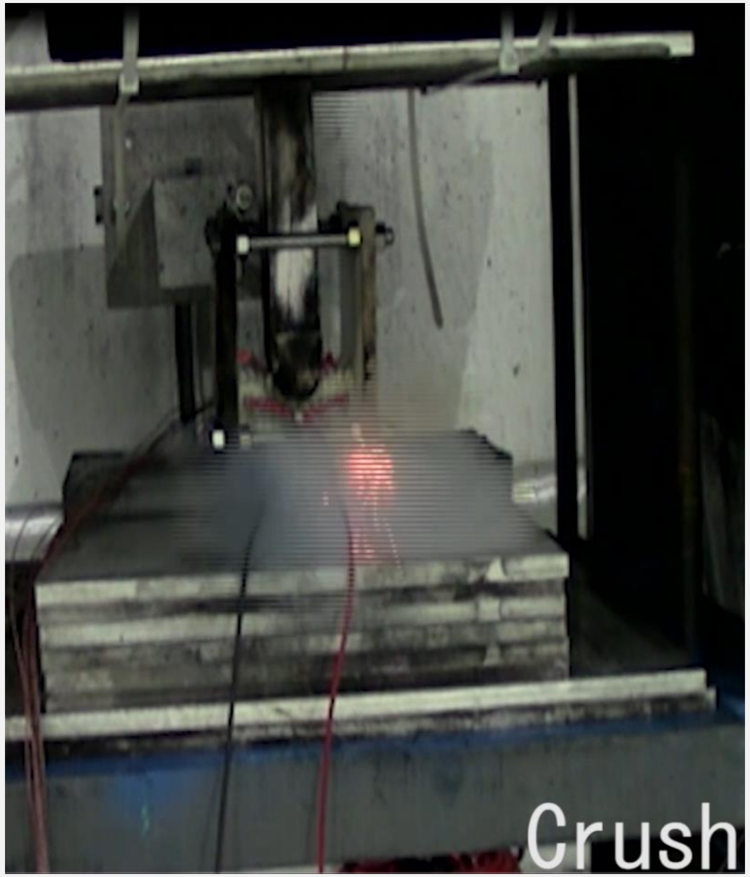
Safety in a battery (pack and beyond)



- Diodes
  - Prevent reverse current (paramount for primary battery)
- PTC devices
  - High current surge protection
- Battery management system
  voltage monitoring system for a multi-cell battery,
  SOC discrepancies
- External Short mitigation
- Ventilation
- Code guidance (NFPA 855) for stationary battery systems
  - ventilation, spill control, neutralization, safety caps on vents, thermal runaway control, explosion control, size and separation requirements for each common ESS chemistry type

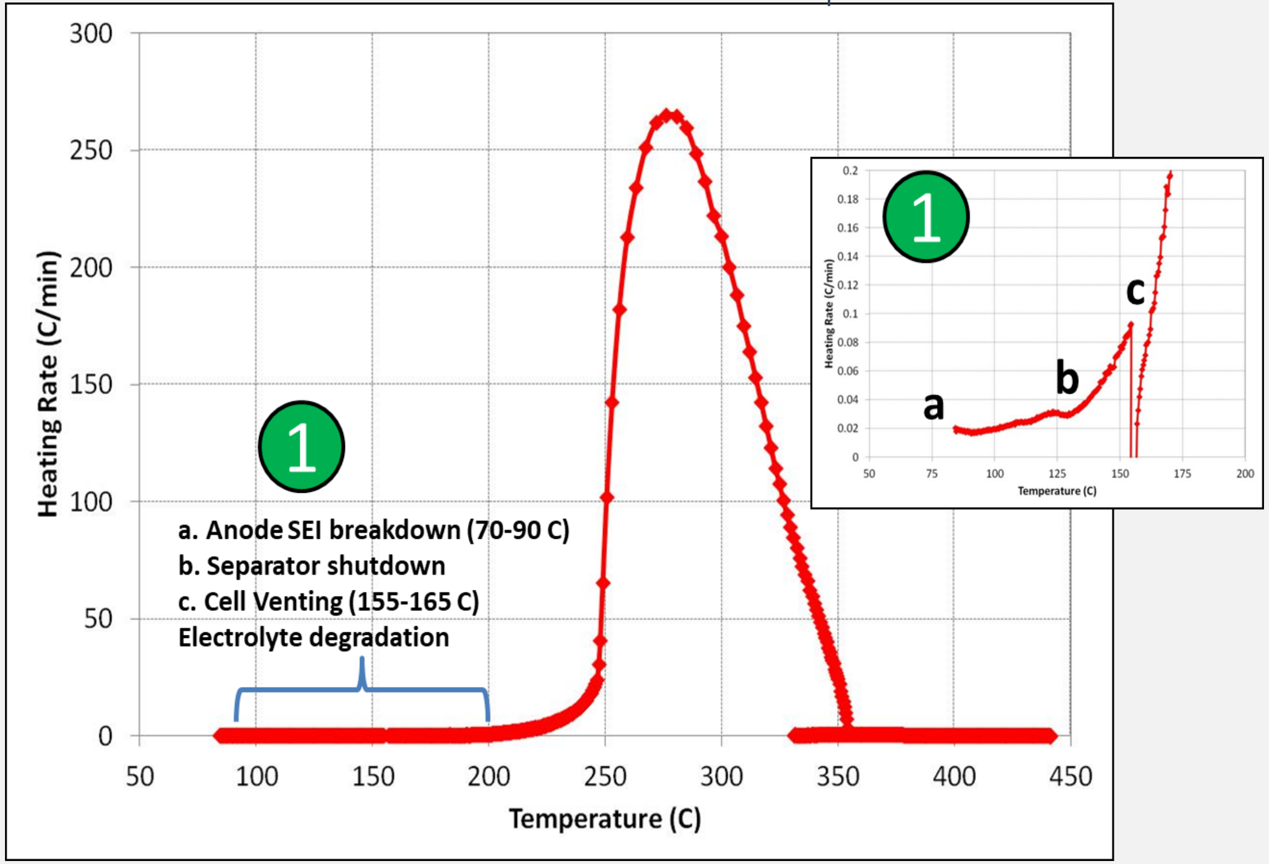
Abusing Cells for Science





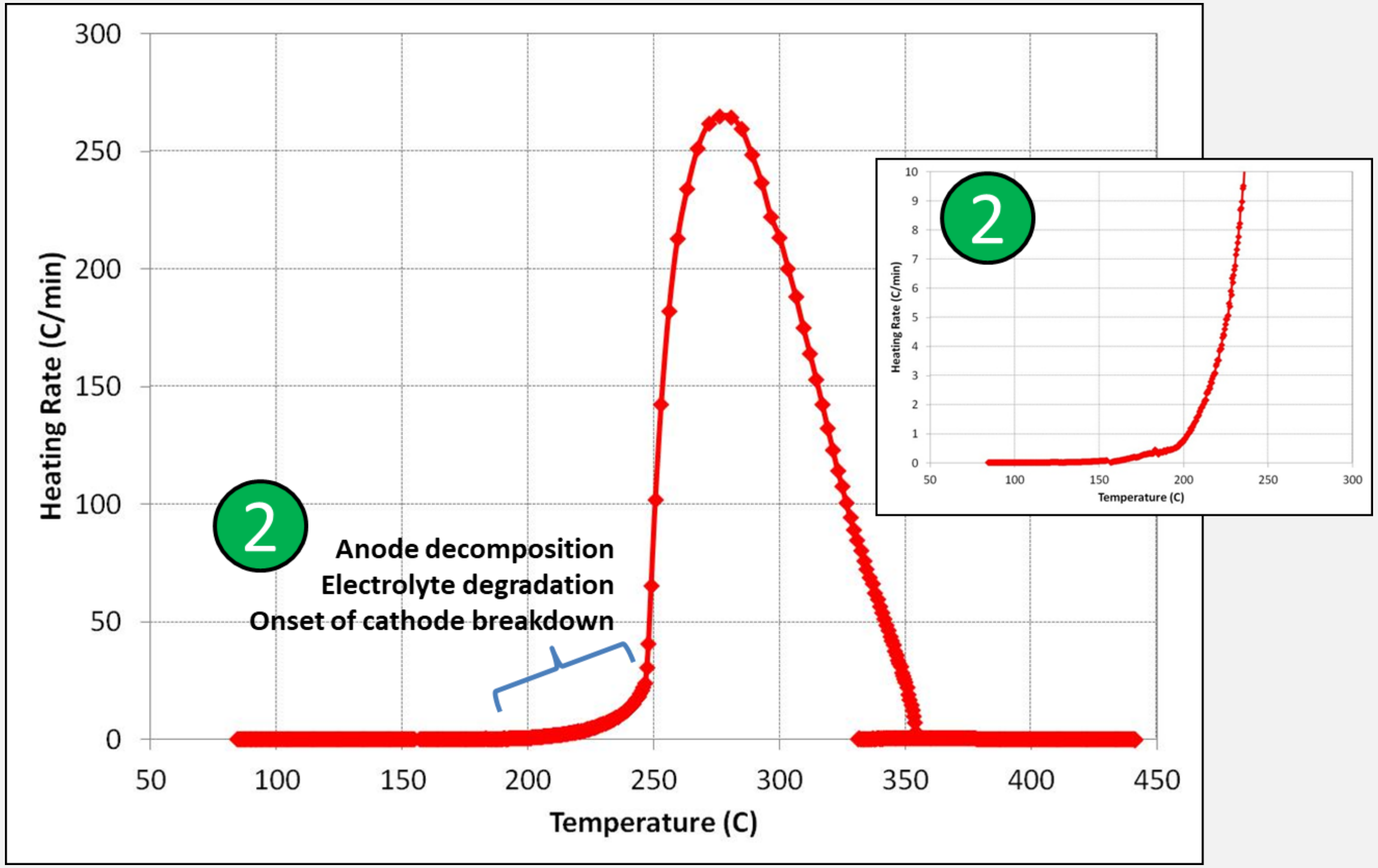
Anatomy of a thermal runaway

- Typical thermal runaway of a Graphite-$LiCoO_2$ cell capture with accelerating rate calorimetry (ARC)
- Low temperature processes include SEI breakdown and decomposition of the electrolyte



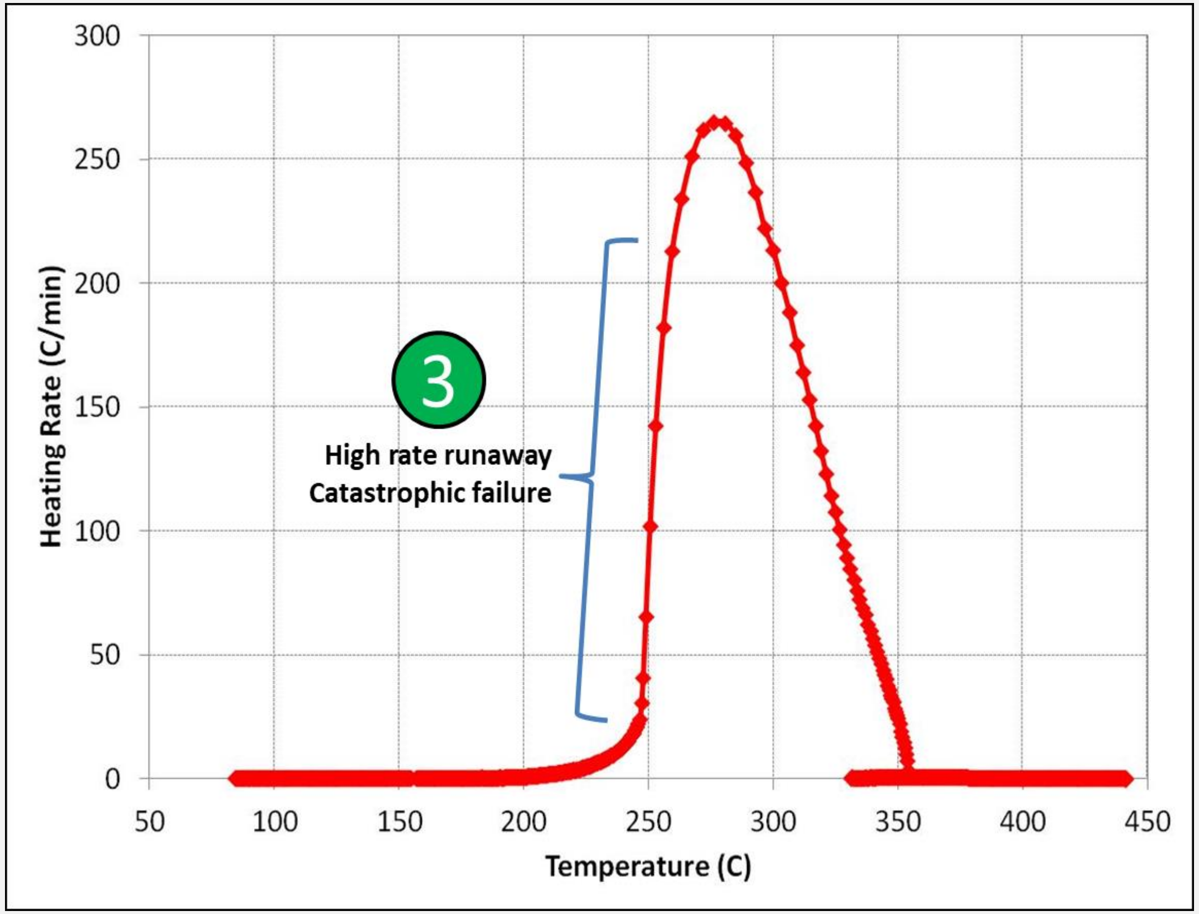
- Chief hazard in this range is release of (often) flammable gas from decomposed electrolyte
- Low excessive temperatures (70-120 °C) will typically permanently degrade performance

Anatomy of a thermal runaway



Anatomy of a thermal runaway

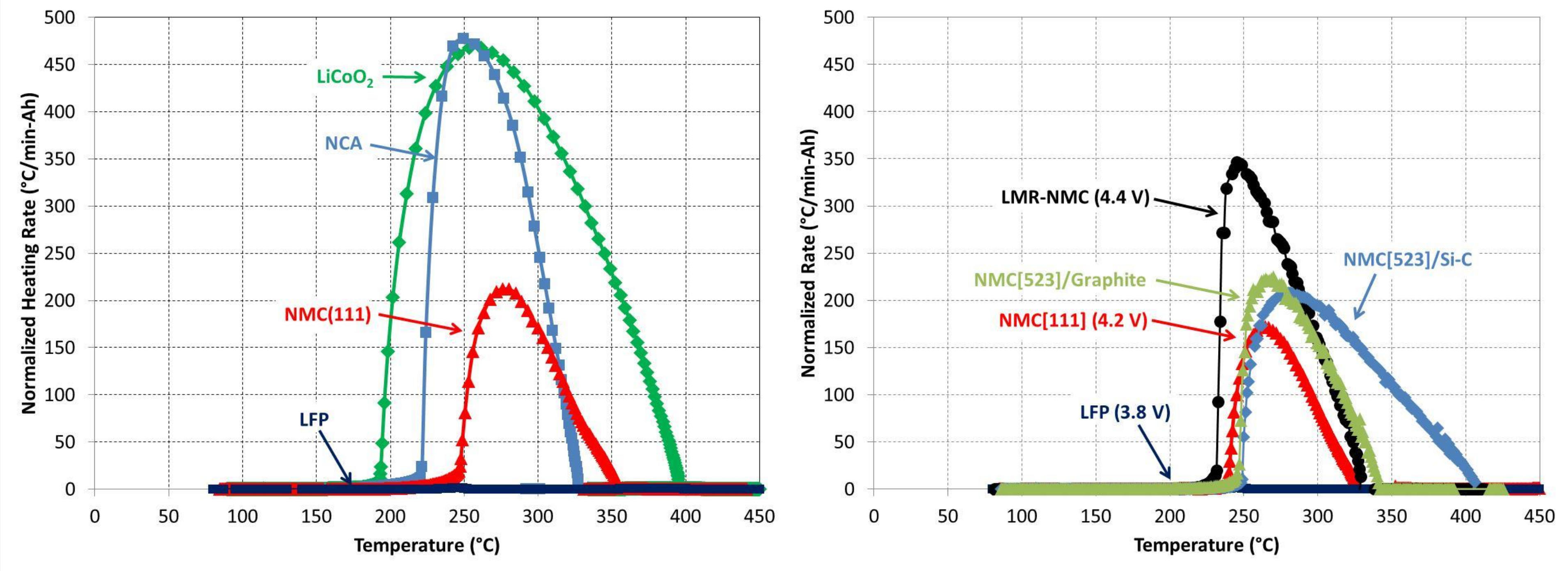
- No stopping thermal runaway



- Best option is stop runaway from impacting other cells

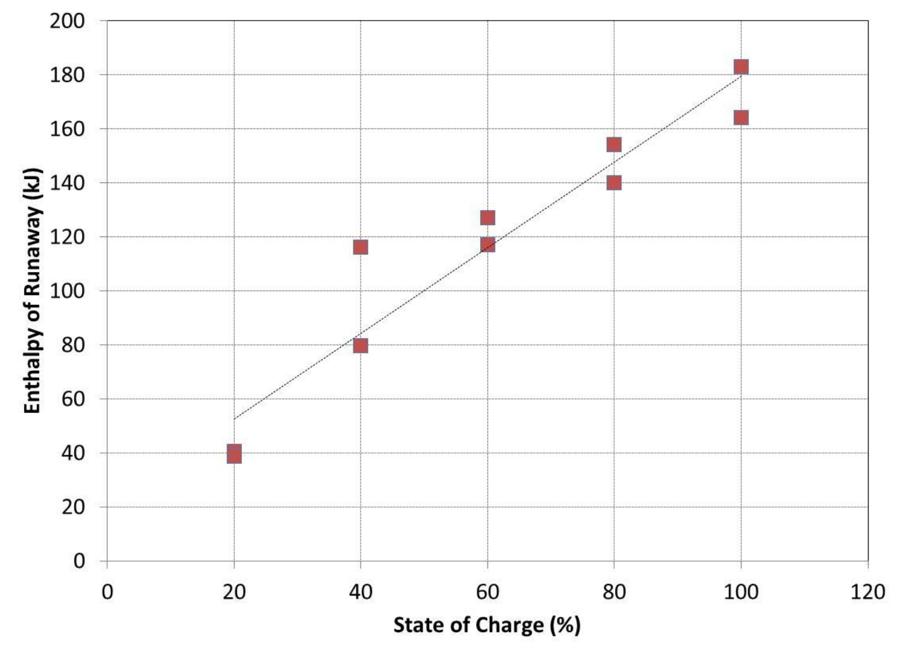
Cathode chemistry impact on safety

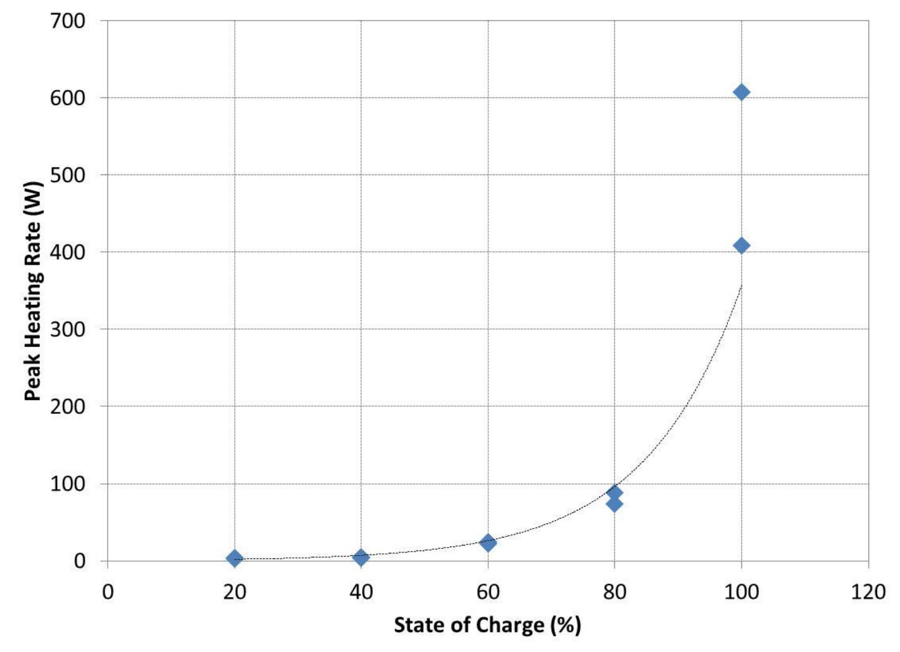
Accelerating rate calorimetry (ARC) of lithium-ion 18650 cells with different cathode materials



- All measurements at 100% SOC and for cells with 1.2 M $LiPF_6$ in EC:EMC (3:7)
- Significant differences in thermal runaway response related to the amount of oxygen released from the cathode material
- 5% silicon composite anode increases the runaway enthalpy by ~10% relative to a graphite cell with the same cathode

Impact of SOC on Runaway

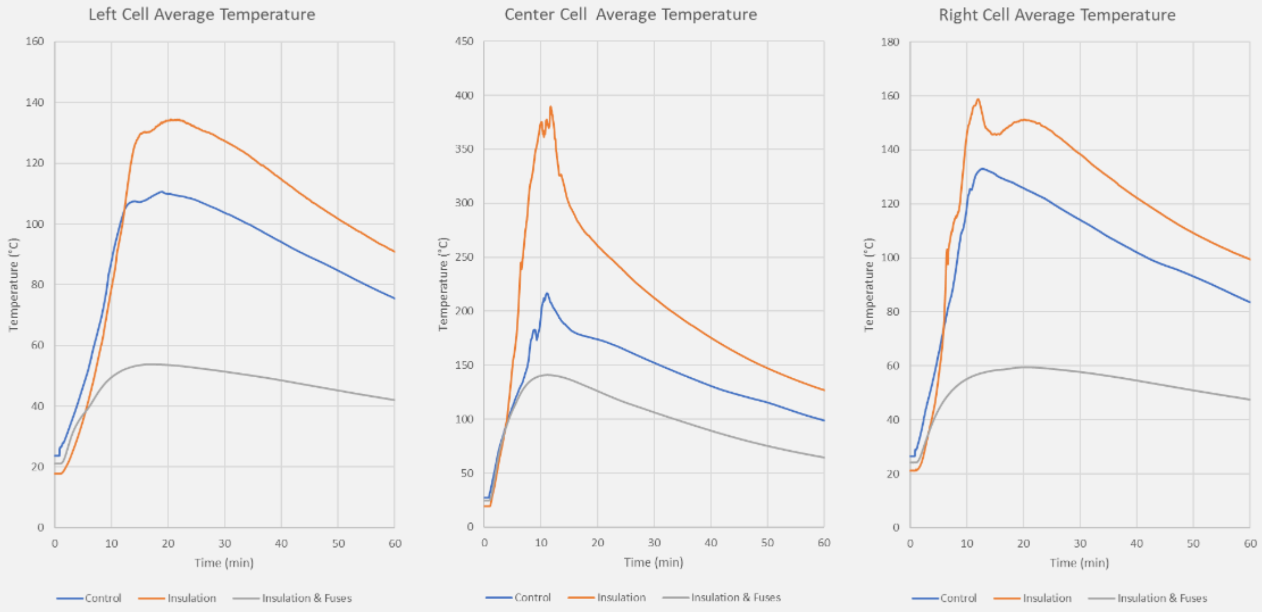




- Results show a nearly linear relationship between total heat release (kJ) and cell SOC – similar to data for cell size this suggests that failure enthalpy is based largely on the stored energy available

- Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship with cell SOC – again this is traditionally thought to cause a greater risk of thermal runaway

Thermal Runaway Protection



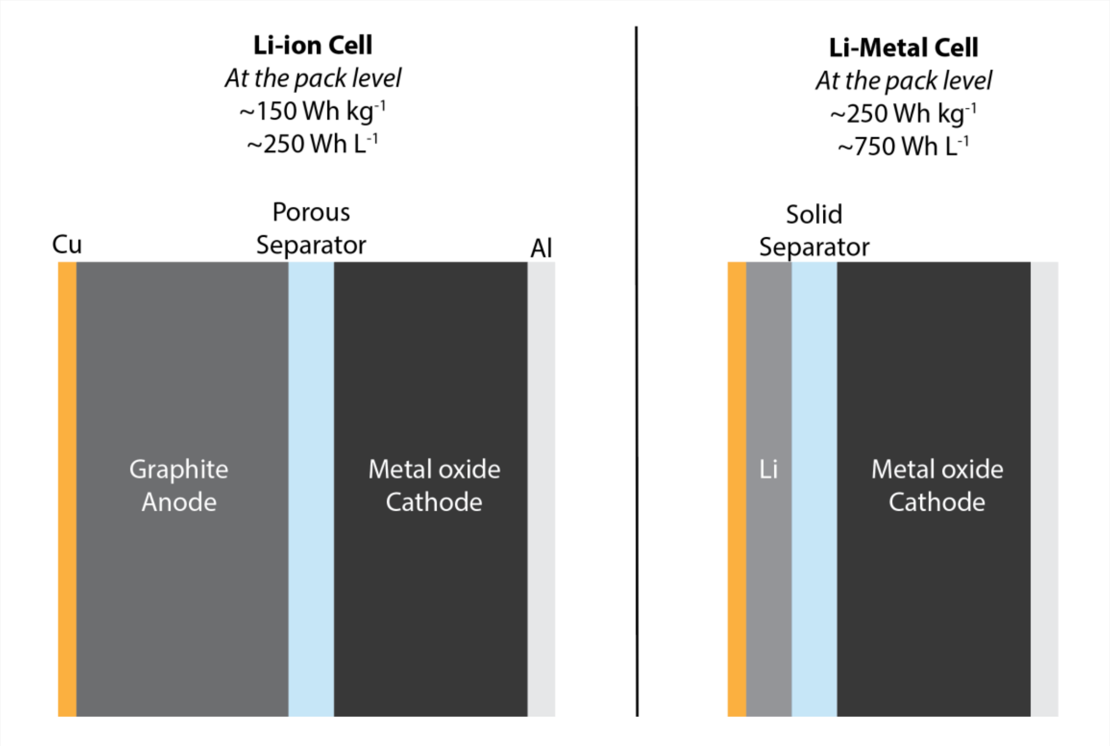
Replacement of Liquid Electrolyte

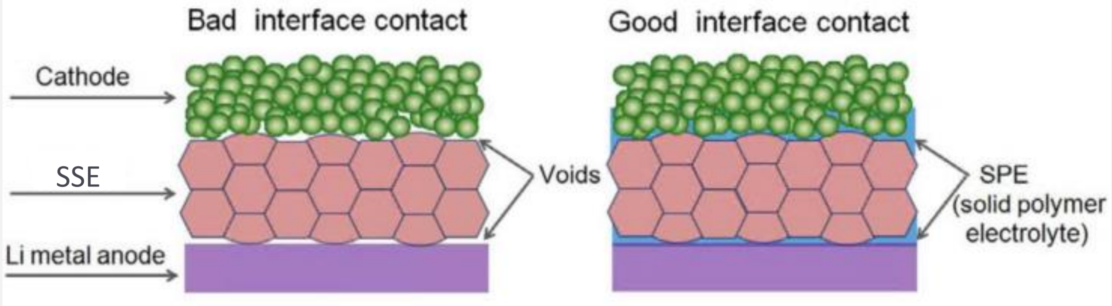
Liquid Electrolyte (LE)

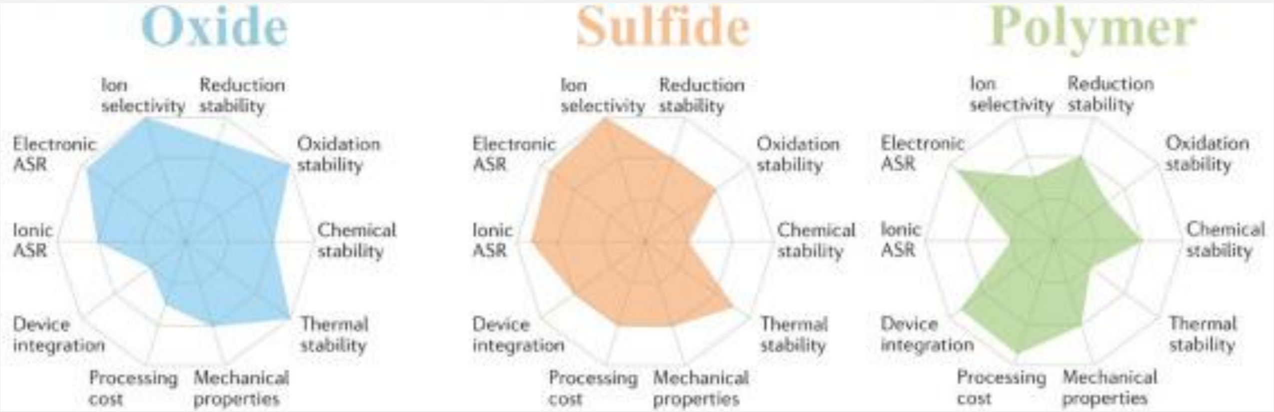
- High ionic conductivity
- Fills void spaces
- Several heat release pathways
- Flammable solvent

Solid Electrolyte (SE)

- OK ionic conductivity
- Energy density (Li-metal anode)
- Safety (no flammable liquid electrolyte)
- Poor interfacial contact







Nat Energy 3, 16–21 (2018).

Journal of Energy Chemistry 50 (2020) 154–177

Heat Release vs. Liquid Volume Fraction (VF)

All solid-state battery are not necessarily safer than liquid Li-ion batteries under short-circuit failure

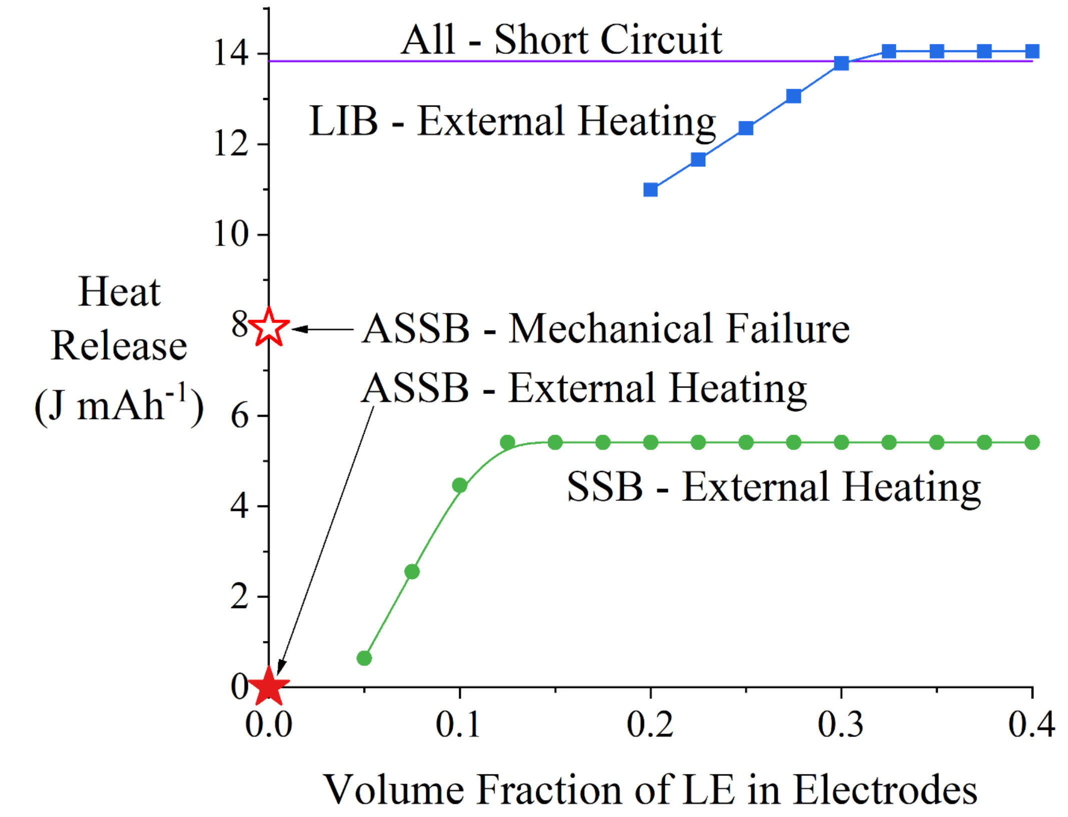
All: short circuit heat release equal

All solid-state battery (ASSB): no heat release from external heating

Li-ion (LIB): heat release dependent on volume fraction 20 to 40%)

Solid-state battery (SSB): Heat release negligible <8% volume fraction

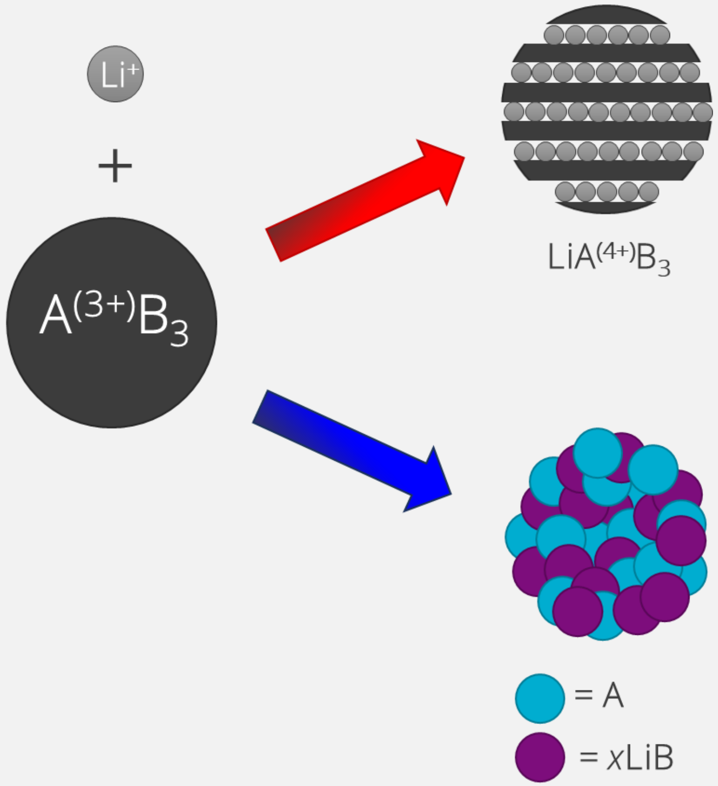
ASSB: large heat release on SE mechanical failure

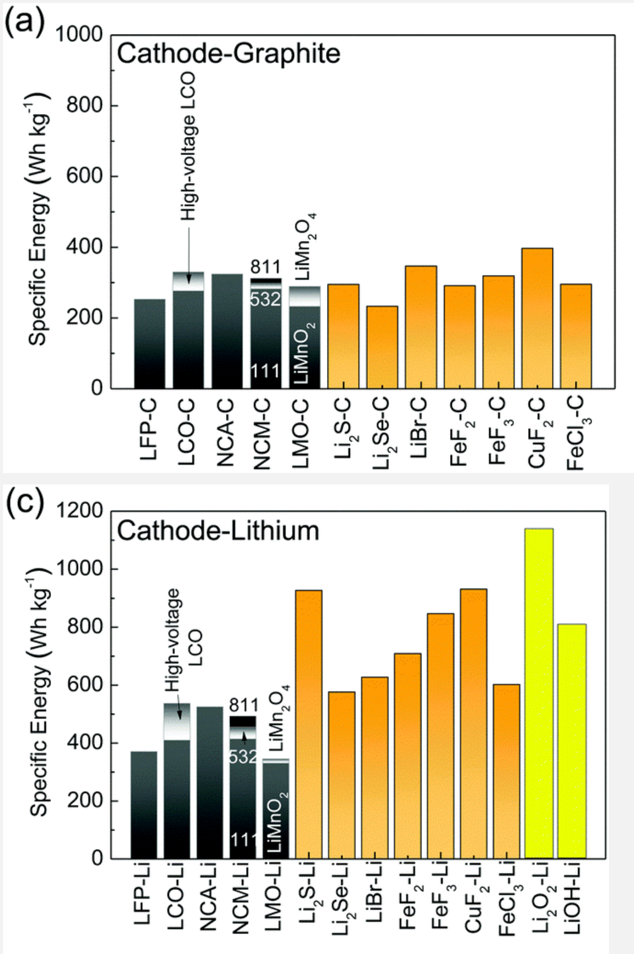


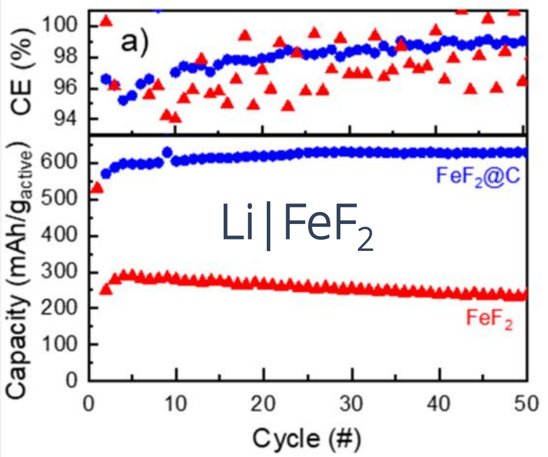
SSB designs with small liquid quantities have improved safety characteristics compared with current LIB designs for scenarios where typical thermal-runaway reactions occur

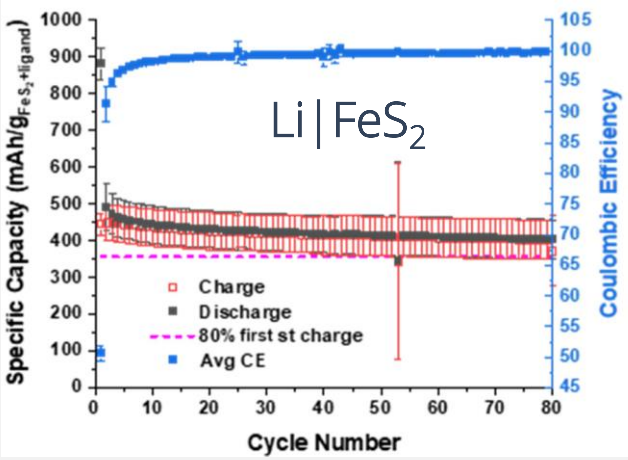
Conversion cathodes for secondary Li batteries

Conversion cathodes typically are more energy density than intercalation materials







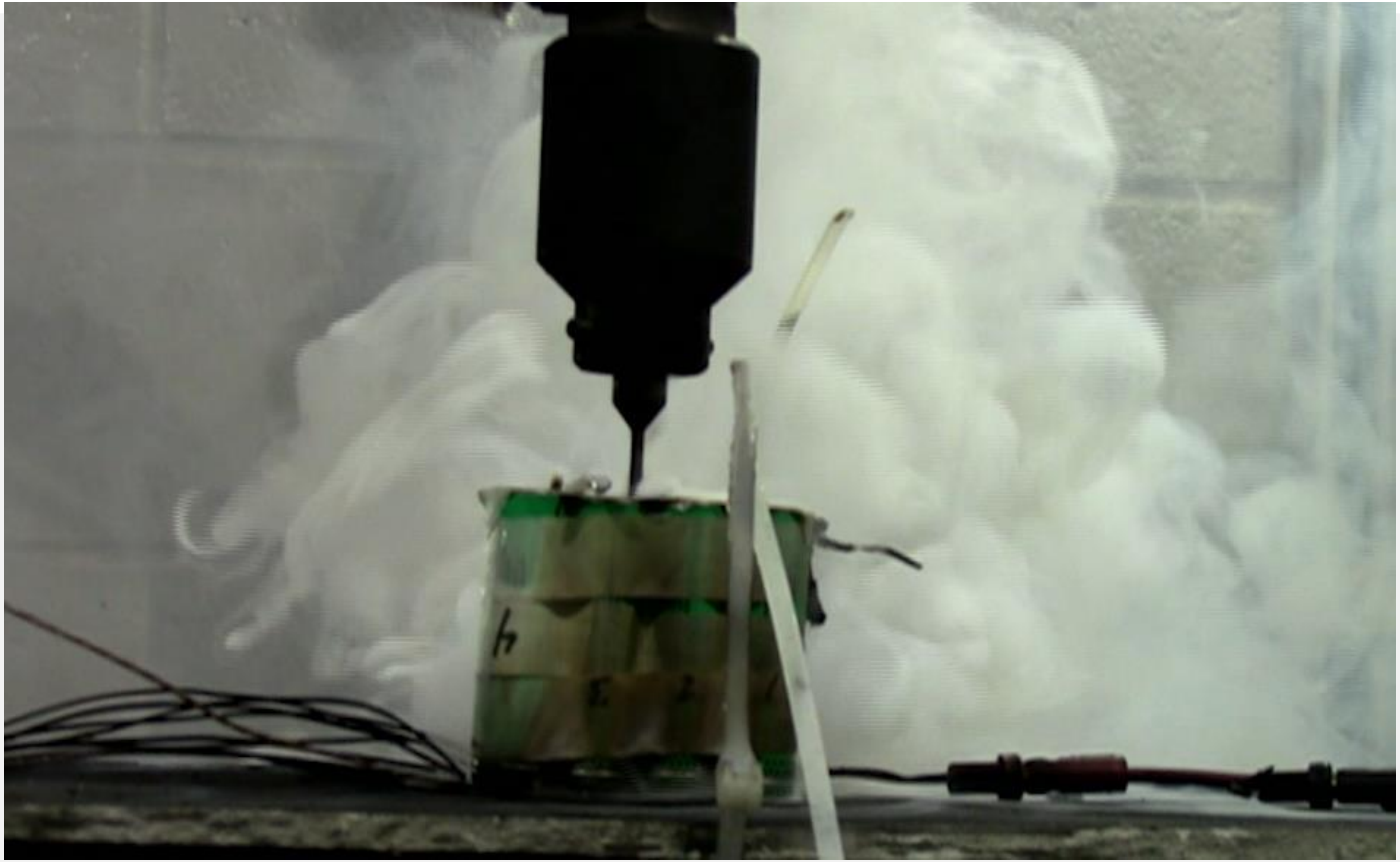


Acknowledgments

- Joshua Lamb
- Kyle Fenton
- Alex Bates
- Katharine L. Harrison
- Brian Perdue
- Mathew Kromer (Harvey Mudd College)
- Kenneth Hernandez-Burgos (DuPont)
- Bryan Wygant
- Loraine Torres-Castro

Sandia National Laboratories

Questions



Backup Slides

Resources

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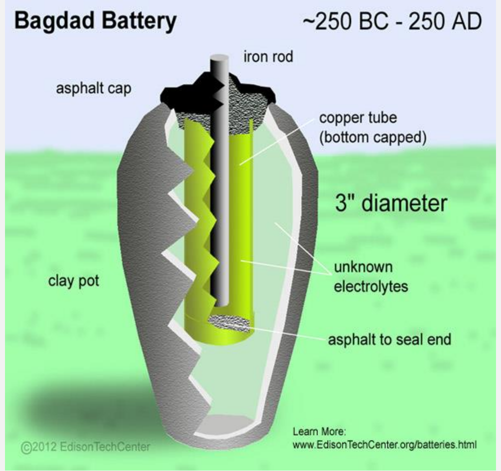
- D. Linden and T. B. Reddy, Handbook of Batteries, Fifth ed., McGraw-Hill, New York, 2002
- What Are Batteries, Fuel Cells, and Supercapacitors Chem. Rev., 2004, Vol. 104, No. 10
- How Batteries Store and Release Energy: Explaining Basic Electrochemistry J. Chem. Educ. 2018, 95, 1801−1810
- Before Li Ion Batteries Chem. Rev. 2018, 118, 23, 11433–11456
- Battery Separators Chem. Rev. 2004, 104, 10, 4419–4462

History of Batteries

250 BC → Today



panasonic.com/global/energy/products/battery/profile/history

macworld.com

Parts of a Battery

A *battery* is a device that converts the chemical energy contained in its active materials directly into electric energy by means of an electrochemical oxidation-reduction (redox) reaction.

The *anode* is the negative electrode of a cell associated with oxidative chemical reactions that release electrons into the external circuit.

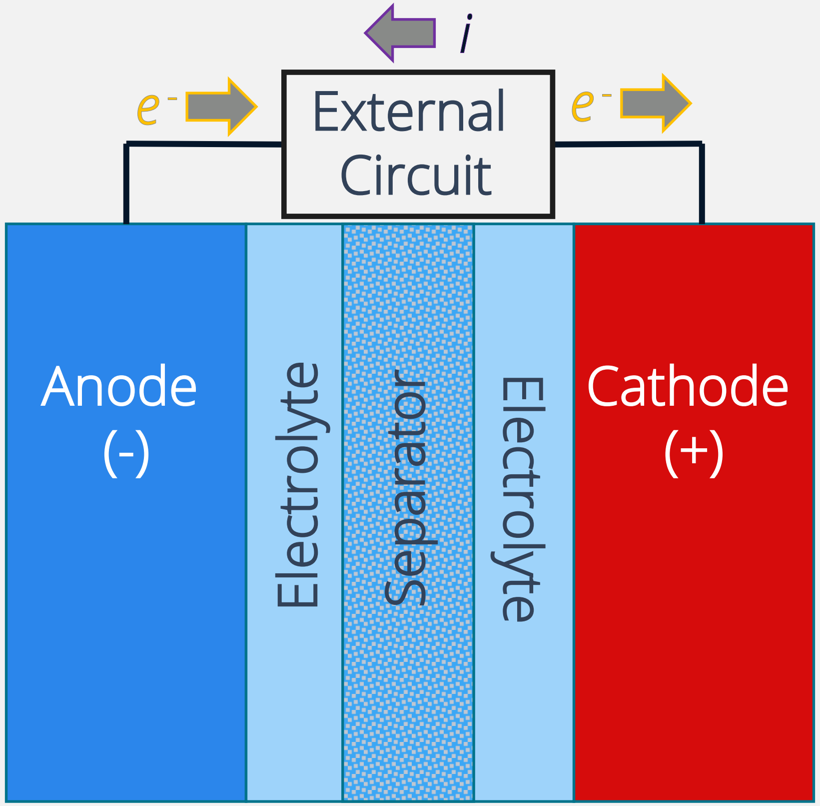
The *cathode* is the positive electrode of a cell associated with reductive chemical reactions that gain electrons from the external circuit.

An *electrolyte* is a material that provides pure ionic conductivity between the positive and negative electrodes of a cell.

A *separator* is a physical barrier between the positive and negative electrodes that must be ionically conductive and electrically insulating.

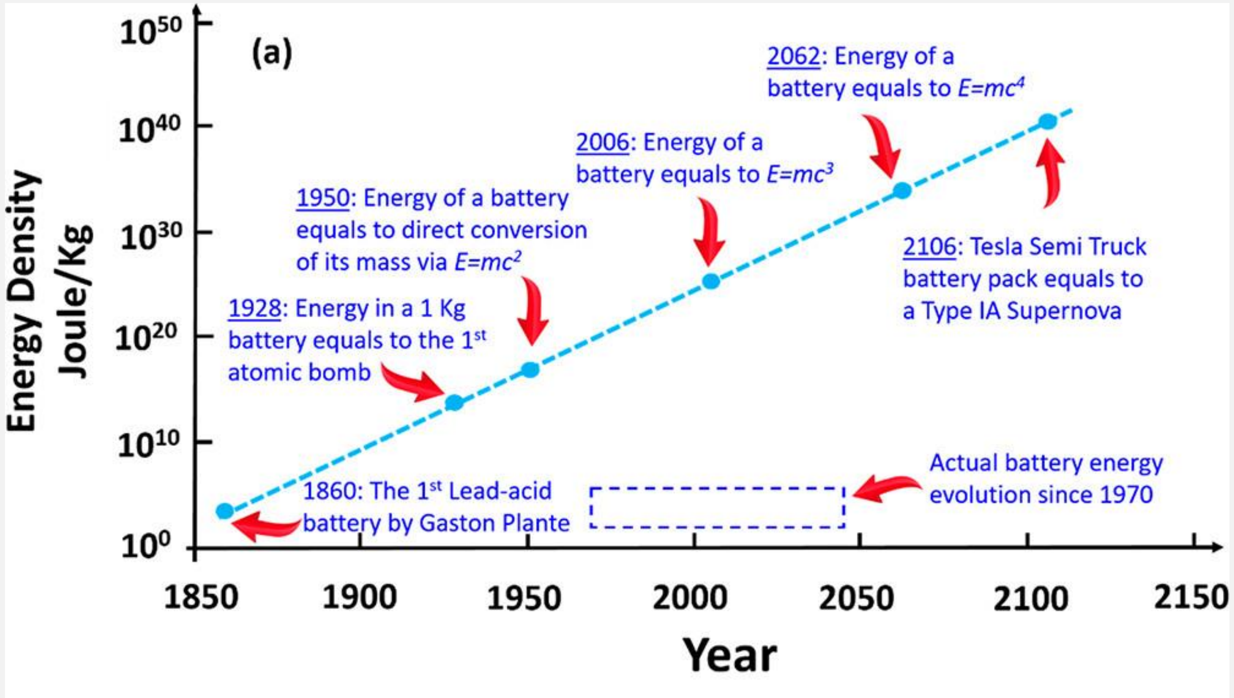
A *current collector* is an inert member of high electrical conductivity used to conduct current from or to an electrode during discharge or charge.

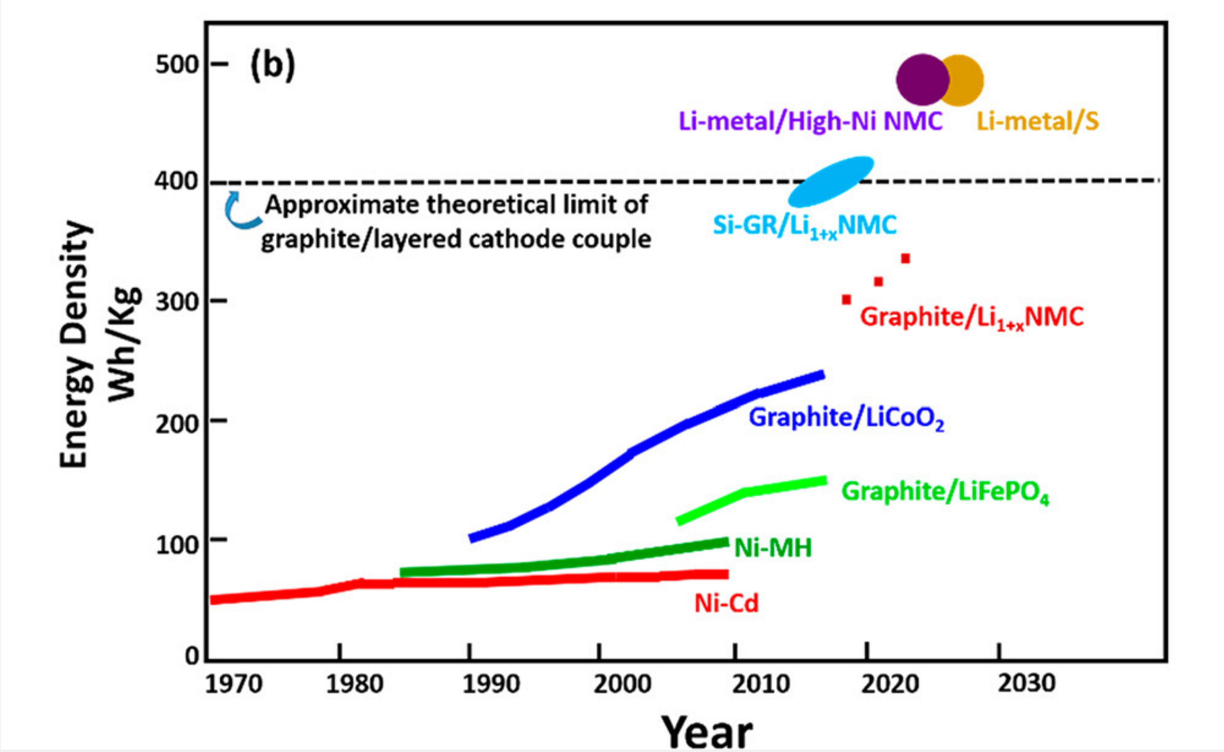
The *casing* is the material that encapsulates the all other components of a battery.



Current → large = fast ; small = slow   *Voltage* → large = more force ; small less force

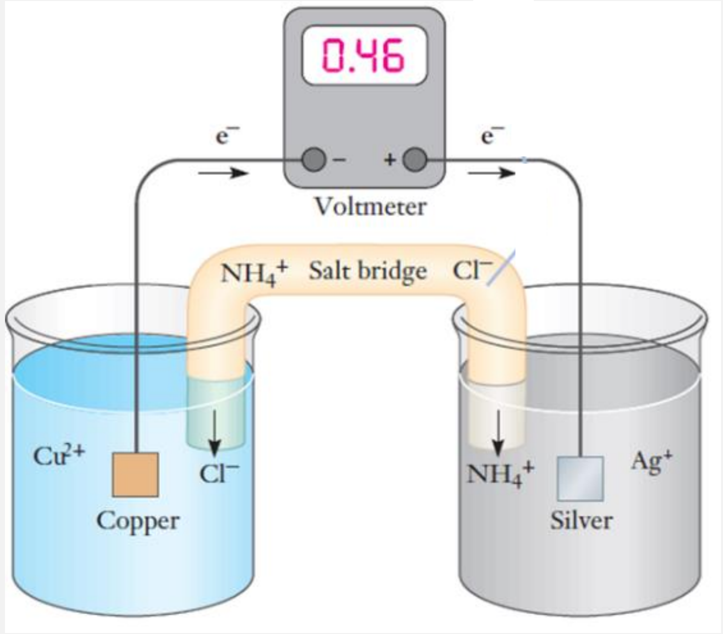
History of Batteries





Chem. Rev. 2018, 118, 23, 11433–11456

Electrons and Electrochemistry



Anode Cathode

- $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
  - Positive E^o spontaneous
- $\Delta G^0 = -nFE^0$
  - Negative ΔG^0 spontaneous
- Nernst equation: $\mathbf{E = E^0 - \frac{RT}{nF}\ln(Q)}$
  - Q ratio of products and reactants
  - R, F constants

- e^-s go from Cu to Ag because E^0_{cell} is positive
- The difference in E^0 from Cu^{2+}/Cu and Ag^+/Ag is ~0.46 V

Electrons and Electrochemistry

"Life is easier when you stand on the shoulders of giants"

Standard Electrode Potentials in Aqueous Solution at 25°C

Half-Reaction	Standard Potential E° (volts)
Li^{+}(aq) + e^{-} -> Li(s)	-3.04
K^{+}(aq) + e^{-} -> K(s)	-2.92
Ca^{2+}(aq) + $2e^{-}$ -> Ca(s)	-2.76
Na^{+}(aq) + e^{-} -> Na(s)	-2.71
Mg^{2+}(aq) + $2e^{-}$ -> Mg(s)	-2.38
Al^{3+}(aq) + $3e^{-}$ -> Al(s)	-1.66
$2H_2O$(l) + $2e^{-}$ -> H_2(g) + $2OH^{-}$(aq)	-0.83
Zn^{2+}(aq) + $2e^{-}$ -> Zn(s)	-0.76
Cr^{3+}(aq) + $3e^{-}$ -> Cr(s)	-0.74
Fe^{2+}(aq) + $2e^{-}$ -> Fe(s)	-0.41
Cd^{2+}(aq) + $2e^{-}$ -> Cd(s)	-0.40
Ni^{2+}(aq) + $2e^{-}$ -> Ni(s)	-0.23
Sn^{2+}(aq) + $2e^{-}$ -> Sn(s)	-0.14
Pb^{2+}(aq) + $2e^{-}$ -> Pb(s)	-0.13
Fe^{3+}(aq) + $3e^{-}$ -> Fe(s)	-0.04
$2H^{+}$(aq) + $2e^{-}$ -> H_2(g)	0.00
Sn^{4+}(aq) + $2e^{-}$ -> Sn^{2+}(aq)	0.15
Cu^{2+}(aq) + e^{-} -> Cu^{+}(aq)	0.16
ClO_4^{-}(aq) + H_2O(l) + $2e^{-}$ -> ClO_3^{-}(aq) + $2OH^{-}$(aq)	0.17
AgCl(s) + e^{-} -> Ag(s) + Cl^{-}(aq)	0.22
Cu^{2+}(aq) + $2e^{-}$ -> Cu(s)	0.34
ClO_3^{-}(aq) + H_2O(l) + $2e^{-}$ -> ClO_2^{-}(aq) + $2OH^{-}$(aq)	0.35
IO^{-}(aq) + H_2O(l) + $2e^{-}$ -> I^{-}(aq) + $2OH^{-}$(aq)	0.49
Cu^{+}(aq) + e^{-} -> Cu(s)	0.52
I_2(s) + $2e^{-}$ -> $2I^{-}$(aq)	0.54
ClO_2^{-}(aq) + H_2O(l) + $2e^{-}$ -> ClO^{-}(aq) + $2OH^{-}$(aq)	0.59
Fe^{3+}(aq) + e^{-} -> Fe^{2+}(aq)	0.77
Hg_2^{2+}(aq) + $2e^{-}$ -> 2Hg(l)	0.80
Ag^{+}(aq) + e^{-} -> Ag(s)	0.80
Hg^{2+}(aq) + $2e^{-}$ -> Hg(l)	0.85
ClO^{-}(aq) + H_2O(l) + $2e^{-}$ -> Cl^{-}(aq) + $2OH^{-}$(aq)	0.90
$2Hg^{2+}$(aq) + $2e^{-}$ -> Hg_2^{2+}(aq)	0.90
NO_3^{-}(aq) + $4H^{+}$(aq) + $3e^{-}$ -> NO(g) + $2H_2O$(l)	0.96
Br_2(l) + $2e^{-}$ -> $2Br^{-}$(aq)	1.07
O_2(g) + $4H^{+}$(aq) + $4e^{-}$ -> $2H_2O$(l)	1.23
$Cr_2O_7^{2-}$(aq) + $14H^{+}$(aq) + $6e^{-}$ -> $2Cr^{3+}$(aq) + $7H_2O$(l)	1.33
Cl_2(g) + $2e^{-}$ -> $2Cl^{-}$(aq)	1.36
Ce^{4+}(aq) + e^{-} -> Ce^{3+}(aq)	1.44
MnO_4^{-}(aq) + $8H^{+}$(aq) + $5e^{-}$ -> Mn^{2+}(aq) + $4H_2O$(l)	1.49
H_2O_2(aq) + $2H^{+}$(aq) + $2e^{-}$ -> $2H_2O$(l)	1.78
Co^{3+}(aq) + e^{-} -> Co^{2+}(aq)	1.82
$S_2O_8^{2-}$(aq) + $2e^{-}$ -> $2SO_4^{2-}$(aq)	2.01
O_3(g) + $2H^{+}$(aq) + $2e^{-}$ -> O_2(g) + H_2O(l)	2.07
F_2(g) + $2e^{-}$ -> $2F^{-}$(aq)	2.87

http://hyperphysics.phy-astr.gsu.edu/

Battery Terminology

Discharge: An operation in which a battery delivers electrical energy to an external load.

Charge: An operation in which the battery is restored to its original charged condition by reversal of the current flow.

Capacity: The total number of Ampere-hours (Ah) that can be withdrawn from a fully charged cell or battery under specified conditions of discharge

Specific Capacity: The ratio of the capacity delivered by a cell or battery to its weight (Ah/kg or mAh/g).

Gravimetric Energy Density: The ratio of the energy output of a cell or battery to its weight (Wh/kg).
Volummetric Energy Density: The ratio of the energy available from a battery to its volume (Wh/L).

Gravimetric Power Density: The ratio of the power delivered by a cell or battery to its weight (W/ kg).
Volummetric Power Density: The ratio of the power available from a battery to its volume (W/ L).

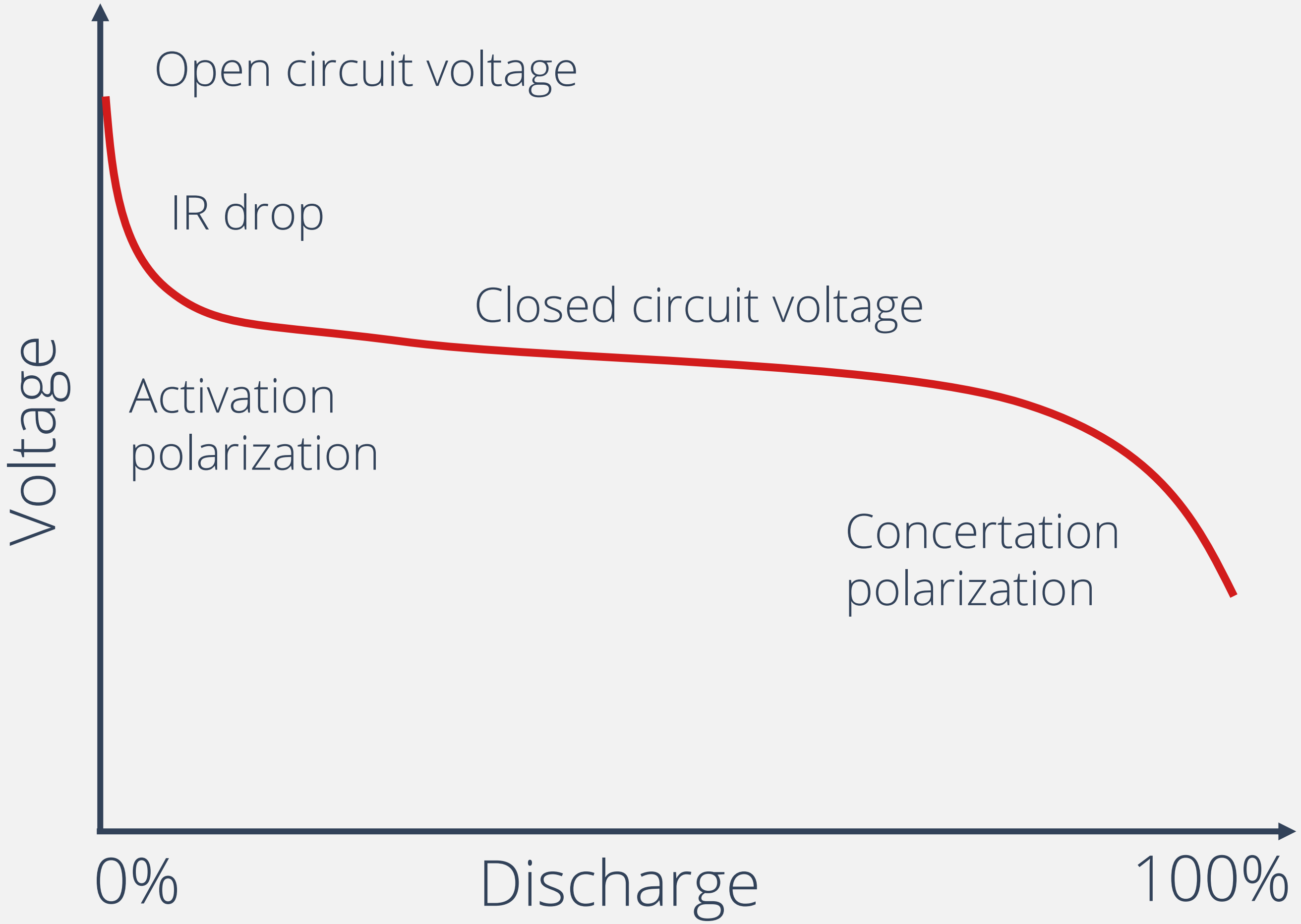
Efficiency: The ratio of the output of a secondary cell or battery on discharge to the input required to restore it to the initial state of charge under specified conditions.

C-Rate: It is the rate of charge or discharge of a cell or battery. Generally, it is expressed by n C.

Example: 0.1 C means the full charge or discharge time is 1/0.1 h (10 h); 10 C is 1/60 h (6 min).

Battery Operation

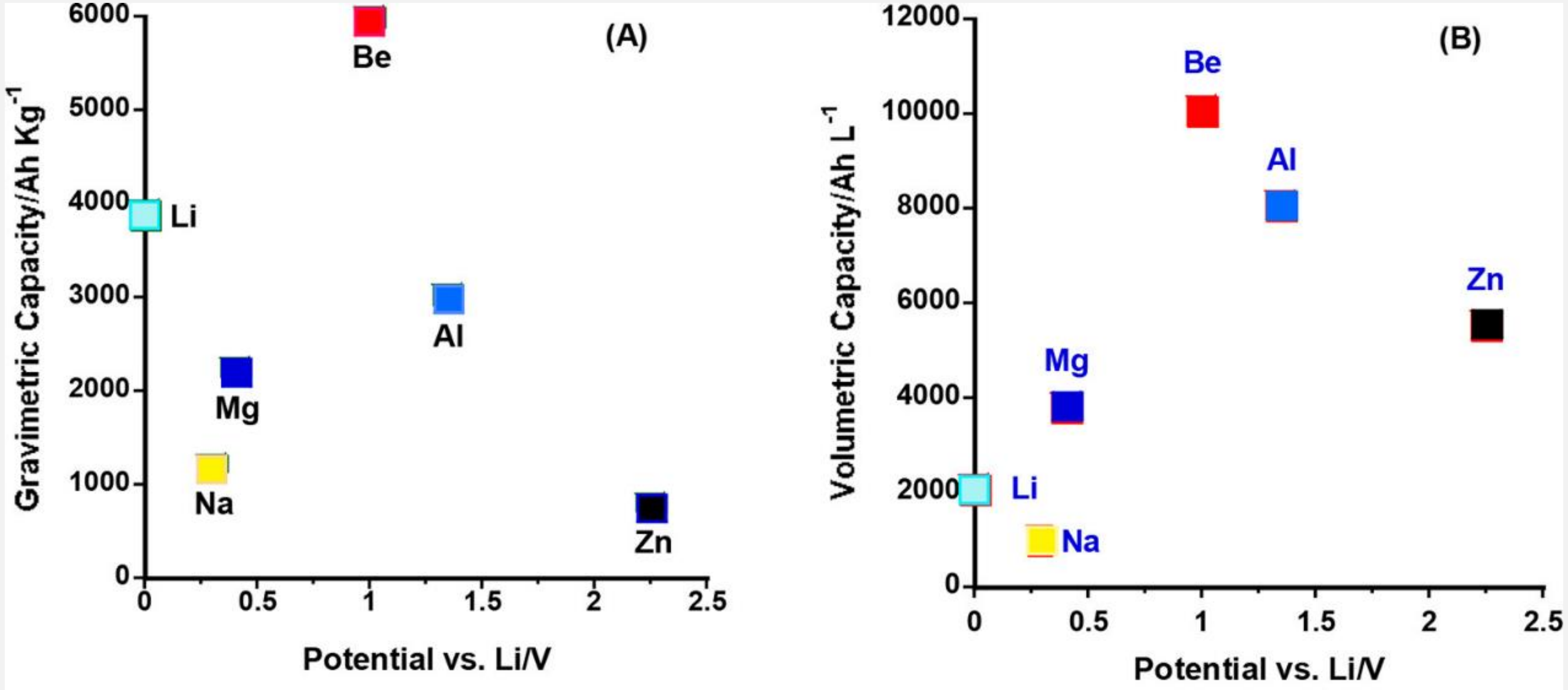
Charge-discharge curve of a battery → Thermodynamics and kinetics in action



- Faraday's law
- Nernst equation
- Sand equation
- Ohm's Law
- Tafel equation
- Butler-Volmer equation

Li

Why Li for batteries?



"The fortuitous combination of a small atomic weight, extremely low reduction potential, and monovalent charge renders Li with such unique qualities that are nearly impossible for other elements or compounds to rival."

Chem. Rev. 2018, 118, 23, 11433–11456

Li-ion vs Li primary

CR Series Manganese Dioxide Lithium Batteries

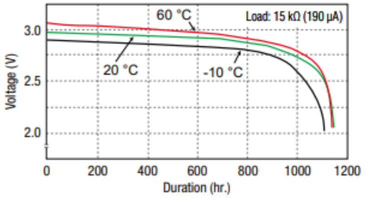
Features

- Offers high-rate pulse discharge
- Available in a range of compact sizes and capacities, from thin-type to high-capacity models
- Excellent low-temperature performance enhanced by manganese-dioxide positive pole

Applications

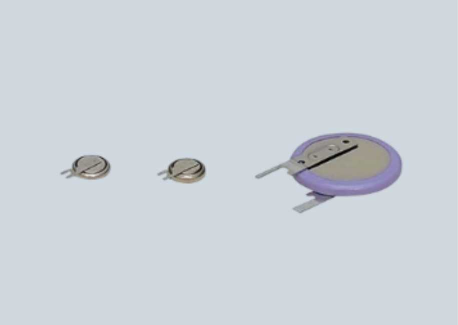
Remote keyless entry, card remote controls, memory backup, security price tags, smart transmitter tags, etc.

■ Discharge temperature characteristics (Example: CR2032)



Model No.	Nominal voltage (V)	Nominal capacity (mAh)*1	Continuous drain (mA)	Dimensions (mm)		Mass (g)	Operating temperature range*2
				Diameter	Height		
CR1025	3	30	0.1	10.0	2.5	0.6	
CR1216		25		12.5	1.6	0.7	
CR1220		35			2.0	0.9	
CR1616		55		16.0	1.6	1.0	
CR1620		75			2.0	1.3	
CR1632		140			3.2	1.9	
CR2012		55		20.0	1.2	1.4	
CR2016		90			1.6	1.6	
CR2025		165			2.5	2.3	

ML Series Manganese Rechargeable Lithium Batteries



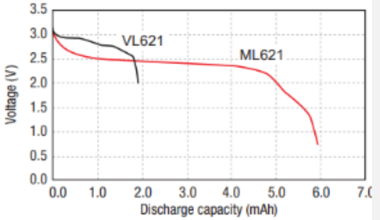
Features

- Ideal for long-term memory backup with extra-high capacity

Applications

Memory backup (drive recorders, PCs, communication/radio, medical equipment, FA equipment), etc.

■ Discharge characteristics (Example: ML621)

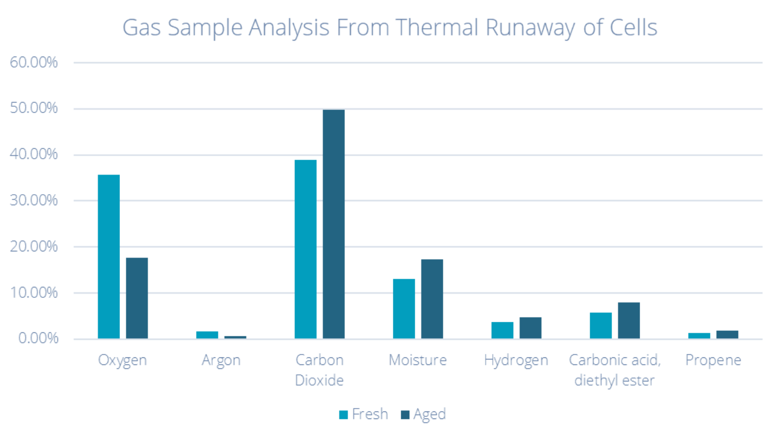


Model No.	Nominal voltage (V)	Nominal capacity (mAh)*1	Continuous drain (mA)	Dimensions (mm)		Mass (g)	Charge voltage (V)	Operating temperature range
				Diameter	Height			
ML421	3	2.3	0.005	4.8	2.1	0.10	2.8 to 3.2	-20 °C to 60 °C
ML614		3.4	0.01	6.8	1.4	0.16		
ML621		5.0			2.1	0.22		
ML920		11.0	0.03	9.5	2.0	0.39		
ML1220		17.0		12.5		0.80		
ML2020		45.0	0.12	20.0		2.20		

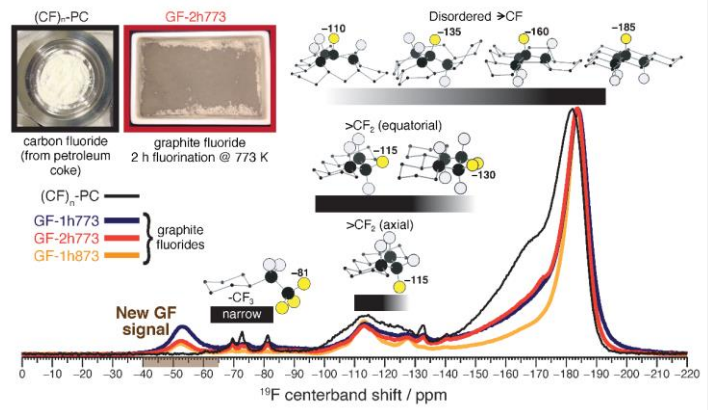
*1 Nominal capacity shown above is based on standard drain and cutoff voltage down to 2.0 V at 20 °C.

Understanding Cell Component Properties

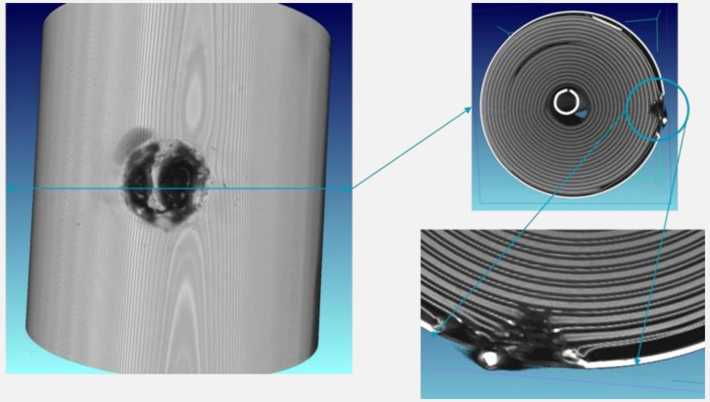
Gas sampling



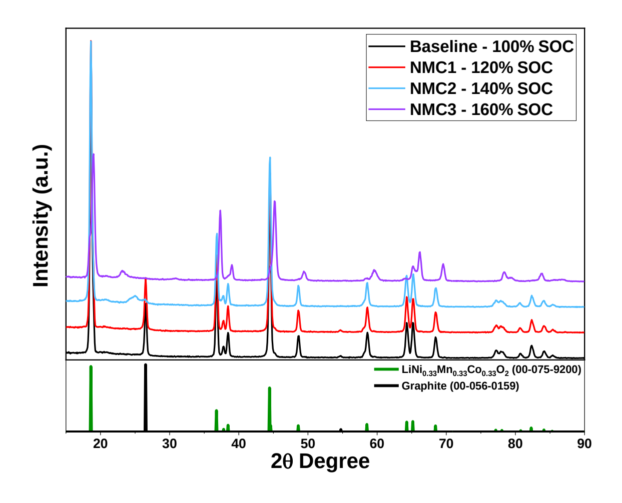
NMR



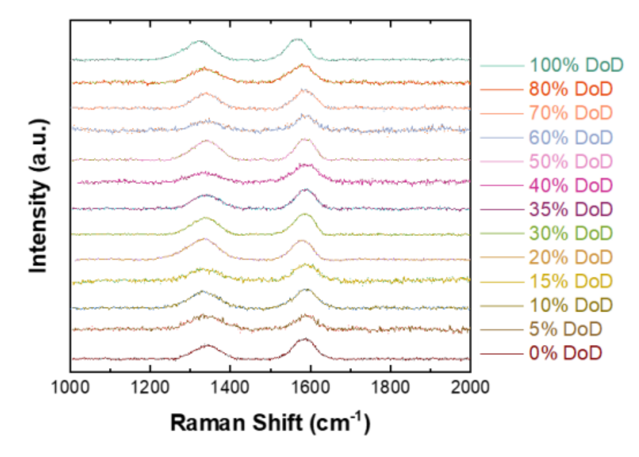
CT scan



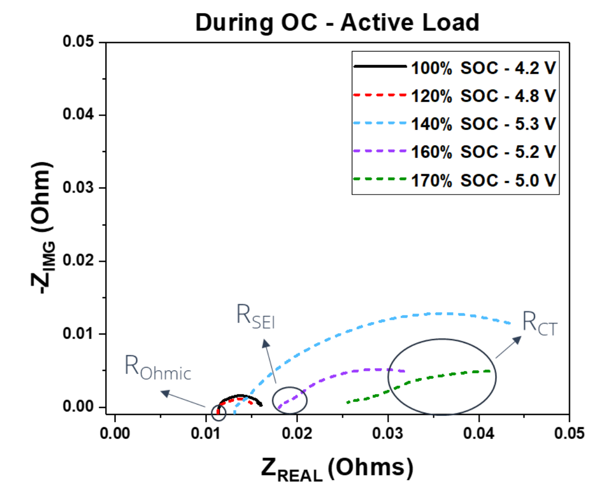
XRD



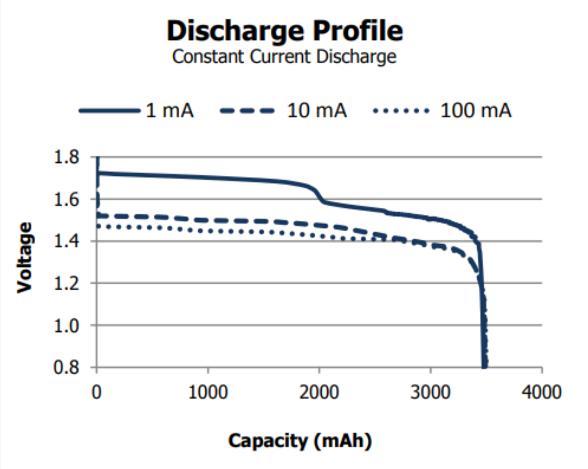
Raman Spectroscopy



Impedance (EIS)



V profiles



Adv. Energy Mater. 2022, 12, 2103196 *Solids* 2022, *3*(2), 237-257

Abusing Cells for Science

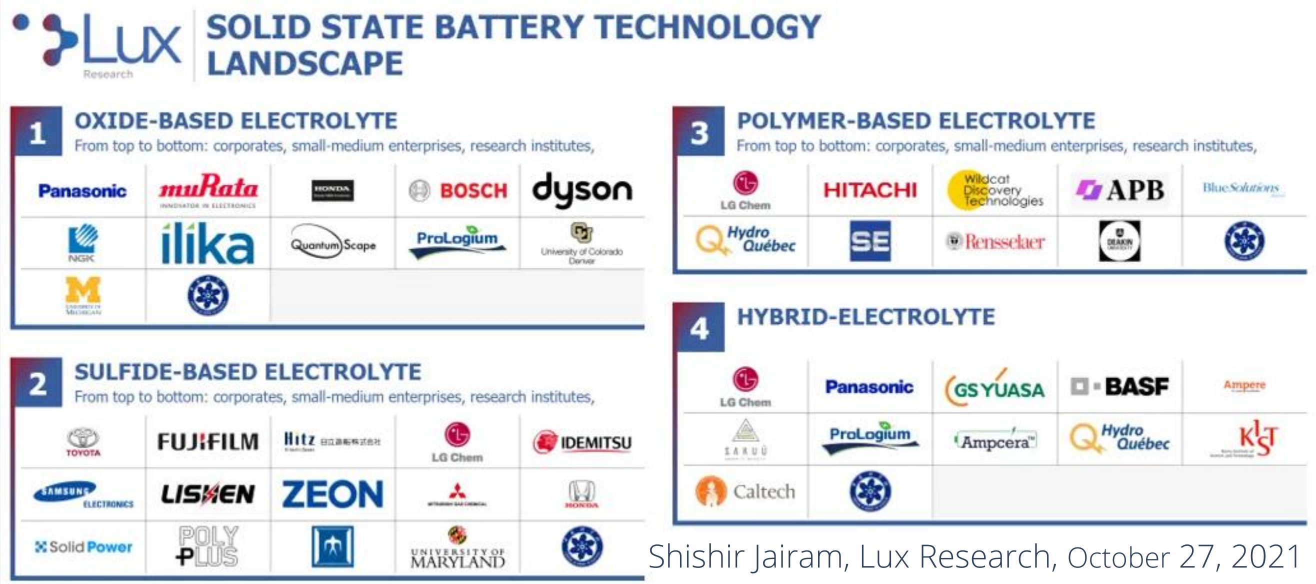
Test	Energy Source	Conditions	Estimated Energy
20 Pulse laser	IR Laser	20 1.9 J pulses	38 J
Nail Penetration	Mechanical	20 mm penetration ~200 lb peak load	1.8 J
Undirected light	Quartz lamp	Exposure to light source through aperture	6000 J*
Thermal Ramp	Thermal	Heat to 200 °C	6300 J**
Overcharge	Electrical	1C to 200% SOC	43200 J***

* Based on radiometer measured flux through aperture
** Calculated for hypothetical 40g cell – larger cells will require more energy
*** Calculated for a hypothetical overcharge at 3 A and 4 V at a 1C rate

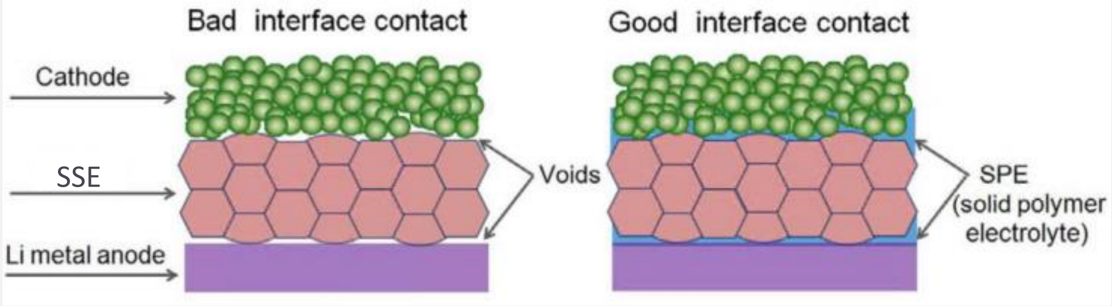
Solid-State Batteries, Why the Excitement?

Two Primary Advantages

- Energy density
  - Li-metal anode
- Safety
  - Replacement of flammable liquid electrolyte



Shishir Jairam, Lux Research, October 27, 2021



Journal of Energy Chemistry 50 (2020) 154–177

Thermal Model

Relevant Reactions

Rxn#	Reaction Description	Reaction Equation
R1	Cathode decomposition	$2MO_2 \rightarrow 2MO + O_2$
R2	Cathode-electrolyte	$2C_4H_8O_3 + 9O_2 \rightarrow 8CO_2 + 8H_2O$
R3	Anode-electrolyte	$4LiC_6 + 2C_4H_8O_3 \rightarrow 4C_6 + 3C_2H_4 + 2H_2 + 2Li_2CO_3$
R4	Cell discharge	$Li + MO_2 \rightarrow LiMO_2$
R5	Anode-oxygen	$4Li + O_2 \rightarrow 2Li_2O$

Failure Modes

Failure Mode	Reactions Involved
External heating	R1, R2, and R3
Short circuit	R4
Mechanical failure	R1 and R5

Shurtz, R.C. (2020). A Thermodynamic Reassessment of Lithium-Ion Battery Cathode Calorimetry.
Shurtz, R.C., and Hewson, J.C. (2020). Review—Materials Science Predictions of Thermal Runaway in Layered Metal-Oxide Cathodes: A Review of Thermodynamics
Shurtz, R. (2021). Lithium-ion Battery Thermodynamic Web Calculator. https://www.sandia.gov/ess-ssl/thermodynamic-web-calculator/.