Lithium Ion Battery Safety

Lloyd Gordon, Nicole Graham, Ray Joggerst

07/24/2017

UNCLASSIFIED

Driver and goal

- Fires and personal injuries from failing lithium ion batteries has received widespread national attention.
- Several lithium ion incidents have occurred at several DOE sites
- It is important for all to be aware of potential risks, counterfeit items, increased regulations, and proper disposal in the use of lithium ion batteries to prevent fire and injury.

Technical Terms - Parameters and Units

Parameter	Symbol	Unit	Symbol
Voltage	V	Volt	V
Current	I	Ampere	A
Time	t	second	s
Power	P	Watt	W
Energy	E	Joule	J
Charge	Q	Coulomb	C
Length	l	meter	m
Capacity		Ampere-hour	A-hr

p = pico = $x10^{-12}$

n = nano = $x10^{-9}$

μ = micro = $x10^{-6}$

m = milli = $x10^{-3}$

k = kilo = $x10^{3}$

M = mega = $x10^{6}$

G = giga = $x10^{9}$

T = tera = $x10^{12}$

Definitions 1

- **Cell -** a single self-contained electrochemical system capable of delivering electrical power and comprising an anode, a cathode, electrolyte, separator, and containing structures.
- **Anode -** the electrode in an electrochemical cell where oxidation takes place. It is the negative electrode of a primary cell.
- **Cathode -** the electrode in an electrochemical cell where reduction takes place. It is the positive electrode of a primary cell.
- **Electrolyte -** a conducting medium in which the flow of electric current takes place by migration of ions.
- **Separator -** porous, nonconductive material interposed between the electrodes of a cell to prevent internal short circuits.
- **Battery -** a single cell or several cells connected in series or parallel.
- **Battery Bank -** several batteries connected in series or parallel.

Definitions 2

- **Primary battery -** a non rechargeable battery
- **Secondary battery -** a rechargeable battery
- **Negative electrode -** the electrode undergoing reduction on charge and/or oxidation on discharge
- **Positive electrode -** the electrode undergoing oxidation on charge and/or reduction on discharge
- **Oxidation -** chemical process in which a substance donates electrons
- **Reduction -** chemical process in which a substance accepts electrons

Definitions 3

- **Capacity -** the total number of ampere-hours that can be withdrawn from a fully charged cell or battery under specified conditions of discharge.
- **Overcharge -** electrical charge or process in which more charge is supplied to a battery than is required to convert the electrodes to the fully charged state.
- **Overvoltage -** difference between the operating voltage of a cell on charge or discharge and the open-circuit voltage of the cell, both at the same state of charge.
- **Polarization -** departure of the voltage of an electrode or of a battery from its equilibrium value.
- **Reversal -** process in which discharge current is forced through a cell after its capacity has been exhausted.

Definition 5

- **Battery Explosion** - an energetic event resulting in a battery coming apart in two or more pieces
- **Venting** - a release of pressure, sometimes with flame, but battery stays together

Lithium Batteries VS. Lithium Ion Batteries

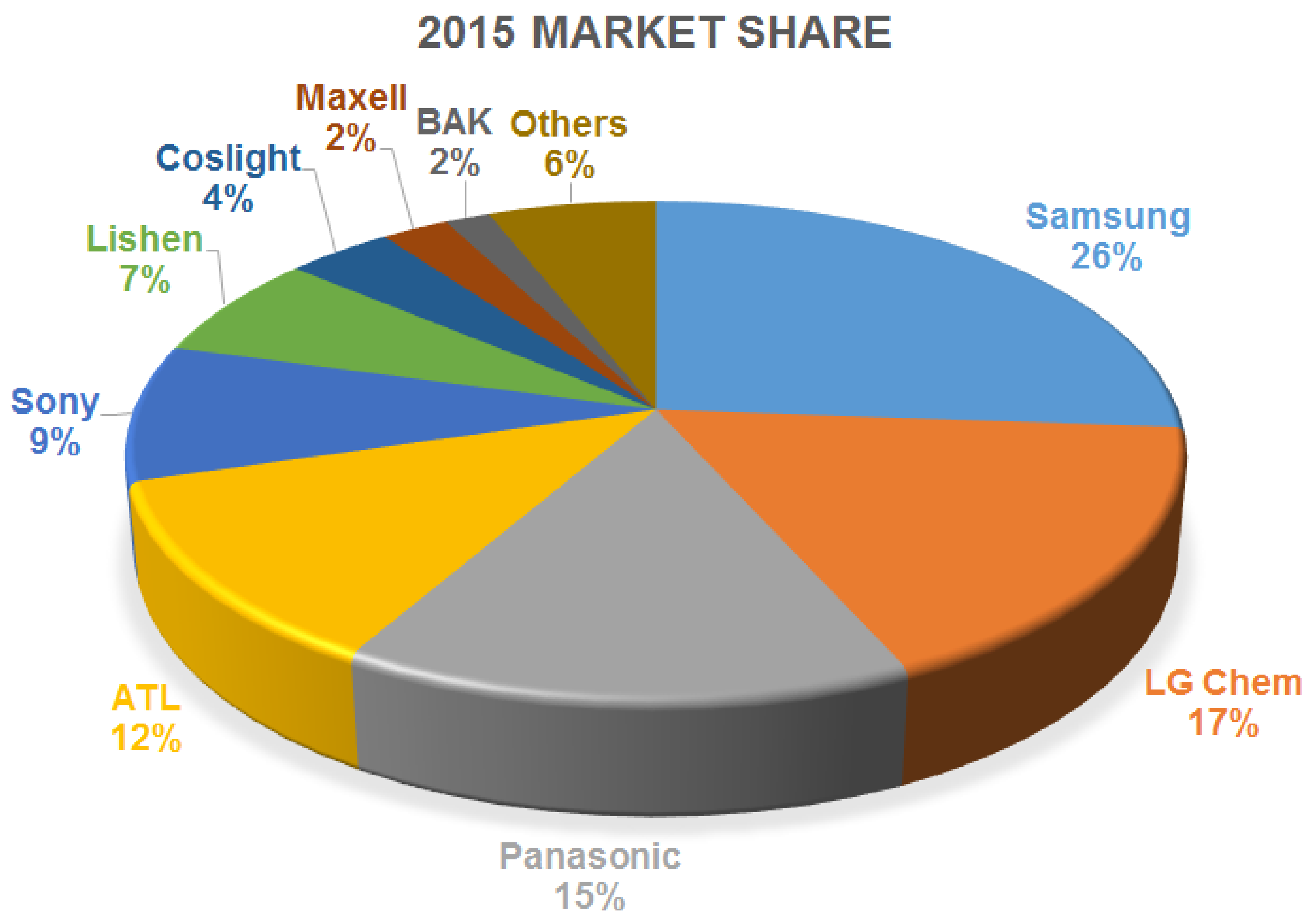
- Lithium batteries, or primary batteries, are single use and incapable of recharge.
- Lithium ion (Li-ion) batteries, or secondary batteries, are rechargeable and used world-wide.
- Both contain highly flammable electrolytes

Lithium Ion Batteries

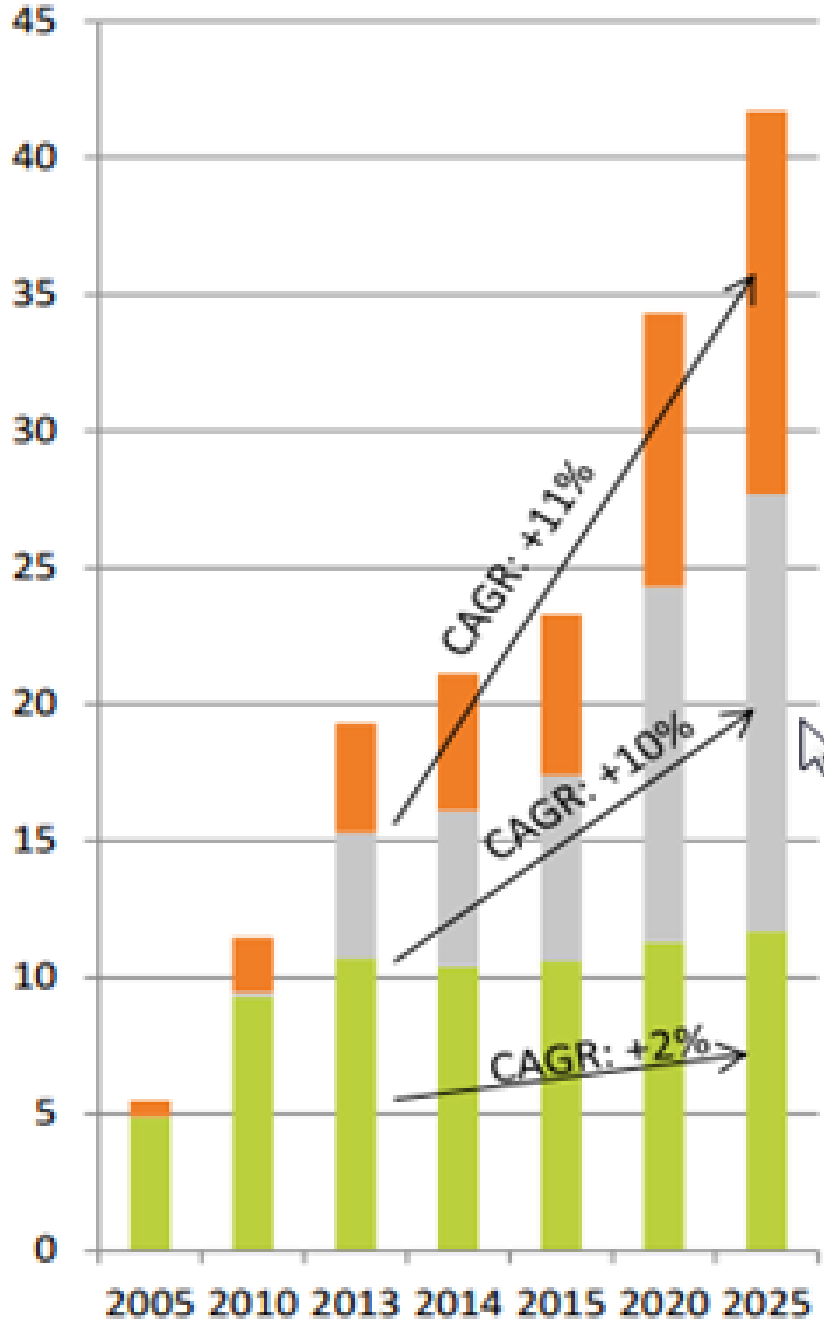
- Lithium-ion (Li-ion) batteries are a relatively new technology that provides the highest energy density (both mass and volumetric) available in a secondary (rechargeable) battery.
- This gives the longest lifetime for a given size for portable devices.
- Li-ion batteries are now used for all laptop, cell phone, and digital camera applications, and are fast becoming the preferred technology for battery powered hand tools, and portable medical emergency equipment.

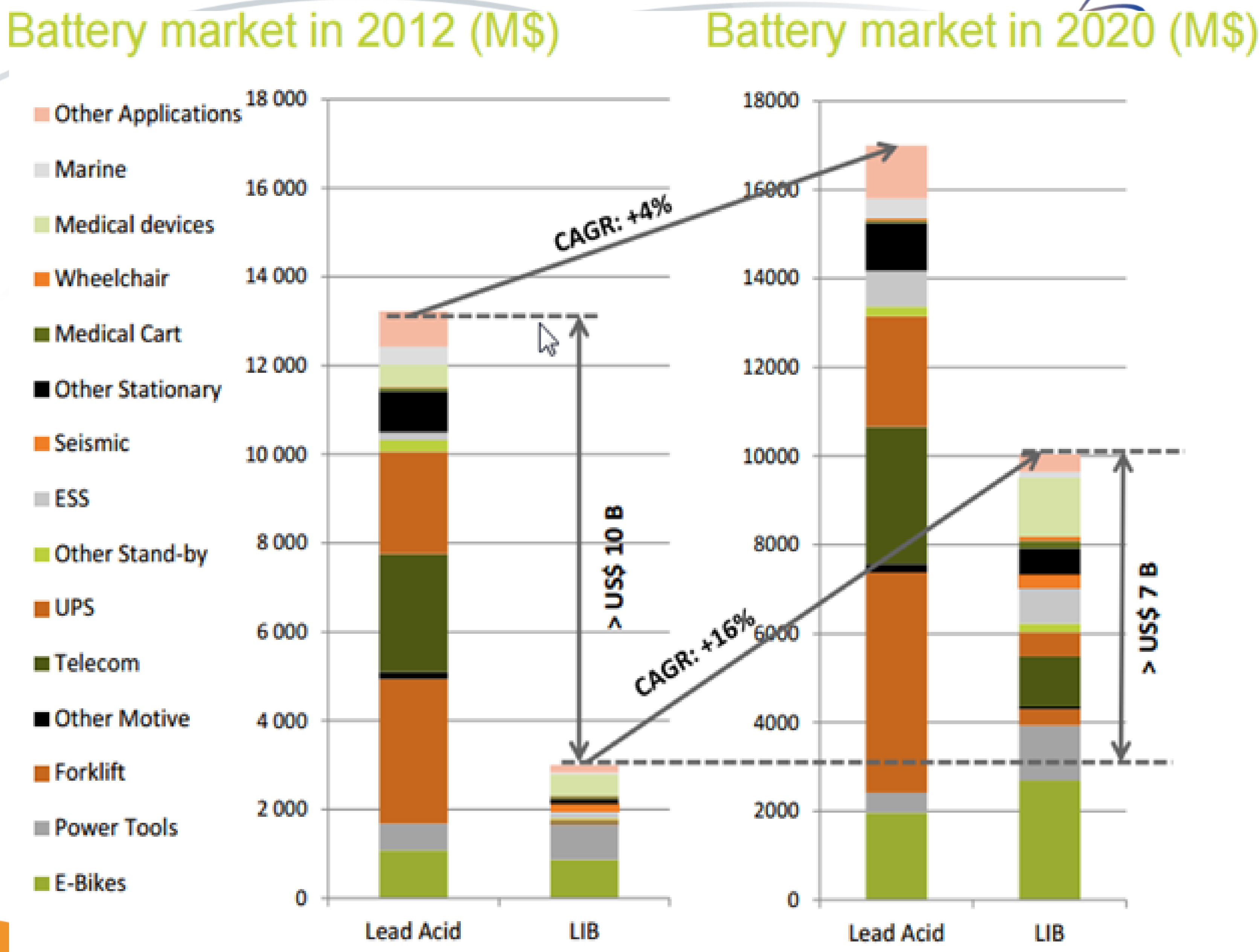
Over 2 billion lithium ion batteries are used annually in the U.S.

- Laptops
- Mobile phones
- Cameras
- Electric vehicles
- Electronic cigarettes
- Battery powered tools
- Portable emergency equipment (AEDs)
- Military
- Toys (e.g., hoverboards)


2015 MARKET SHARE
Maxell
2%
BAK
2%
Others
6%
Coslight
4%
Lishen
7%
Samsung
26%
Sony
9%
ATL
12%
LG Chem
17%
Panasonic
15%

Li-ion Pack market[1] (B$)




Battery market in 2012 (M$)
Battery market in 2020 (M$)
Other Applications
Marine
Medical devices
Wheelchair
Medical Cart
Other Stationary
Seismic
ESS
Other Stand-by
UPS
Telecom
Other Motive
Forklift
Power Tools
E-Bikes
18 000
16 000
14 000
12 000
10 000
8 000
6 000
4 000
2 000
0
Lead Acid
LIB
CAGR: +4%
CAGR: +16%
> US$ 10 B
> US$ 7 B
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
Lead Acid
LIB

Classes of lithium-ion cells

- Cylindrical
  - 18650, 20650, 21700 (18 mm dia x 650 mm long)
- Prismatic
- Laminate (polymer)

Laptop Lithium-Ion Batteries

UNCLASSIFIED

Lithium-Ion and Lithium-Polymer Batteries

Suitable for diverse wearable devices

Flat · Mini · Curved Cell Technology

Flat Cell

Mini Cell

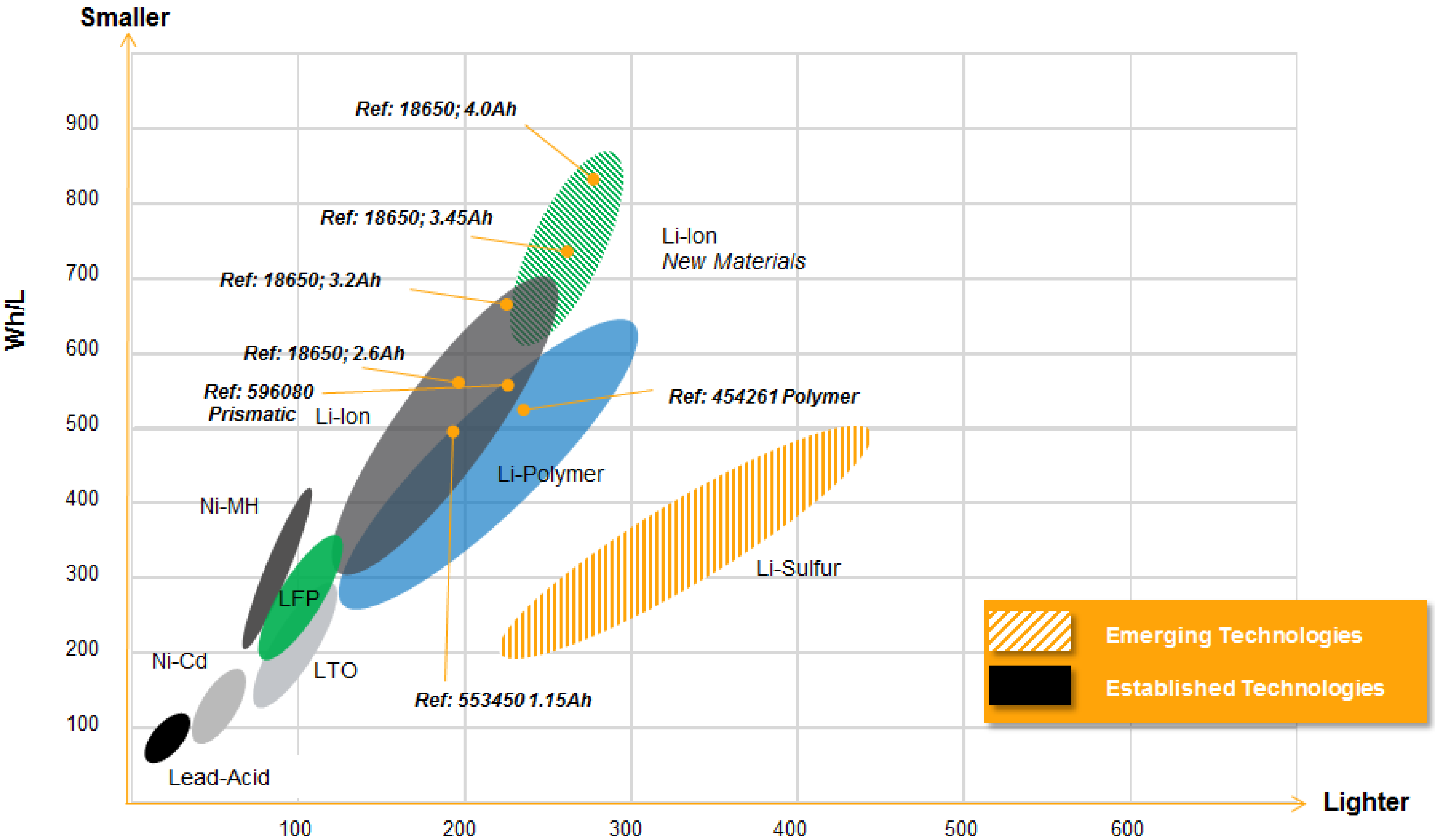
Curved Cell

Smart Watch

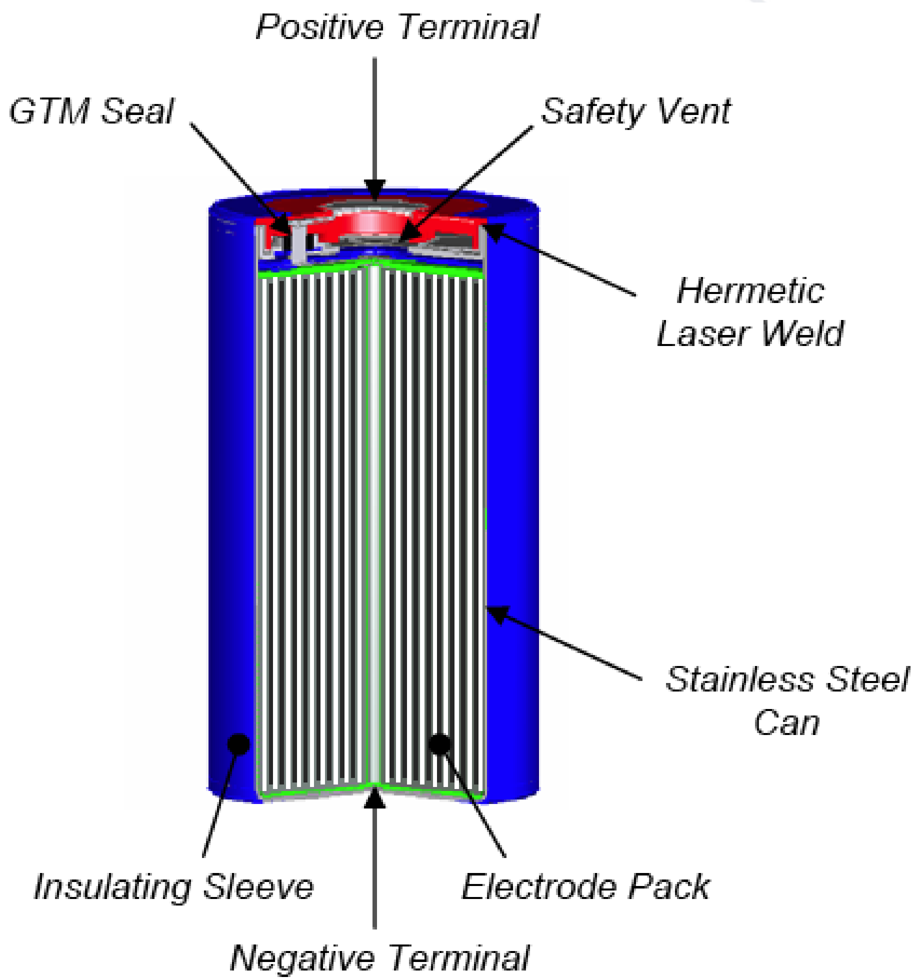
Smart Band

Action Camera

Smart Glasses


Smaller
Wh/L
900
800
700
600
500
400
300
200
100
Ref: 18650; 4.0Ah
Ref: 18650; 3.45Ah
Ref: 18650; 3.2Ah
Ref: 18650; 2.6Ah
Ref: 596080
Prismatic
Li-Ion
Li-Ion
New Materials
Ref: 454261 Polymer
Li-Polymer
Ni-MH
LFP
Li-Sulfur
Ni-Cd
LTO
Ref: 553450 1.15Ah
Lead-Acid
Emerging Technologies
Established Technologies
100
200
300
400
500
600
Lighter

Li-Ion battery construction



Lithium-ion technology

- There are many different chemistries. Some are safer than others.
- Li ions are transported
  - to/from carbon anode
  - to/from $LiCoO_2$ cathode
  - through a liquid organic electrolyte (flammable)
  - electrodes are held apart by a porous separator
- During normal use, in a healthy state, there is no metallic lithium
- Lithium-ion batteries are fragile and can have violent failure modes
- With proper care and protection, Li-ion battery technology is SAFE
- The fastest growing, and highest energy density battery technology

Characteristics of the Lithium-ion cell

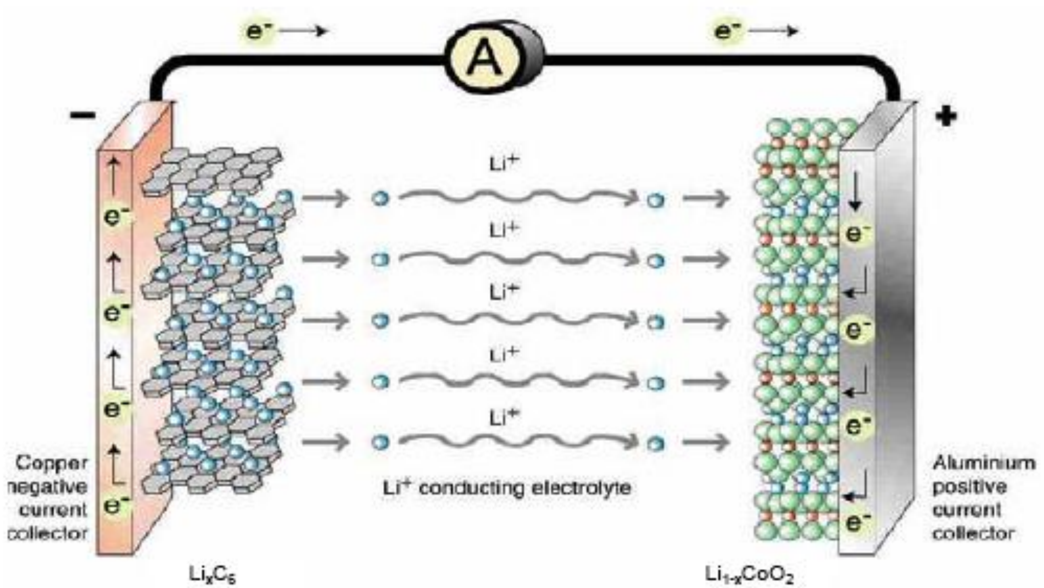
- Full charge voltage - 4.2 V
- “nominal” voltage - 3.6 V
- Rated in AmpHours (Ah)
- Charge and discharge measured in “C”
  - 1 C is the current that discharges the battery in 1 hour
  - for a 5.2 Ah cell, 1 C = 5.2 A, 2 C = 10.4 A, 0.5 C = 2.6 A
- The most common Lithium-ion technology
  - Cobalt Lithium-ion
  - Used for laptops, cell phones, cameras

Lithium-ion cycle

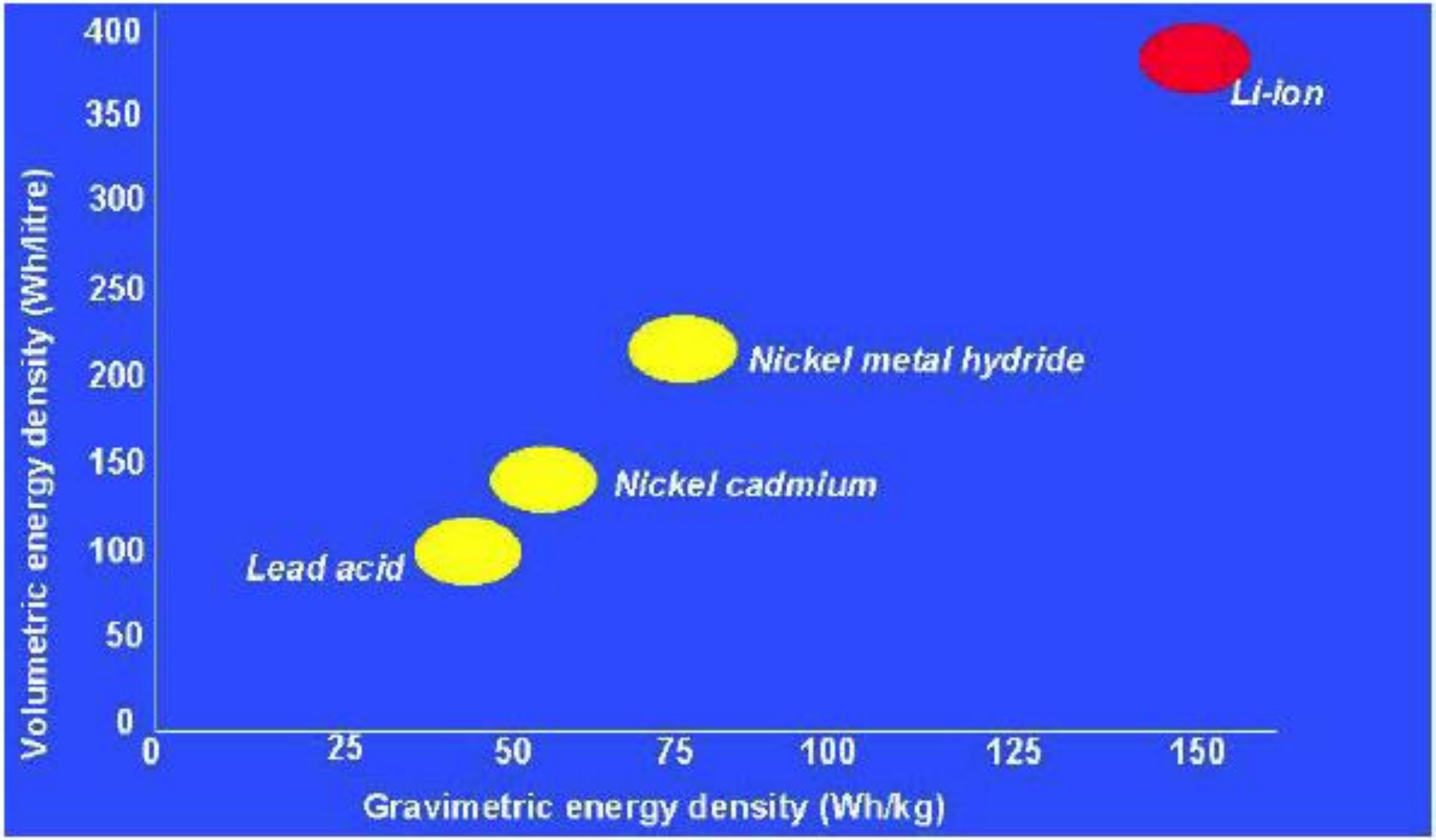
Discharging→

$$2Li_{1-x}CoO_2 + Li_{2x}C_6 \longleftrightarrow 2Li_{1-dx}CoO_2 + Li_{2dx}C_6$$

← Charging



Energy Density Comparison Chart



Lithium Ion Battery Safety

- Li-ion batteries are a safe technology if certain precautions in design and use are followed.
- If such precautions are not taken, Li-ion batteries can fail dramatically causing equipment damage, fire and possible personal harm.

Cause of failure

- Errors in manufacturing.
  - You will not be able to detect these problems before the battery starts failing.
- Over heating.
- Charging while the battery is too cold.
- Charging or discharging too fast.
- Mechanical damage.
- Shorting the battery.

Li-ion Safety

- Several mechanisms of abuse can cause metallization of the lithium ions (lithium ions bond together into a metallic form)
- Several mechanisms of abuse can cause thermal runaway, leading to:
  - further metallization of lithium
  - reduction of cathode creating oxygen
  - boiling of electrolyte
- Failure mode can be catastrophic
  - Once the metallized lithium melts, a violent, energetic chemical reaction occurs, with high temperatures and potentially high pressures

Protection of Li-ion batteries

- To prevent hazardous failure, and to maintain safe use, the following protections must be employed
  - protection against overcharge (V < 4.3 V)
  - protection against undercharge (V > 2.5 V)
  - protection against over charging (less than 1 C in)
  - protection against over discharging (less than 1 C out)
  - protection against over temperature
  - protection against over pressure
- Each cell in a battery pack must be protected
- Series configurations are the most susceptible to failure

Battery Manufacturer (AGM) Design Guides

- Lithium-ion cells must always be operated within strict voltage limits.
- Minimum protection requirements
  - individual cell voltage monitoring
  - prevention of over-charge, of any single cell
  - prevention of over-discharge, of any single cell
  - prevention of over-current
- Warning in Battery Manufacturer's Design Guide

NEVER, UNDER ANY CIRCUMSTANCES, PRODUCE BATTERIES THAT DO NOT INCORPORATE THESE MINIMUM PROTECTION REQUIREMENTS.

Voltage Limits on Li-ion Batteries

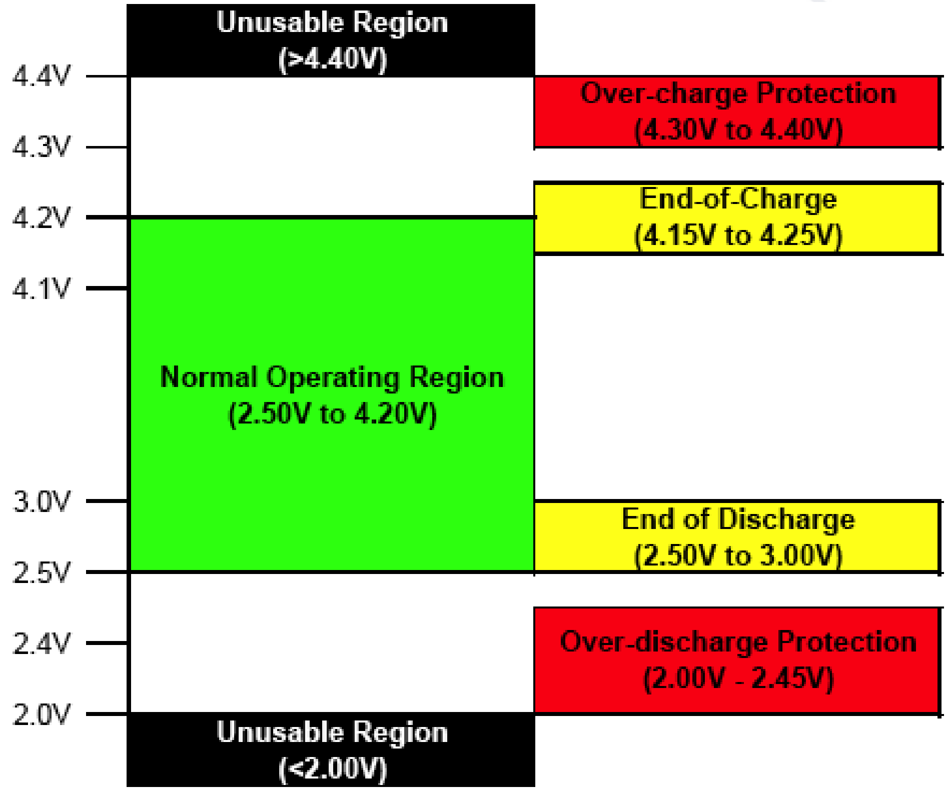


Figure 2: Typical lithium-ion cell voltage limits

Typical Battery Manufacturer (AGM) Design Guides - cont.

- Battery Charging
  - Limit the charging current to 1.73 A for the 5.2 Ah rated cell.
  - Higher charge currents will shorten the cell life
  - Limit the c

TYPICAL CHARGE GRAPH

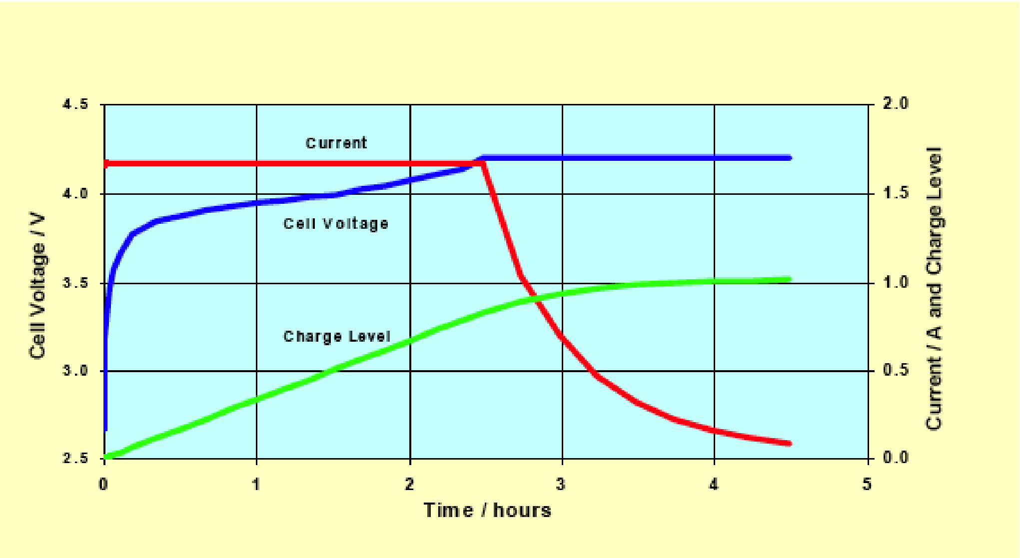


Figure 3: Typical CCCV charge graph (C/3 + 2h)

Failure modes

- Lithium ions plate out as lithium metal, create a short and catch on fire.
- Small metallic particles, introduced as contamination in manufacturing, create a short and catch on fire.
- The separator, often only 24µm thick, punctures, creating a short and catching on fire.
- Battery swells with CO_2, bursts exposing lithium to water in the air, which then catches on fire.
- Over charging causes $LiCoO_2$ to release O_2, which reacts with the electrolyte and catches on fire.
- In all above cases the electrolyte catches on fire.

Failure process of Li-ion Batteries

- Without protection, cells in a series configuration are very susceptible to failure
- Continued charging and discharging in series led to a cell failure
- Premature cell failure was likely enhanced by:
  - using a charger with 20% higher current than recommended by battery manufacturer
  - using a charger with x 2 more charge time at 4.2 V
  - could have led to gradual metallization and/or corrosion due to overcharge
- Gradual failure probably occurred over weeks

Failure process of Li-ion Batteries - part 2

- No two batteries are alike, even starting with all new batteries of identical model
- As batteries age naturally, or under stress, one battery begins to show more degradation than the others
- In a series string, the weakest battery is stressed by the other batteries
- Ultimately the weakest battery begins to lose the capacity to charge, ultimately dropping below 2.5 V
- Without protection, when a Li-ion battery fails to the point of less than 2.0 V, copper shunts develop that can short the cell
- The copper shunts lead to a cell with close to 0 V, or even reverse polarization (even at 1 - 2 V)

Failure process of Li-ion Batteries - part 3

- When recharging a series string with a weak cell (less than normal voltage), without protection, with a fixed charging voltage:
- Excess voltage is applied to the other cells
- This was compounded by holding that excess voltage for 4 hours
- With overcharging (> 4.2 V/cell) lithium metallization at the anode occurred on the "good" cells

Failure process of Li-ion Batteries - part 4

- A combination of copper shunt growth in the weakest cell, plus lithium metallization in the over voltaged cells, ultimately led to a thermal runaway
- As thermal runaway develops
  - temperature rises
  - chemical processes accelerate
  - the metallized lithium begins to melt
  - the cathode reduces generating oxygen
  - the electrolyte begins to boil
- Once the lithium melts and the electrolyte boils a catastrophic runaway even occurs resulting in
  - rapid pressure buildup
  - rapid temperature increase
- The battery explodes

Failure process of Li-ion Batteries- part 5

- Once a single cell in a battery pack goes into thermal runaway, it quickly heats adjacent cells causing a cascade effect.
- A string of batteries in a cascade failure process can destruct in milliseconds to minutes.

Other Li-ion Battery Failure Modes

- Shorting out, piercing, crushing, applying a reverse current, or heating a Li-ion battery can lead to very high case temperatures or battery explosion.
- Allowing a Li-ion battery to remain in a discharged state for a prolonged time will irreversibly damage the battery.
- A Li-ion battery loses 1 to 5 % of its charge per month when not in use.
- Storing a Li-ion battery for 18 months (when starting with a full charge) or 3 months (when starting in a low charge state) can irreversibly damage the battery.

Example of Li-ion Battery damage to laptops

Incidents at LANL

- August 6th, 2007: Lithium Ion battery explosion.
- January 21st, 2010 Lithium Ion Phosphate battery explosion.
- January 6th, 2016: Electronic Cigarette Incident

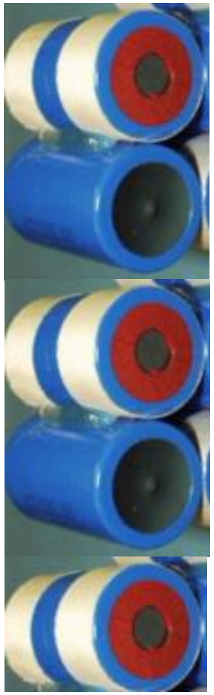
Lithium Ion Battery Accident on LANL R&D equipment in 2007

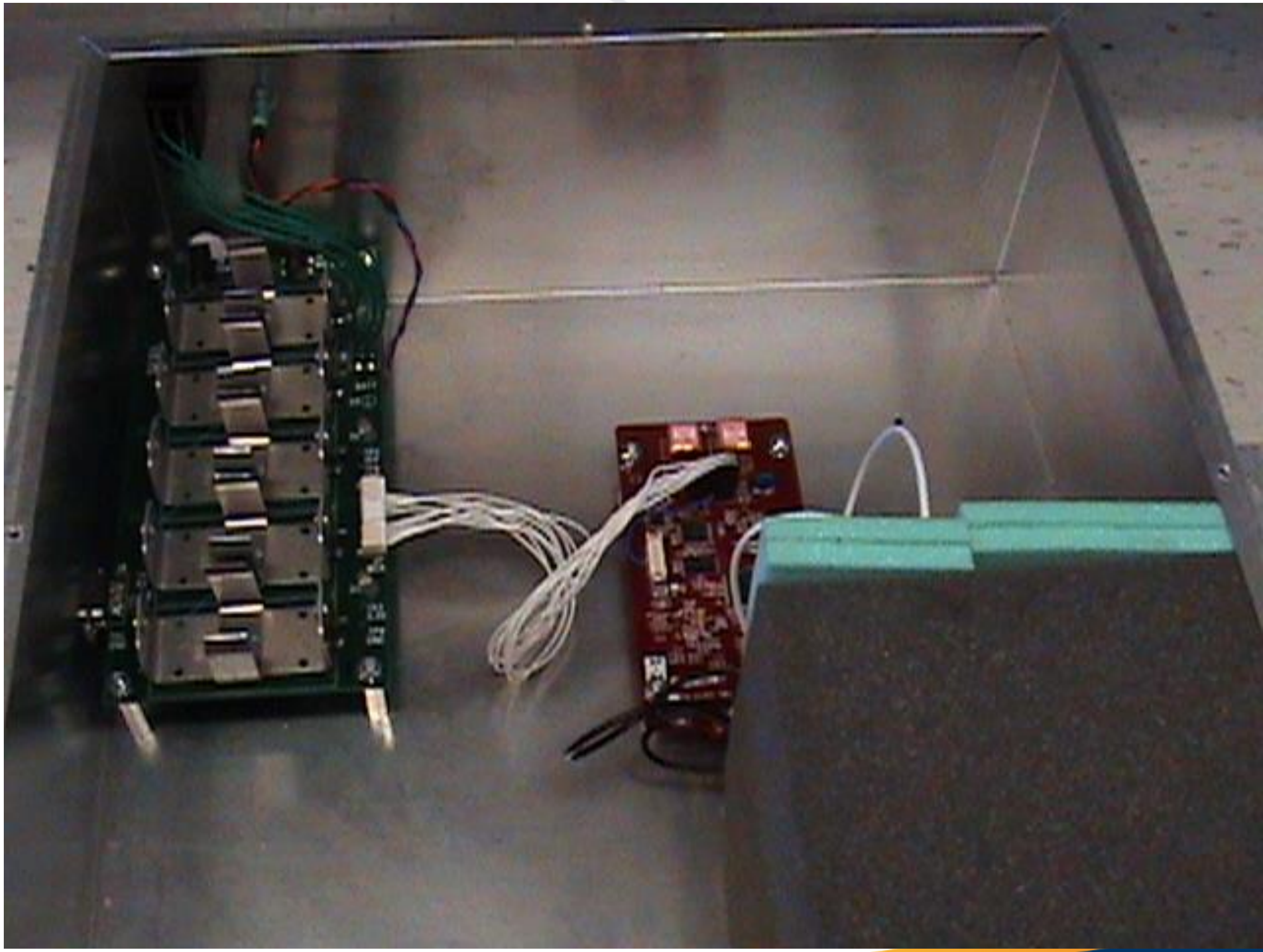
- Improperly matched charger to a series of 5 lithium ion batteries
- Lithium metallization over 3 months
- Battery explosion at 11 pm, no one present

Lithium Ion Battery Accident on LANL R&D equipment - August 6, 2007

- Portable radiation detection instruments under development and testing
- Powered by 5 Lithium Ion batteries in series
- Charger was not properly matched to the batteries
- Over three months stress to batteries led to metallization of the lithium
- Explosion occurred at 11 pm at night, no one present

Inside of Test Equipment prior to Event



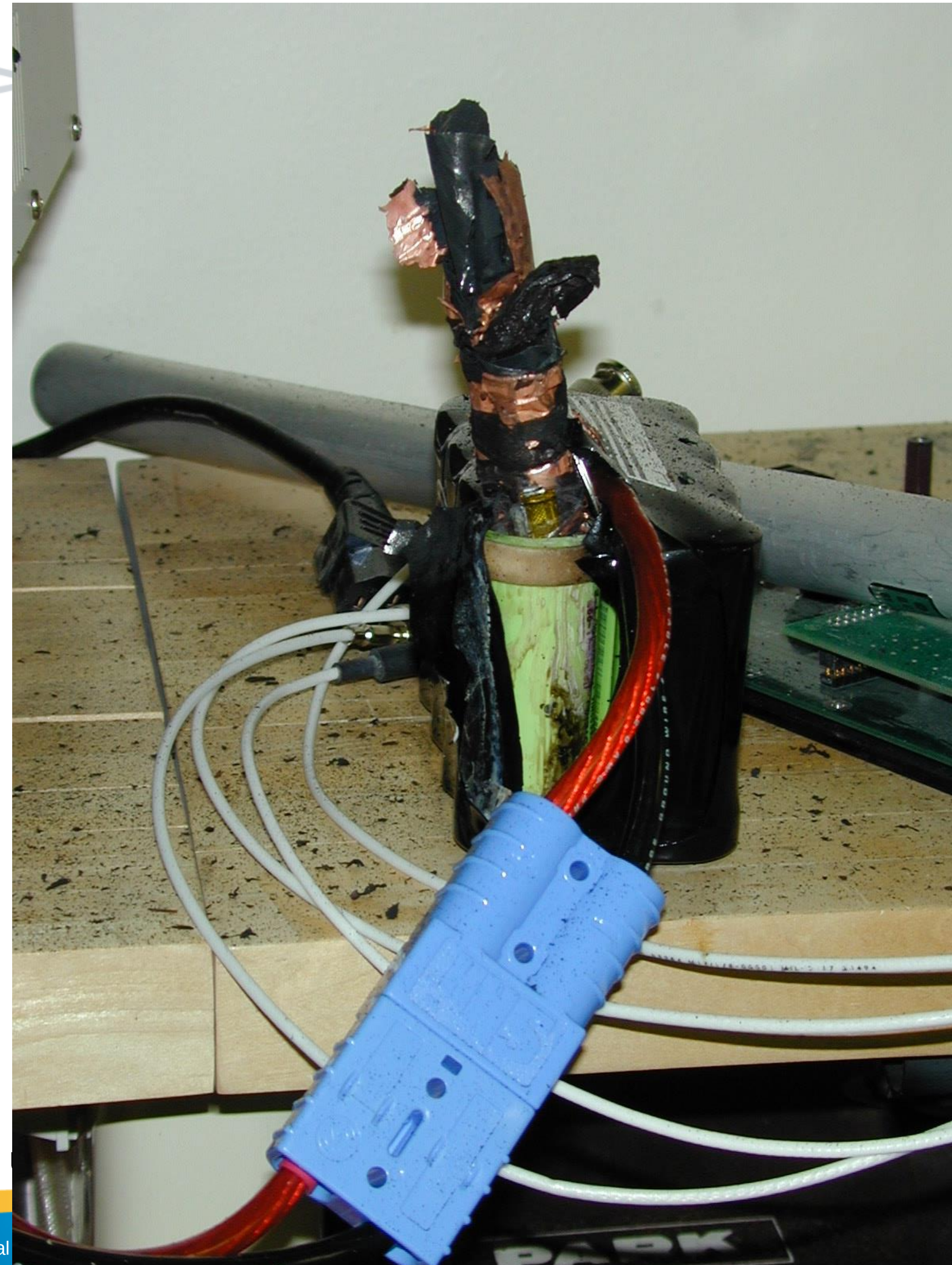


Showing cover plate blown open

View inside, showing charred remains

Inside, showing one remaining battery in clip

Lithium Ion Phosphate battery explosion on January 21, 2010



Lithium Ion Battery "fire" NISC building Tuesday, January 5, 2016

Lloyd B. Gordon, CESO

January 7, 2016

Summary of Facts from Lithium-Ion Battery failure STO FOD Fact Finding, Wednesday, January 6, 2016

- Facts
  - A worker had personal electronics at work (electronic cigarette, four batteries, and charger)
  - The cigarette uses two LiIon batteries, in series
  - While taking the used pair of batteries out of a holder, in preparation for recharging, one battery began to heat and vent, with flame
  - The worker dropped the battery onto the floor
  - The battery spun around, spewing sparks, “flame” and smoke
  - Coworkers put out the “fire” with a class ABC fire extinguisher
  - There was no injury to any personnel, no damage to the facility.
  - The fire extinguisher products triggered the facility smoke detector
  - The worker had purchased the LiIon batteries from Ebay
- Note: the words “flame” and “fire” are not classical heat induced combustion, in the normal use of the words, but a rapid exothermic reaction between Lithium metal and oxygen and/or water. No heat source is required to start this reaction once water or oxygen reaches lithium metal. This is known as a alkali metal fire or reaction. The primary byproduct of this reaction is hydrogen, which then rapidly burns in the presence of oxygen.

Analysis of Incident

- The Chief ESO met with the worker following the fact finding, and reviewed the equipment and specifications.
- The following is subject to further validation:
  - The Lithium Ion batteries, purchased from Ebay likely did NOT have protective circuitry, which is required of all LiIon batteries to prevent the plating out of lithium metal, which is normally only in Ion form (non metallic) in a healthy LiIon battery.
  - The charger seemed to be built safely to prevent overcharging.
  - The cigarette had been modified by the worker to produce more power in the vaporization of the material
  - It is very probable that the battery load (the electronic cigarette) caused the LiIon batteries to over discharge (dropping below 2.5 V per cell) causing the lithium to plate on the electrodes in metal form.
  - After repeated over discharging, and the plating of sufficient lithium metal, one battery went into thermal runaway, where it began to heat, which caused more heat, and ultimately caused the electrolyte (a liquid polymer) to decompose creating some oxygen and water products.
  - Once the water/oxygen reached the lithium, the lithium reaction started.

Conclusions

- Lithium Ion battery fires have recently received additional press due to new products coming out, that are not being built to existing lithium ion battery safety standards. Many injuries and fires have been reported, including from electronic cigarettes. This includes products such as hover boards and electronic cigarettes.
- The combination of purchasing cheap or possibly even counterfeit LiIon batteries without protective circuitry, plus modification of the product by the user, caused damage to the batteries, leading to the fire.
- The worker did not violate any existing laboratory policy or requirement.

Vented Lithium Ion battery

Closeup of battery

Electronic Cigarette Incident Summary

- An employee's electronic cigarette contained two lithium ion batteries. One battery ignited.
- Batteries had been purchased from ebay and had no protective circuitry.
- Electronic cigarette had been altered for much higher output, which impulse loaded the batteries.
- No injuries or LANL policies violated.

Lithium Ion Batteries Nationwide

- Lithium ion battery fires have recently received additional press due to new products that have caused many reported injuries and fires, including hover boards, and mobile phones.

Regulations for Lithium Ion Batteries

- Despite numerous recalls on lithium ion battery products due to fire hazard, the Consumer Product Safety Commission (CPSC) currently has no regulations, mandatory standards, or bans on lithium ion batteries.

Regulations for Lithium Ion Batteries

- According to USA today more than 30 universities now ban hover boards on campus due to fire hazard, including:
  - University of New Mexico
  - Purdue University
  - Vanderbilt University
  - University of Massachusetts Amherst

U.S. Regulations relevant to batteries

- Federal Hazardous Substances Act (FHSA)
- Federal Hazardous Substances Act Regulations
- Federal Hazardous Packaging Act (PPPA)
- Federal Trade Commission, Fair Packaging and Labeling Act.
- U.S. Dept. of Commerce, NIST, Model State Packaging and Labeling Regulations

Covers batteries that contain toxic, corrosive, irritational, flammable or combustible, and pressure-generating substances.

Regulations for Lithium Ion Batteries

- Amazon complies with the following regulations when shipping lithium batteries:
- U.S. Department of Transportation
- United States Postal Service
- IATA's Dangerous Goods Regulations (DGR)
- IATA's Lithium Batteries Guidance
- ICAO's Technical Instructions for the Safe Transport of Dangerous Goods by Air

Regulations for Lithium Ion Batteries

- Federal Aviation Agency (FAA) regulations:
  - Spare lithium ion and lithium metal batteries must be carried in carry-on baggage
  - 2 grams of lithium per battery and 100 Whr limit
  - Batteries for further sale or distribution are prohibited
  - With airline approval up to 2 larger lithium ion batteries (101-160 Whr) may be carried on board.

Recommended Actions

1. Understand general lithium ion battery safety
2. Know how to identify a counterfeit battery
3. Know what to do in case of a lithium ion battery fire
4. Understand lithium ion battery disposal

Recommendations - Design

1) Li-ion batteries (individual cells) and battery packs (multiple cells connected together) should be properly protected for
   1) under voltage
   2) over voltage
   3) excess charging rate
   4) excess discharging rate
   5) over temperature
   6) over pressure
2) Design, installation, protection, maintenance, and use of Li-ion batteries in equipment should be well-documented, and a rigorous design review should be conducted prior to release for use.

Recommendations - Care and use - page 1

Do not dip or wet a Li-ion battery in water, seawater, or other liquid.

Do not put a Li-ion battery into a fire.

Do not heat a Li-ion battery.

Do not install a Li-ion battery backwards (in reverse polarity) both in the equipment, and in a charger.

Do not short a Li-ion battery.

Do not apply any heavy impact to a Li-ion battery, throw or drop it.

Recommendations - Care and use - page 2

Do not solder the battery directly.

Do not drive a nail into, hammer, or stamp on a Li-ion battery.

Do not disassemble or alter a Li-ion battery or battery pack.

Do not use or leave a Li-ion battery near fire, heaters, inside an automobile in hot weather, or under strong sunshine.

When charging a Li-ion battery, do not use any battery charger not specified by the manufacturer. Always follow the charge conditions specified by the manufacturer.

Do not connect a Li-ion battery directly to any electrical outlet in the home, office, car, etc.

Recommendations - Care and use - page 3

Do not put a Li-ion battery into a microwave oven or a pressure cooker.

Do not use Li-ion batteries with any primary (non rechargeable) battery.

Replace all Li-ion batteries in a multi-battery system at the same time.

Do not mix Li-ion batteries in a multi-battery system with any other type of battery.

Use the same brand, capacity, size, and type of Li-ion batteries in a multi-battery system.

If you notice any unusual odor, heat, discoloration, deformation, or any other abnormal characteristic while using, charging, or storing a Li-ion battery, take it out of the equipment or charger, and avoid using it. Dispose of properly.

If the Li-ion battery leaks or emits an unusual odor, remove it from the vicinity of any heat source. The electrolyte is flammable.

Recommendations - Care and use - page 4

Do not allow leaked electrolyte to come into contact with the eyes. In the event of such contact, flush the eyes with plenty of water immediately, and consult a doctor.

If the battery leaks and its electrolyte comes into contact with skin or clothing, wash the contact area well with tap water or other clean water right away.

When the Li-ion battery is expected not to be used for a long time, take the battery out of the equipment and store it in a less humid area.

Do not store Li-ion batteries in a discharged state.

After long periods of storage without being used, the battery should be charged before use.

If a Li-ion battery does not accept a charge, or if the charger indicates a failed, bad, or invalid battery, do not use the battery, and dispose of it properly.

1. Understand General Lithium Ion Battery Safety

- Store batteries at room temperature
- Do not expose batteries to high temperatures such as could be achieved in a parked car in the sun
- Use a charger designed for the battery or device
- When feasible, do not leave a battery charging unattended
- Store batteries separately from anything hazardous, such as explosives, combustibles, or any other highly flammable material
- Avoid over-charging, over discharging, or shorting
- Watch for signs of failure such as discoloration or swelling
- Dispose of the battery before the expiration date or when the battery is no longer functioning properly

2. Know How to Identify a Counterfeit Battery

- Compare your batteries with pictures on listed website
- Buy your batteries from a reputable source
- Measure and weigh the batteries, compare to spec sheet
- Look for unusual wear and tear like burns, rust, or excessive scratches

3. Know What To Do In Case of a Lithium Ion Battery Fire

- For Lithium (primary, non- rechargeable) batteries: Use Class D extinguishing agent with copper powder. DO NOT use water
- For Lithium-Ion (secondary, rechargeable) batteries: Use an ABC dry chemical fire extinguisher or, for small batteries, use water to keep the fire from spreading.

4. Know What To Do In Case of Exposure to a Lithium Ion Battery

In case of contact with electrolyte, gases, or combustion byproducts from a lithium battery or lithium ion battery release:

- Immediately flush eyes with a direct stream of water for at least 15 minutes and seek immediate attention
- Flush skin with cool water or shower for at least 15 minutes and seek medical attention if necessary
- Move to fresh air and monitor breathing and circulation. Take appropriate first aid or CPR actions as necessary and seek immediate medical attention

Q&A