Battery energy density, safety, and LENRs

Global quest to improve performance drives battery R&D toward ever-higher energy densities

High gravimetric energy density rewards battery users with lighter portable or mobile power sources and longer operating times between recharges

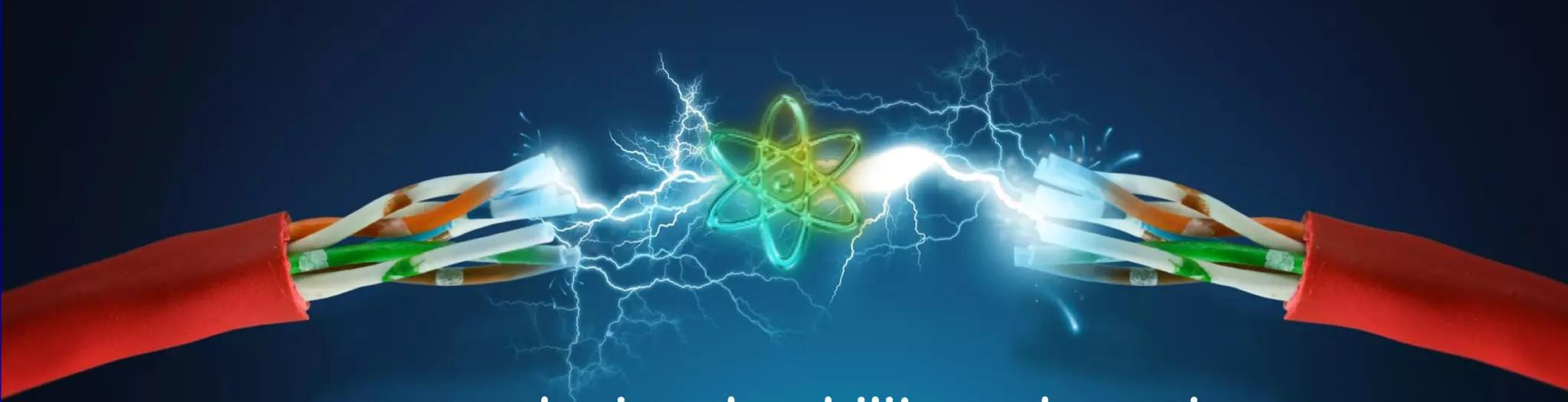
Product safety & reliability could be the hidden costs --- higher energy density is two-edged sword that cuts both ways

Lewis Larsen
President and CEO
Lattice Energy LLC
April 14, 2016

Contact: 1-312-861-0115   Chicago, Illinois USA
lewisglarsen@gmail.com

LENRs = ultralow energy neutron reactions

Internal electrical shorts, hot sparks, and catastrophic electric arcs …



… are reducing durability and causing thermal runaways, fires, and even explosions in Lithium-ion batteries

Competition pushing batteries to ever-higher energy density

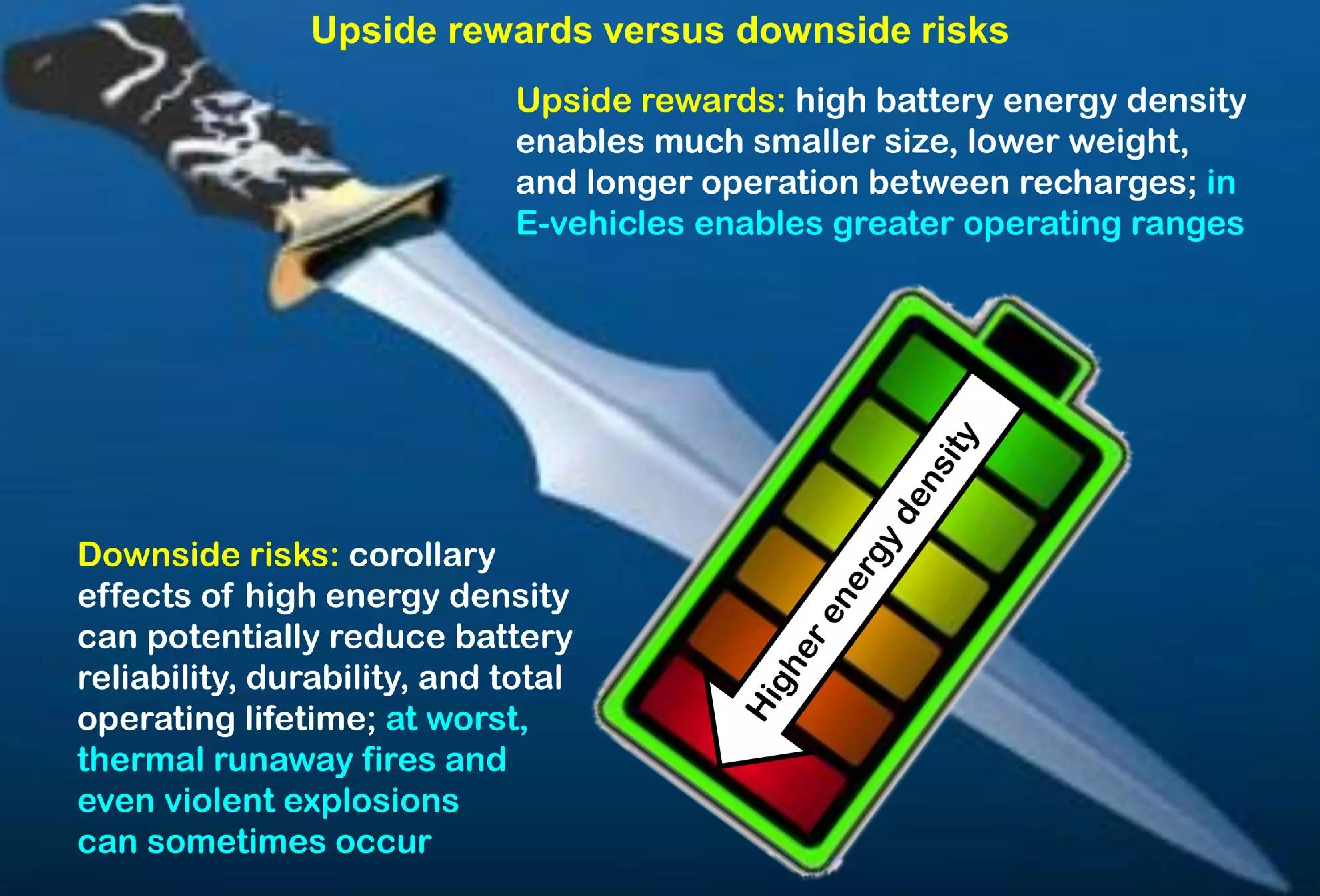
Thermal runaways fires and explosions

LENRS may cause some of these extreme events

Engineering for LENR effects
could help improve battery safety and durability

Higher battery energy density is a two-edged sword

Upside rewards versus downside risks



Upside rewards: high battery energy density enables much smaller size, lower weight, and longer operation between recharges; in E-vehicles enables greater operating ranges

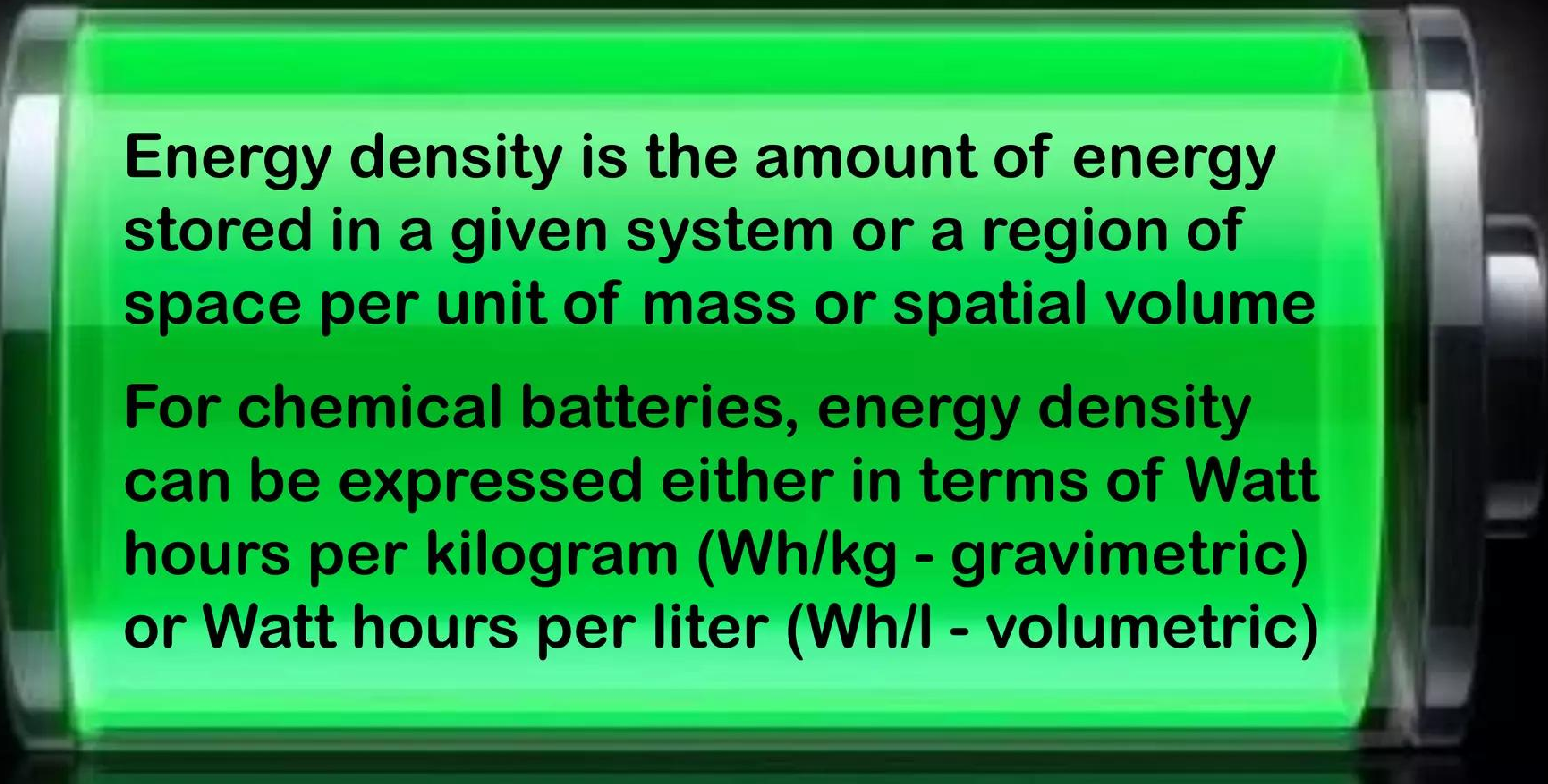
Downside risks: corollary effects of high energy density can potentially reduce battery reliability, durability, and total operating lifetime; at worst, thermal runaway fires and even violent explosions can sometimes occur

Contents

Energy storage is key component of global energy system

Dominant storage technology is chemical batteries that store electricity

Companies strive to boost energy density because it increases storage capacity



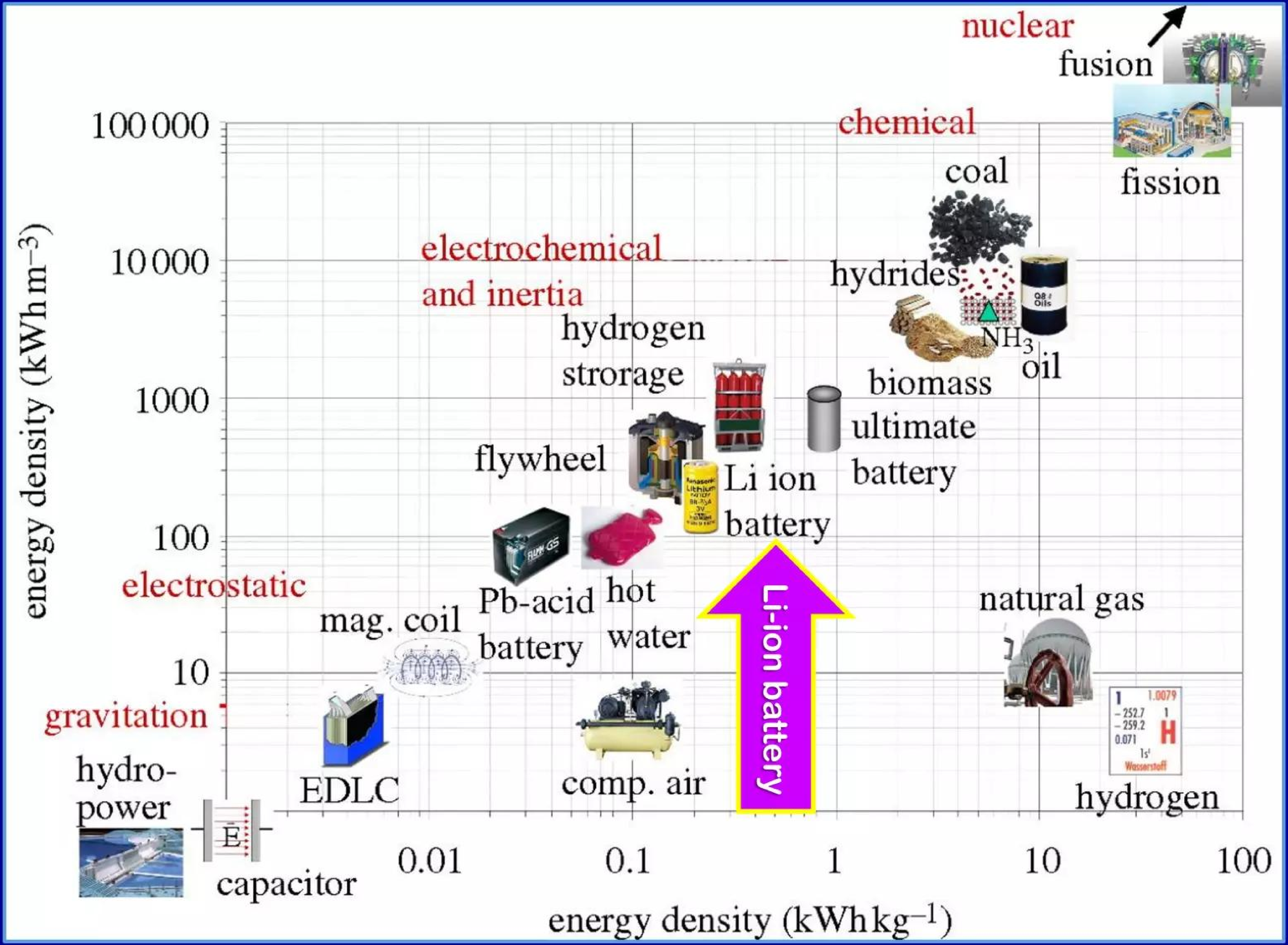
Energy density is the amount of energy stored in a given system or a region of space per unit of mass or spatial volume

For chemical batteries, energy density can be expressed either in terms of Watt hours per kilogram (Wh/kg - gravimetric) or Watt hours per liter (Wh/l - volumetric)

Batteries have become indispensable in modern life

Energy density of technologies from hydropower to fusion

Fig. 7 in "Hydrogen: the future energy carrier" A. Zuttel *et al.* *Phil. Trans. R. Soc. A* 368 pp. 3329 - 3342 (2010)



Energy density of technologies from batteries to nuclear

Energy density upper bound for today's battery technology ~1 kWh/kg

This estimate was made in 2010; as of 2016 this value has still not been achieved

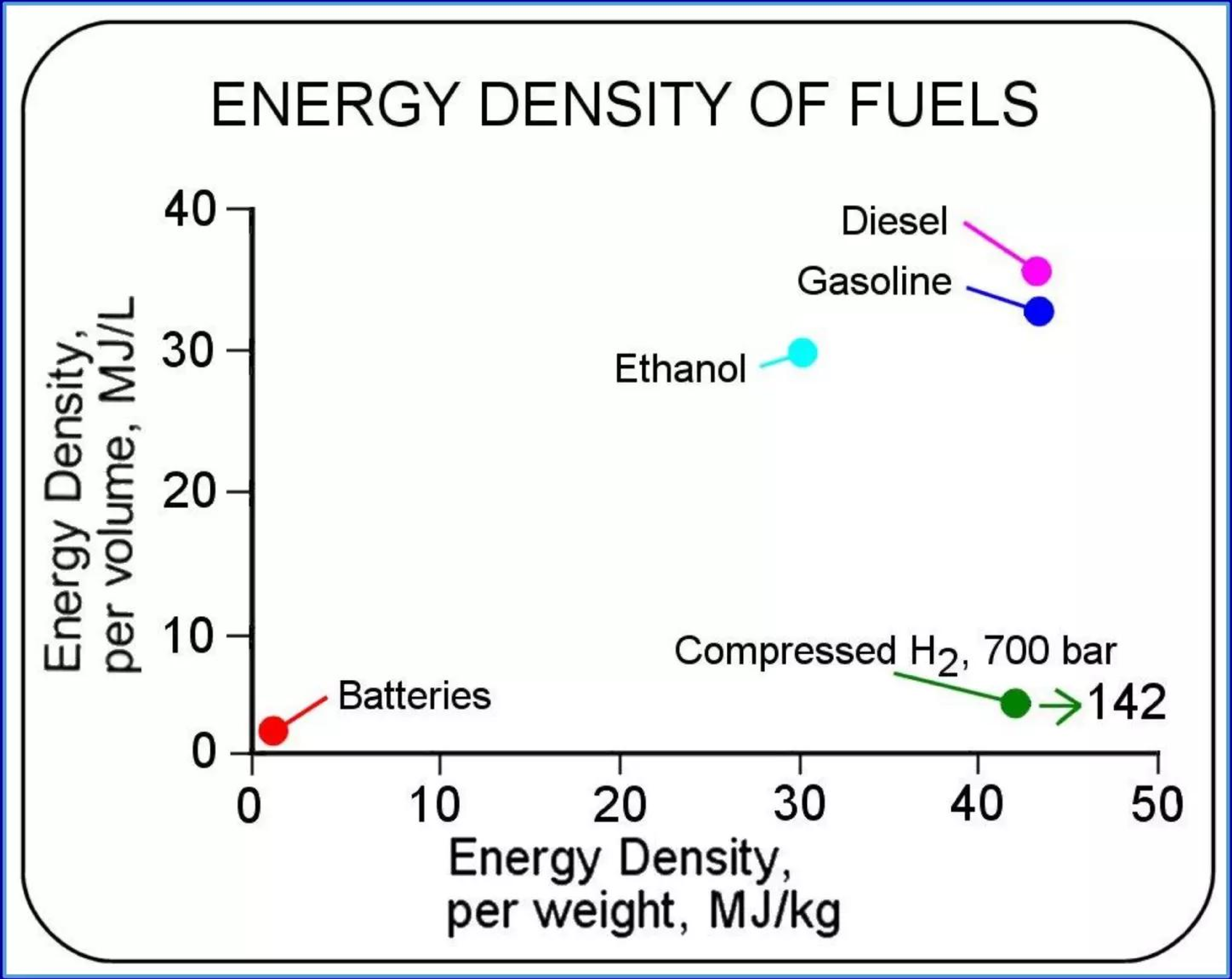
THE ROYAL SOCIETY
PUBLISHING

"Hydrogen: the future energy carrier" A. Zuttel *et al.*,
Phil. Trans. R. Soc. A 368 pp. 3329 - 3342 (2010)

http://rsta.royalsocietypublishing.org/content/roypta/368/1923/3329.full.pdf

"Only hydrides and ammonia exhibit an energy density close to that of fossil fuels, as shown in **figure 7**; all other energy carriers are at least an order of magnitude less dense in energy except for nuclear reactions, i.e. fission and fusion. However, nuclear reactions are stationary, i.e. very system demanding for the application and continuous delivery of power. In addition, fusion is still not carried out in a controlled efficient way in a reactor. The energy density in batteries is very limited (less than 0.2 kWh kg^{-1} in a Li ion battery today). Furthermore, batteries exhibit time constants in the range of several minutes to hours. The potential for the improvement of current battery technology is estimated to be approximately 1 kWh kg^{-1}. Such an ultimate battery could be derived from the Zn-air battery by replacing the Zn with lithium in a set-up with a non-aqueous electrolyte. New types of batteries, e.g. metal-air, where the energy is stored in metal clusters suspended in a non-aqueous electrolyte combined with an oxygen (air) electrode, have the potential for a significantly increased energy density and the cluster suspension would allow the battery to be refueled."

Battery energy density is less than Hydrogen or fossil fuels



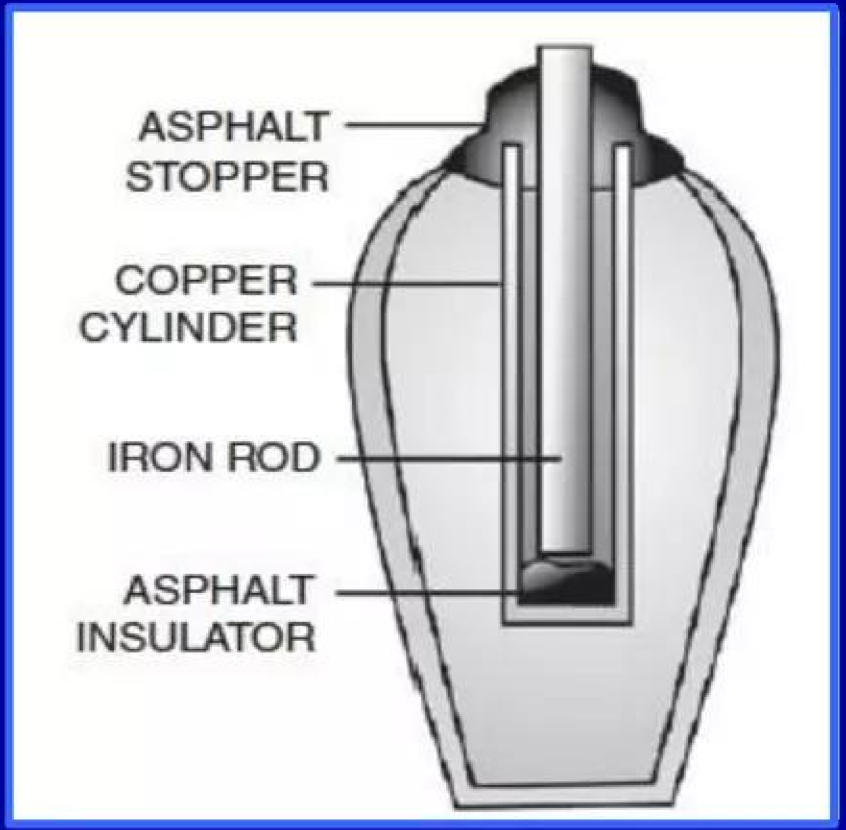
http://simanaitissays.com/2013/03/17/ev-good-news/

Physical sizes of all internal battery structures have shrunk

Huge decrease in distance separating battery anodes from cathodes

Ancient battery

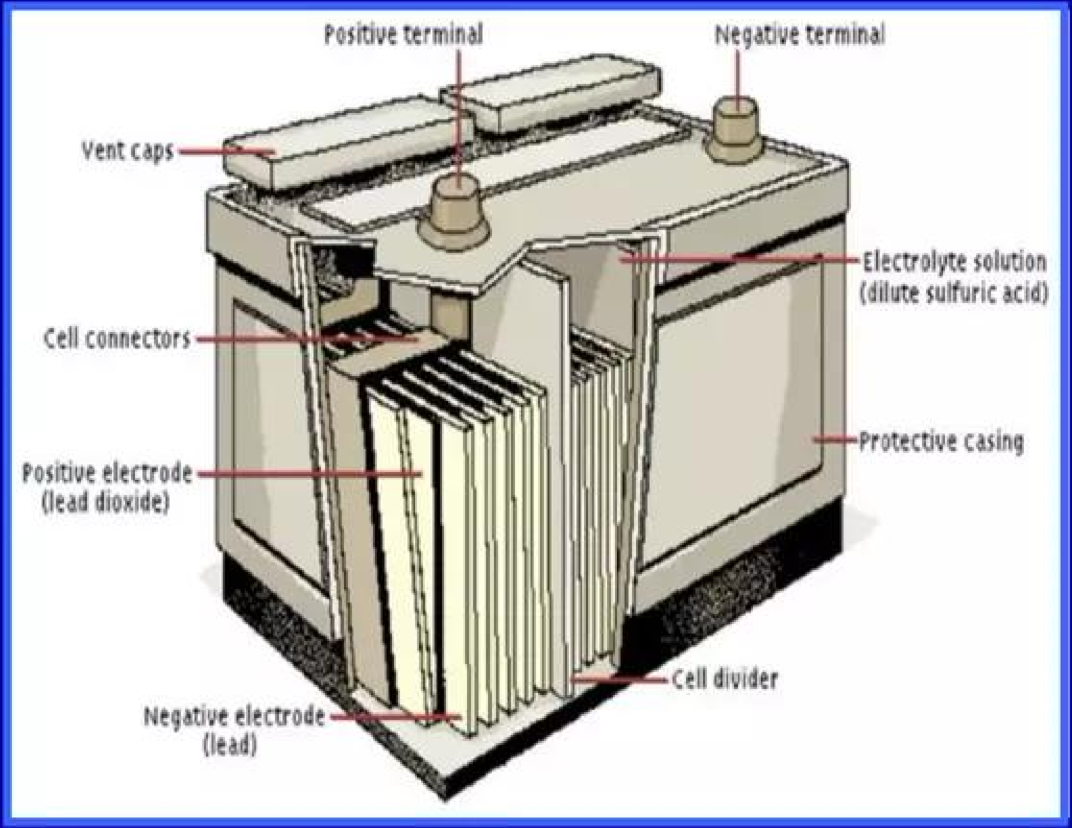
centimeter (1.0 cm)



Baghdad battery ~ 250 BCE?

Lead-acid car battery

millimeter-scale (.01 cm)

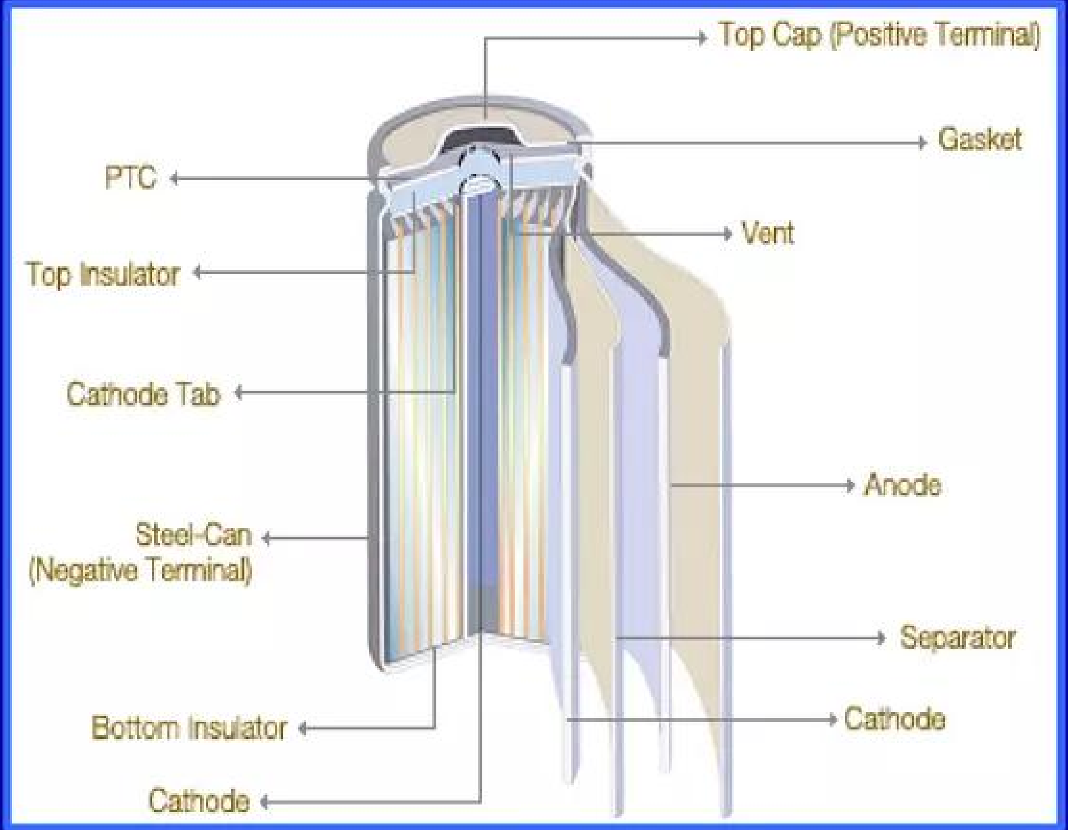


20th century lead-acid starter battery

Resistant to μ–scale LENRs

Li-ion jelly roll battery

micron-scale (.001mm)



Contemporary Lithium-ion battery

Jelly roll architecture maximizes internal surface area

Separators between anode and cathode can be very thin

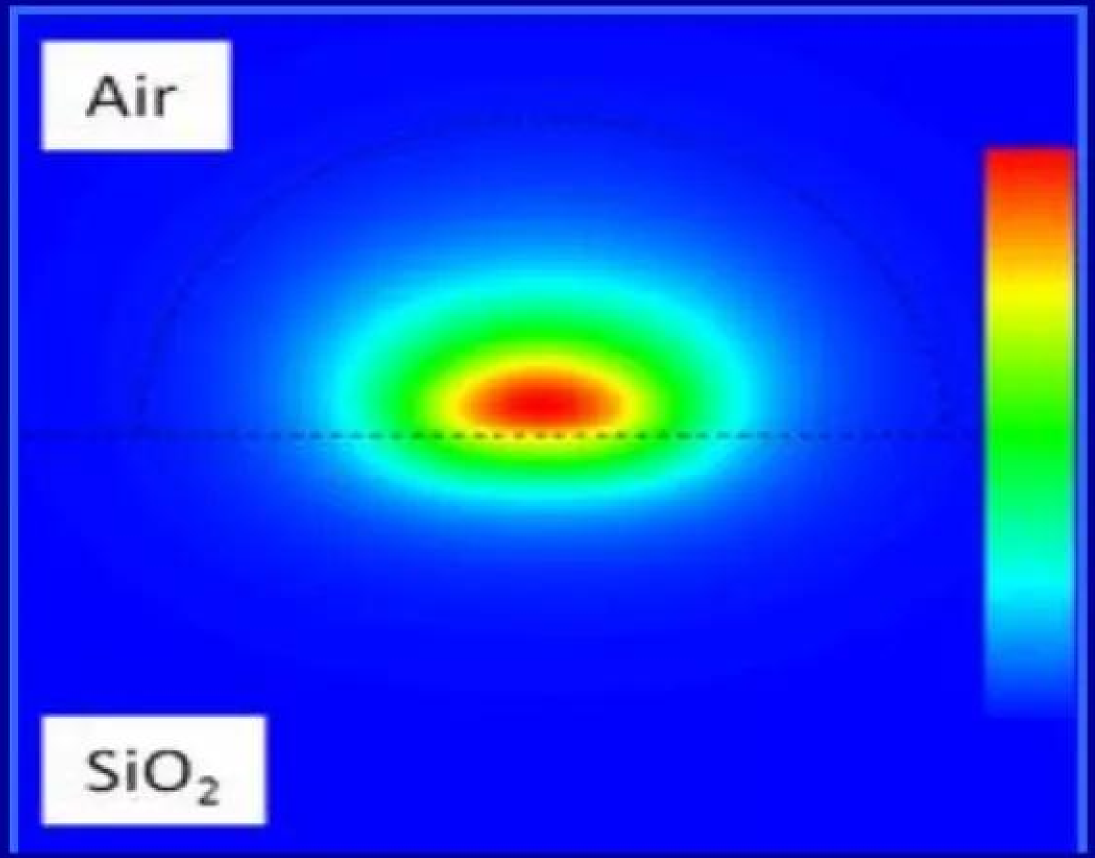
Internal battery structures shrunk to boost energy density

Jelly roll architecture and thin separators boosted Li-ion energy density

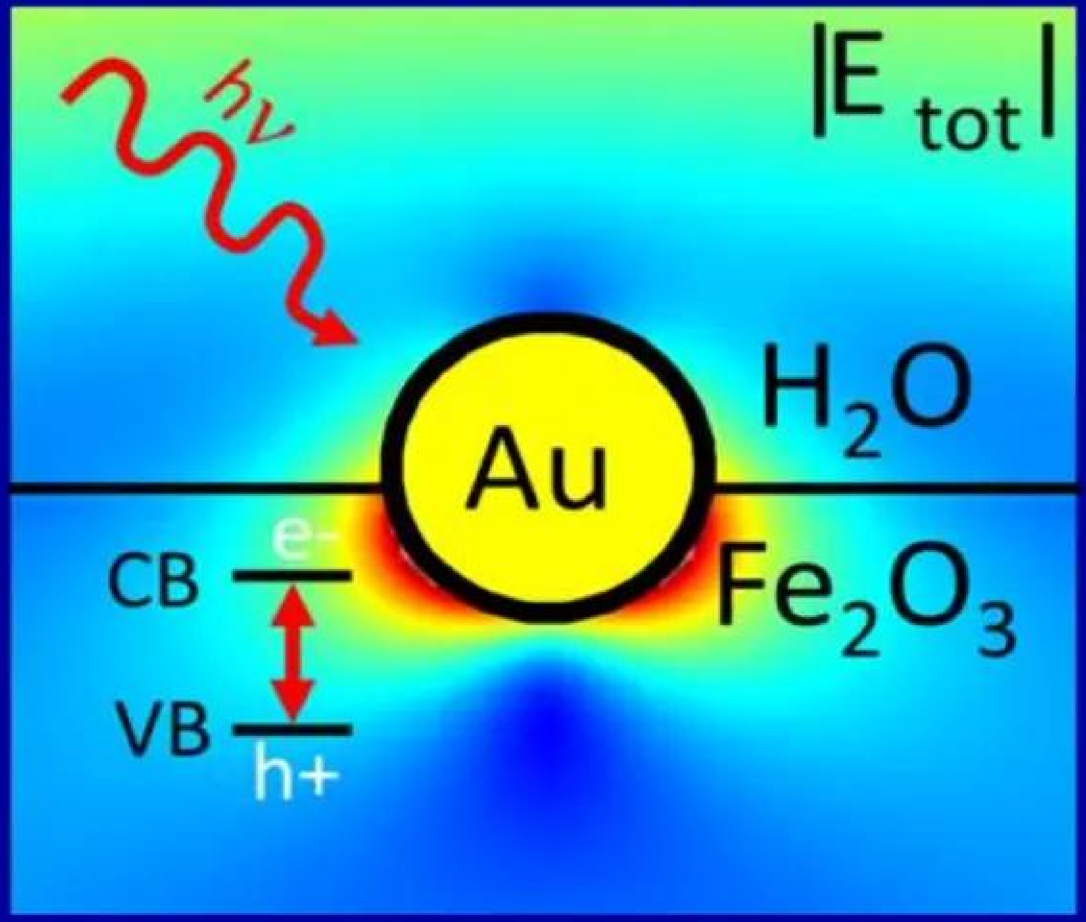
Nanotechnology now utilized by advanced batteries and nano-energetic materials

- ✓ **Battery performance is diffusion-rate-limited through intervening materials and across internal interfaces. To improve this parameter and increase overall energy density of battery cells, researchers invented the "jelly roll" architecture and shrank the thicknesses of dielectric plastic separators located between anode and cathode from centimeters to microns (thousand-fold decrease). To further boost performance and some energy density parameters, batteries are increasingly utilizing nanotechnology and developing many new types advanced battery chemistries, e.g., Lithium-sulfur and Lithium-oxygen**
- ✓ **Independently of batteries, technologists working to improve energy density and performance metrics of energetic chemical materials used in thermal igniters, propellants, and certain types of advanced explosives are increasingly utilizing much of the same areas of nanotechnology --- this relatively new area of R&D is called "nano-energetic materials"**

High E-field nm-scale hot spots near interfaces



Credit: *Scientific Reports* 3 paper #2335 (2013)



Credit: Thomann Group at Rice University

“Increasing battery energy density is a top priority”

Current R&D focuses on new chemistries with higher capacity & voltage

“Effects of inhomogeneities --- nanoscale to mesoscale --- on the durability of Li-Ion batteries”
S. Harris (Lawrence Berkeley National Lab) and P. Lu (General Motors)
The Journal of Physical Chemistry C 117 pp. 6481 - 6492 (2013)

http://lithiumbatteryresearch.com/pdf/Inhomogeneities-and-Durability.pdf

“Increasing energy density is a top priority for vehicle batteries since a higher energy density translates directly to a greater range. Current research focuses on new electrode chemistries with higher capacity and voltage, but the energy density is the product of three terms: energy density = charge capacity (Ah/kg) × voltage × mass density (kg/L). The third term offers as great an opportunity to improve energy density as the first two terms. (Volumetric energy density is more important than gravimetric energy density in commercial systems.)”

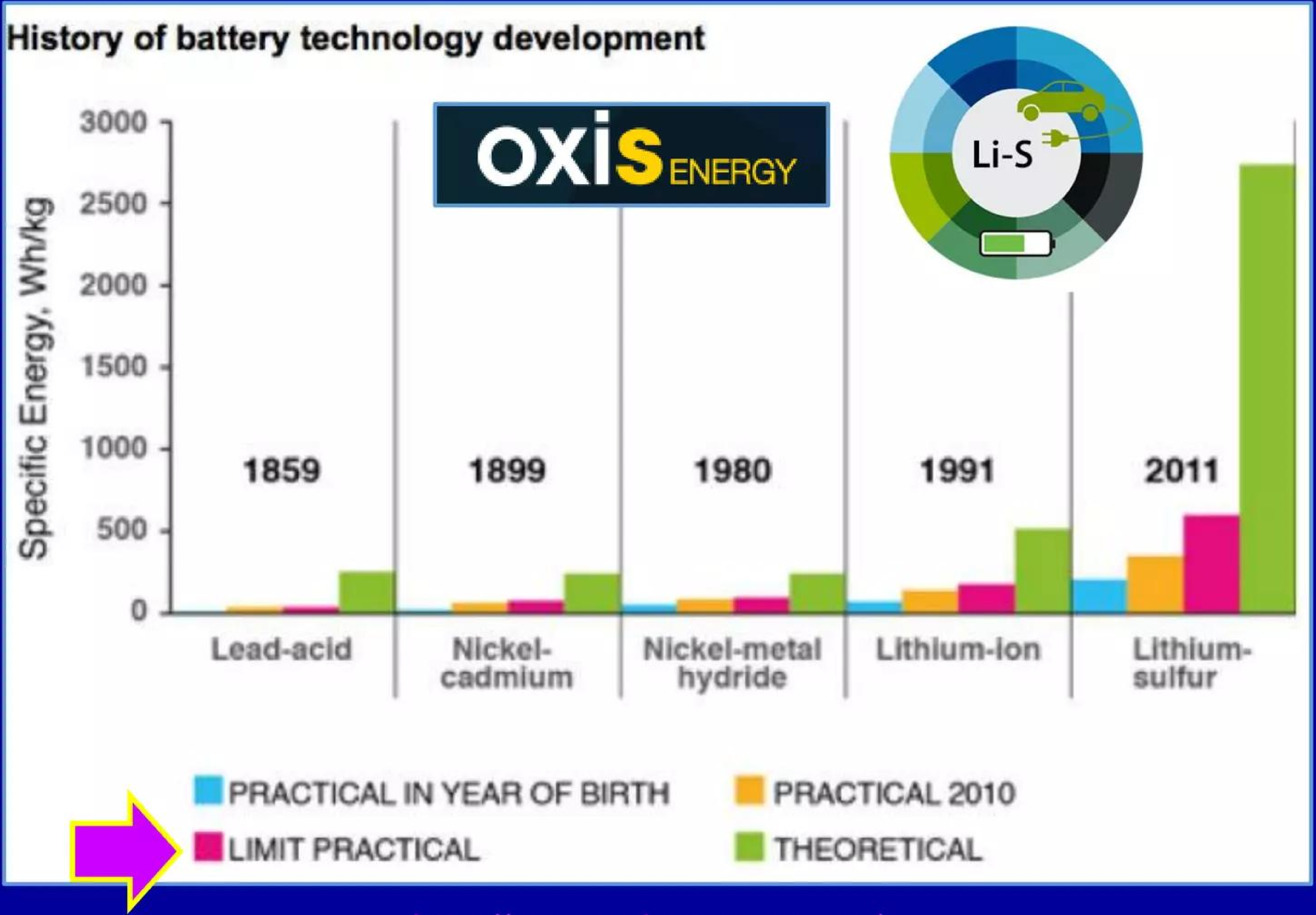
“We review work from our laboratory that suggests to us that most Li-ion battery failure can be ascribed to the presence of nano- and microscale inhomogeneities that interact at the mesoscale, as is the case with almost every material, and that these inhomogeneities act by hindering Li transport. (Li does not get to the right place at the right time.) … We propose new research approaches to make more durable, high energy density lithium-ion batteries.”

Series of major battery chemistries from 1859 up to today

Lead-acid was invented in 1859; still dominates for auto starter batteries

Lithium-based chemistries presently dominate high performance battery products

Lithium-sulfur along with Lithium-air are higher energy density challengers to Li-ion



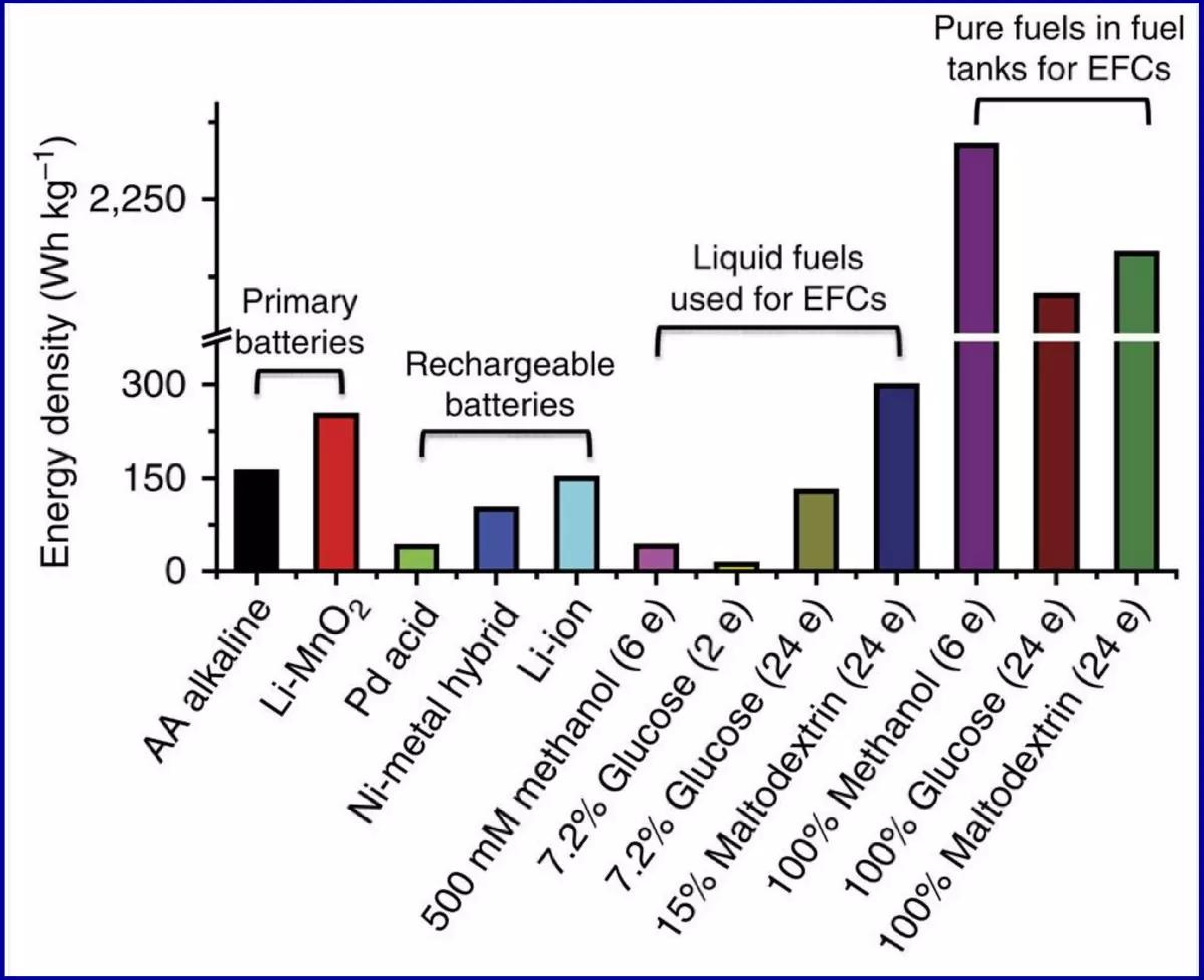
http://www.oxisenergy.com/

Energy densities: batteries versus enzymatic fuel cells

Enzymatic fuel cells (EFC) have higher energy densities vs. batteries

Early-stage technology: enzymes - not precious metals - are used to oxidize fuels

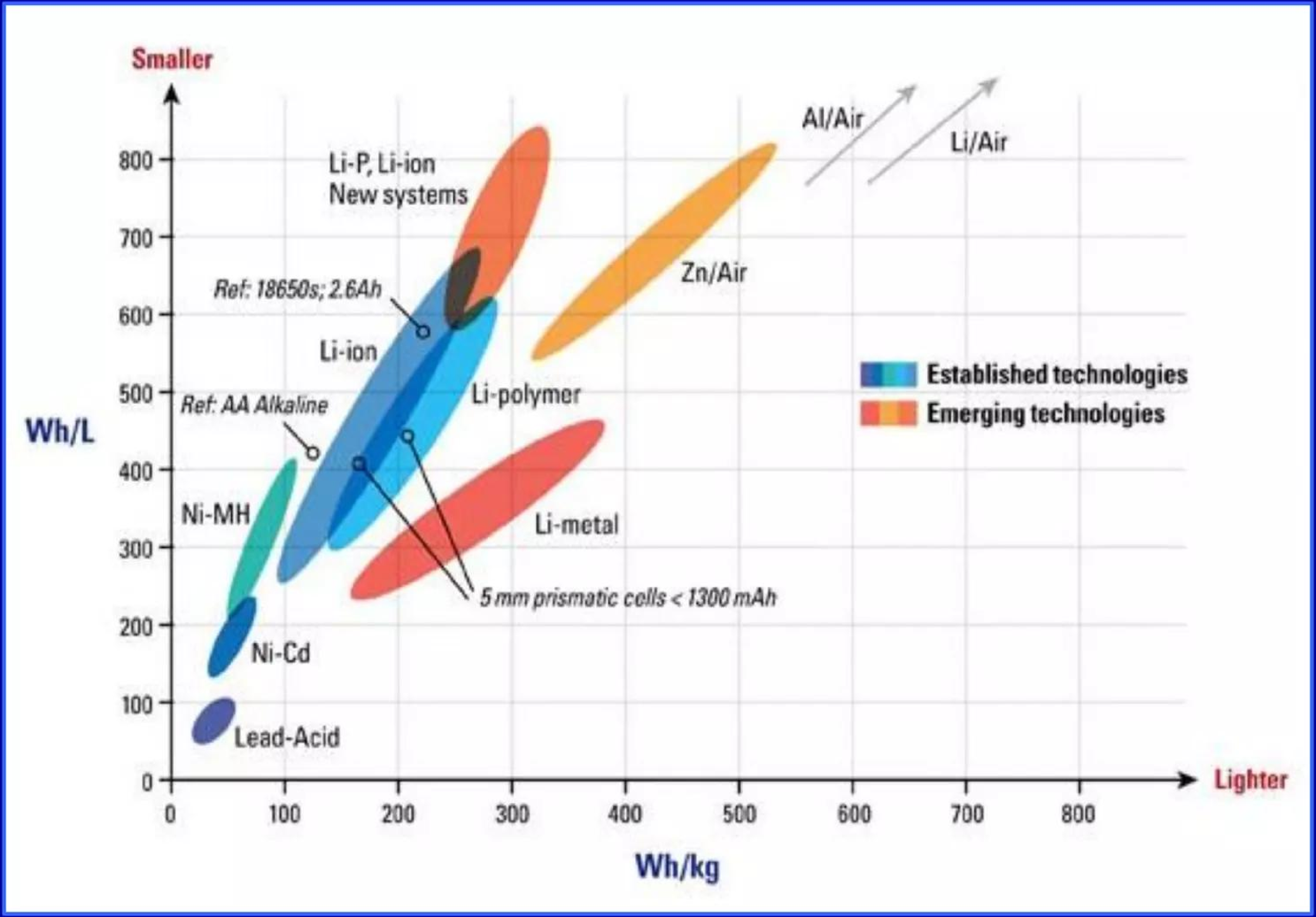
"A high-energy-density sugar biobattery based on a synthetic enzymatic pathway" Z. Zhu et al. *Nature Communications* 5 #3206 (2014)



Battery energy densities increased by ~10x over 157 years

Achieved by improving battery chemistries; Lithium is dominant today

Lead-acid chemistry first invented back in 1859; still used in auto starter batteries

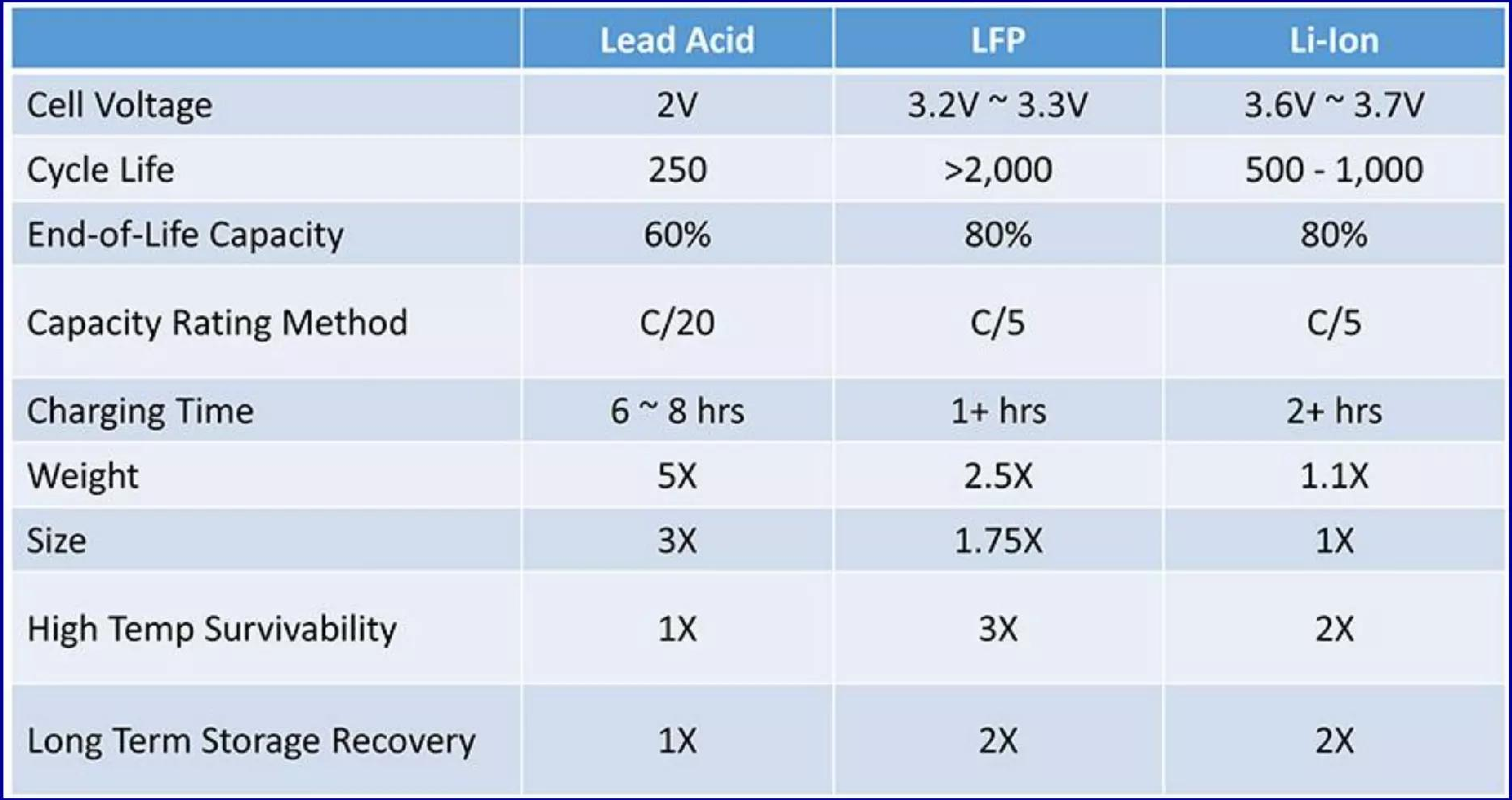


http://www.estquality.com/technology

Comparison of three very important battery chemistries

Lead-acid (1859), Lithium Iron Phosphate (1997), and Lithium-ion (1991)

Each of these 3 different chemistries now dominates certain segments of markets

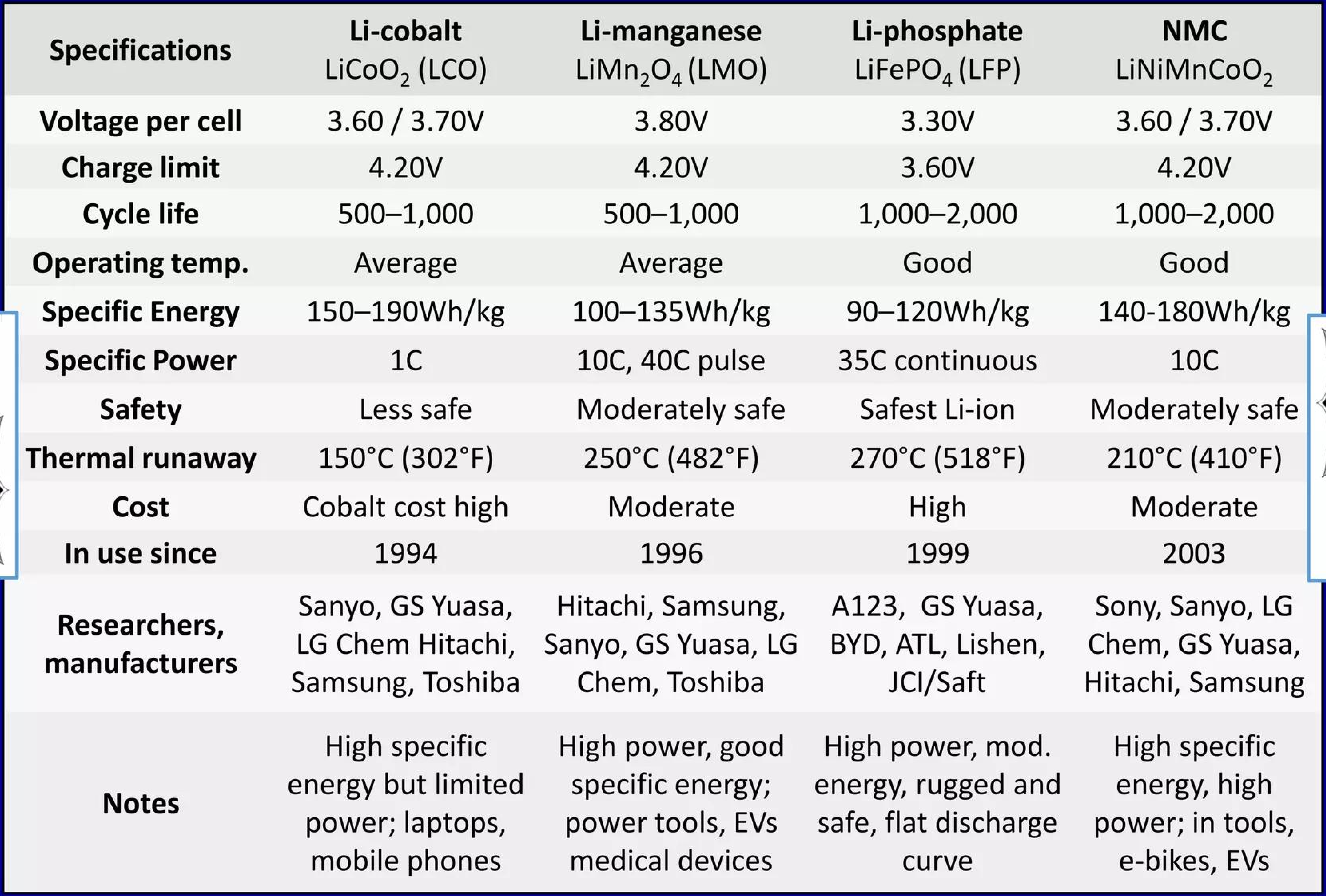


	Lead Acid	LFP	Li-Ion
Cell Voltage	2V	3.2V ~ 3.3V	3.6V ~ 3.7V
Cycle Life	250	>2,000	500 - 1,000
End-of-Life Capacity	60%	80%	80%
Capacity Rating Method	C/20	C/5	C/5
Charging Time	6 ~ 8 hrs	1+ hrs	2+ hrs
Weight	5X	2.5X	1.1X
Size	3X	1.75X	1X
High Temp Survivability	1X	3X	2X
Long Term Storage Recovery	1X	2X	2X

http://www.datacenterjournal.com/lithiumion-power-data-storage-servers/

Characteristics of 4 common Lithium-ion battery chemistries

Source: Battery University (see URL further below)



Specifications	Li-cobalt $LiCoO_2$ (LCO)	Li-manganese $LiMn_2O_4$ (LMO)	Li-phosphate $LiFePO_4$ (LFP)	NMC $LiNiMnCoO_2$
Voltage per cell	3.60 / 3.70V	3.80V	3.30V	3.60 / 3.70V
Charge limit	4.20V	4.20V	3.60V	4.20V
Cycle life	500–1,000	500–1,000	1,000–2,000	1,000–2,000
Operating temp.	Average	Average	Good	Good
Specific Energy	150–190Wh/kg	100–135Wh/kg	90–120Wh/kg	140-180Wh/kg
Specific Power	1C	10C, 40C pulse	35C continuous	10C
Safety	Less safe	Moderately safe	Safest Li-ion	Moderately safe
Thermal runaway	150°C (302°F)	250°C (482°F)	270°C (518°F)	210°C (410°F)
Cost	Cobalt cost high	Moderate	High	Moderate
In use since	1994	1996	1999	2003
Researchers, manufacturers	Sanyo, GS Yuasa, LG Chem Hitachi, Samsung, Toshiba	Hitachi, Samsung, Sanyo, GS Yuasa, LG Chem, Toshiba	A123, GS Yuasa, BYD, ATL, Lishen, JCI/Saft	Sony, Sanyo, LG Chem, GS Yuasa, Hitachi, Samsung
Notes	High specific energy but limited power; laptops, mobile phones	High power, good specific energy; power tools, EVs medical devices	High power, mod. energy, rugged and safe, flat discharge curve	High specific energy, high power; in tools, e-bikes, EVs

http://batteryuniversity.com/learn/article/possible_solutions_for_the_battery_problem_on_the_boeing_787

Lithium chemistry enabled batteries with high energy density

Lower density Lead-acid batteries not practical for small smartphones

Generally speaking, in portable electronics markets, batteries having the highest energy densities and duration of electrical power output will usually win price/performance contests in energy storage markets

+

= No

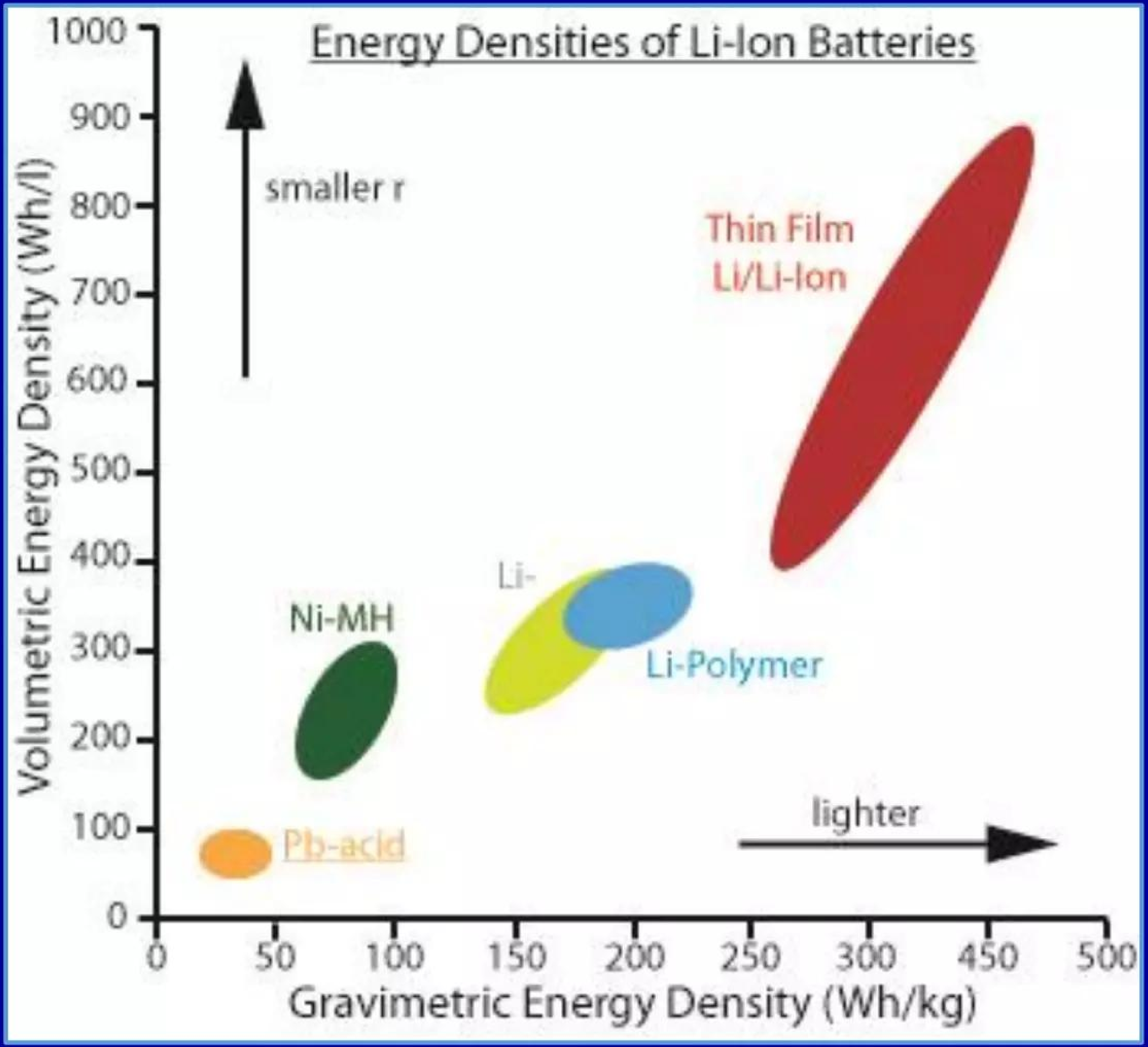
Using 30 lb. DieHard Lead-acid batteries to power 4-ounce Apple iPhones is impractical for end-user customers

Utilizing advanced chemistries beyond Lead-acid technology allows more electrical charge to be stored inside a battery casing that is much smaller in volume and weighs vastly less; i.e. with higher volumetric energy density

Lithium-based batteries are an integral part of modern life

Very strong competitive pressures to further increase energy densities

High level of safety is important because of ubiquitous use in consumer products



Credit: Chem511grpThinLiBat

Lithium-based batteries are an integral part of modern life

$LiCoO_2$

$LiFeS_2$

$Li/AlMnO_2$

$LiFeS$

$LiFePO_4$

$LiPbCuS$

Li_2S

$LiCuO$

$LiFeS_2$

$LiCu_4O(PO_4)_2$

$LiSO_2Cl_2$

$Li\text{-}Cu_4O(PO_4)_2$

Lithium-based batteries come in many different chemistries

$LiAg_2CrO_4$

$Li(CF)_x$

$LiCuCl_2$

$LiSOCl_2$

$LiBi_2O_3$

$Li_4Ti_5O_{12}$

Li-air

$LiAg_2V_4O_{11}$

$LiMnO_2$

$LiBi_2Pb_2O_5$

$LiAg_2CrO_4$

$LiPbCuS$

Lithium-based batteries are an integral part of modern life

Small portable electronic devices have become a ubiquitous, indispensable part of daily life in modern societies

Vast majority of all such products use chemical batteries for power sources

Lithium-based batteries are an integral part of modern life

Lithium-based batteries come in many different shapes and sizes

Lithium-based batteries are an integral part of modern life

Secondary

Primary

Primary batteries CANNOT be recharged safely (fully discharged only once); secondary batteries are designed to be rechargeable

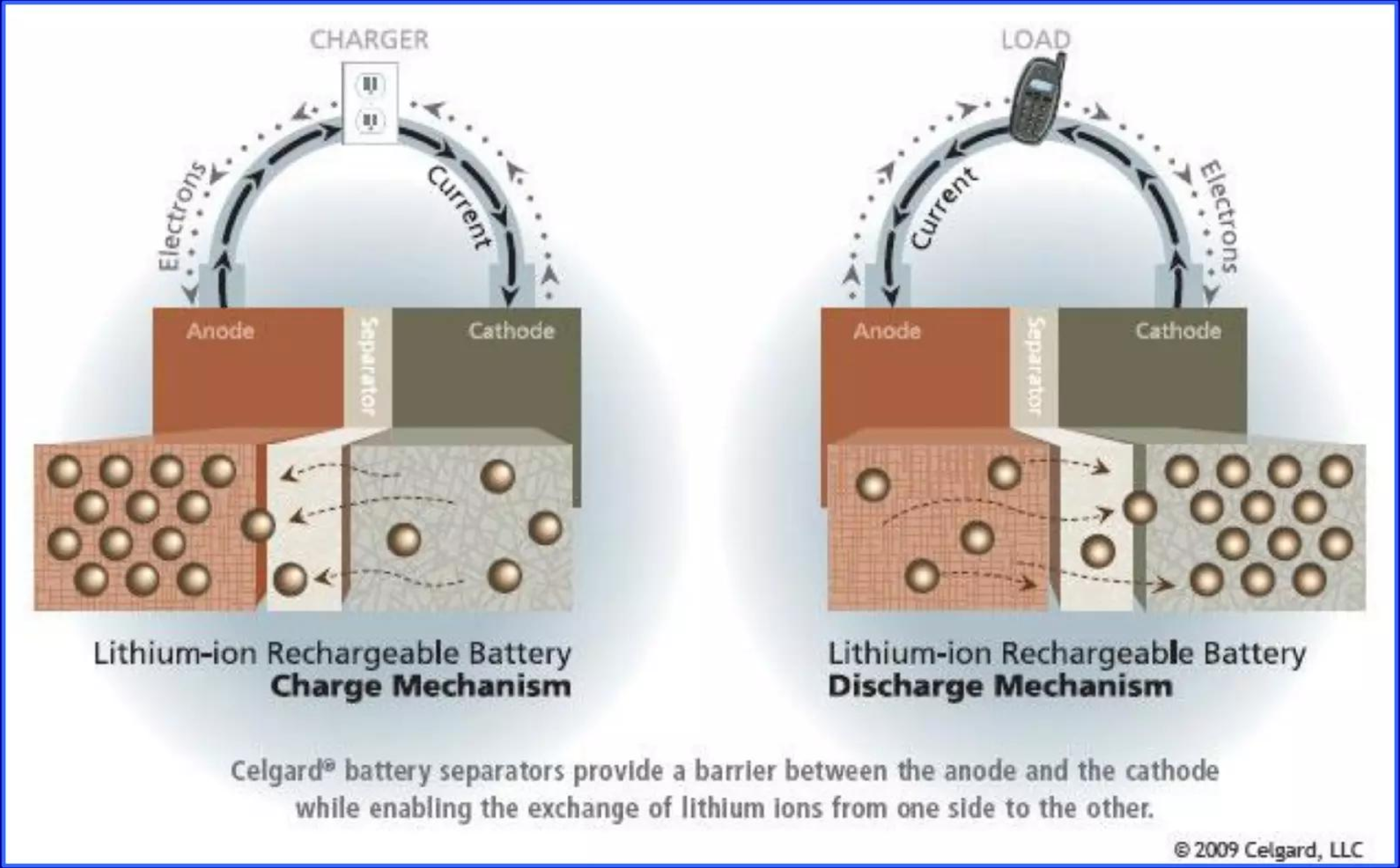
Primary

Secondary

Primary

Conceptual overview of a commercial Lithium-ion battery

Lithium ion battery: "A typical lithium-ion rechargeable battery. The battery consists of a positive electrode (green) and a negative electrode (red), with a layer (yellow) separating them. When in use, lithium-ions (Li+, blue) travel from the negative electrode (anode) to the positive (cathode). During charging, the process is reversed and lithium ions are transferred back to the anode."



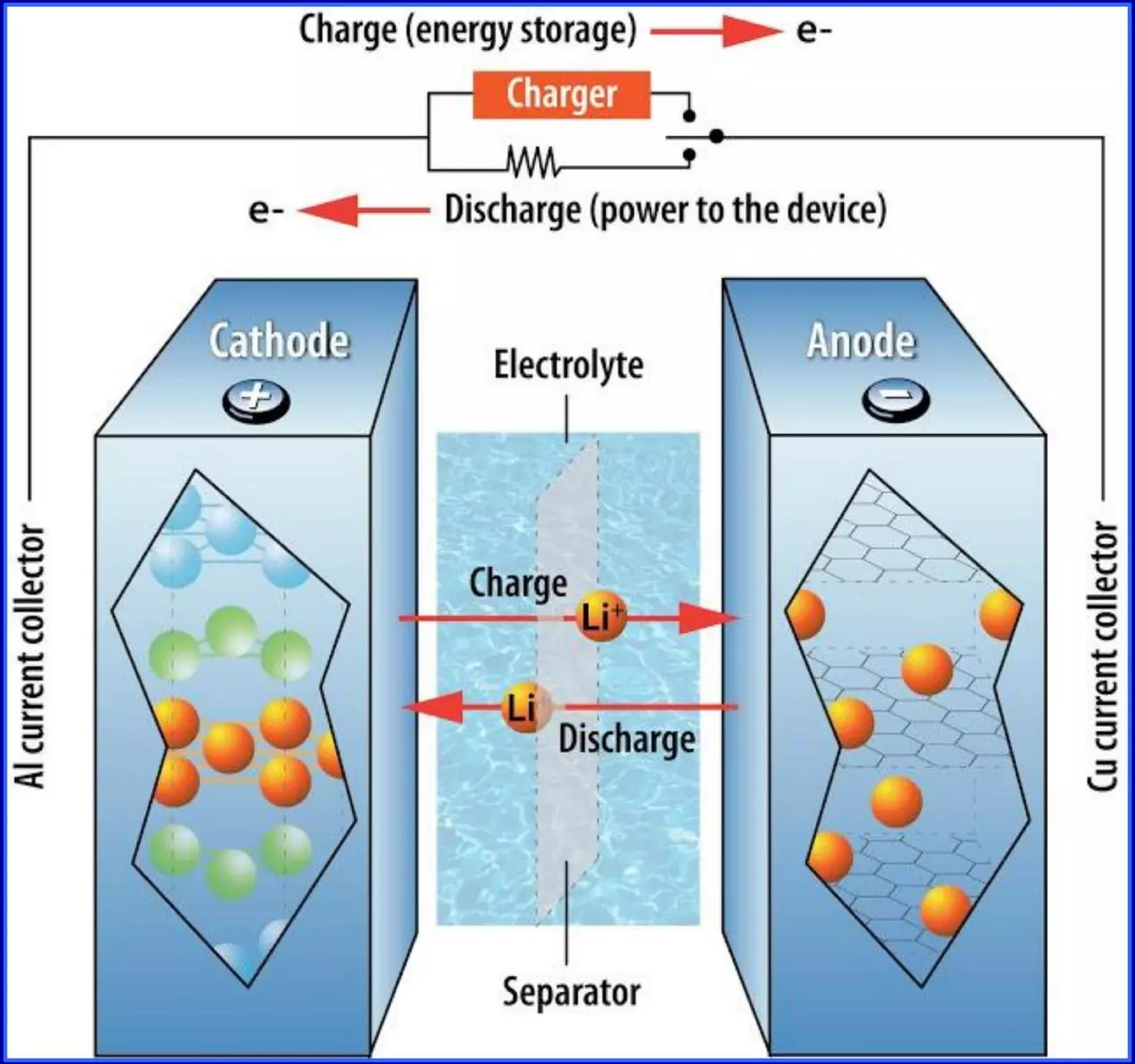
Lithium-ion Rechargeable Battery
Charge Mechanism

Lithium-ion Rechargeable Battery
Discharge Mechanism

Celgard® battery separators provide a barrier between the anode and the cathode while enabling the exchange of lithium ions from one side to the other.

© 2009 Celgard, LLC

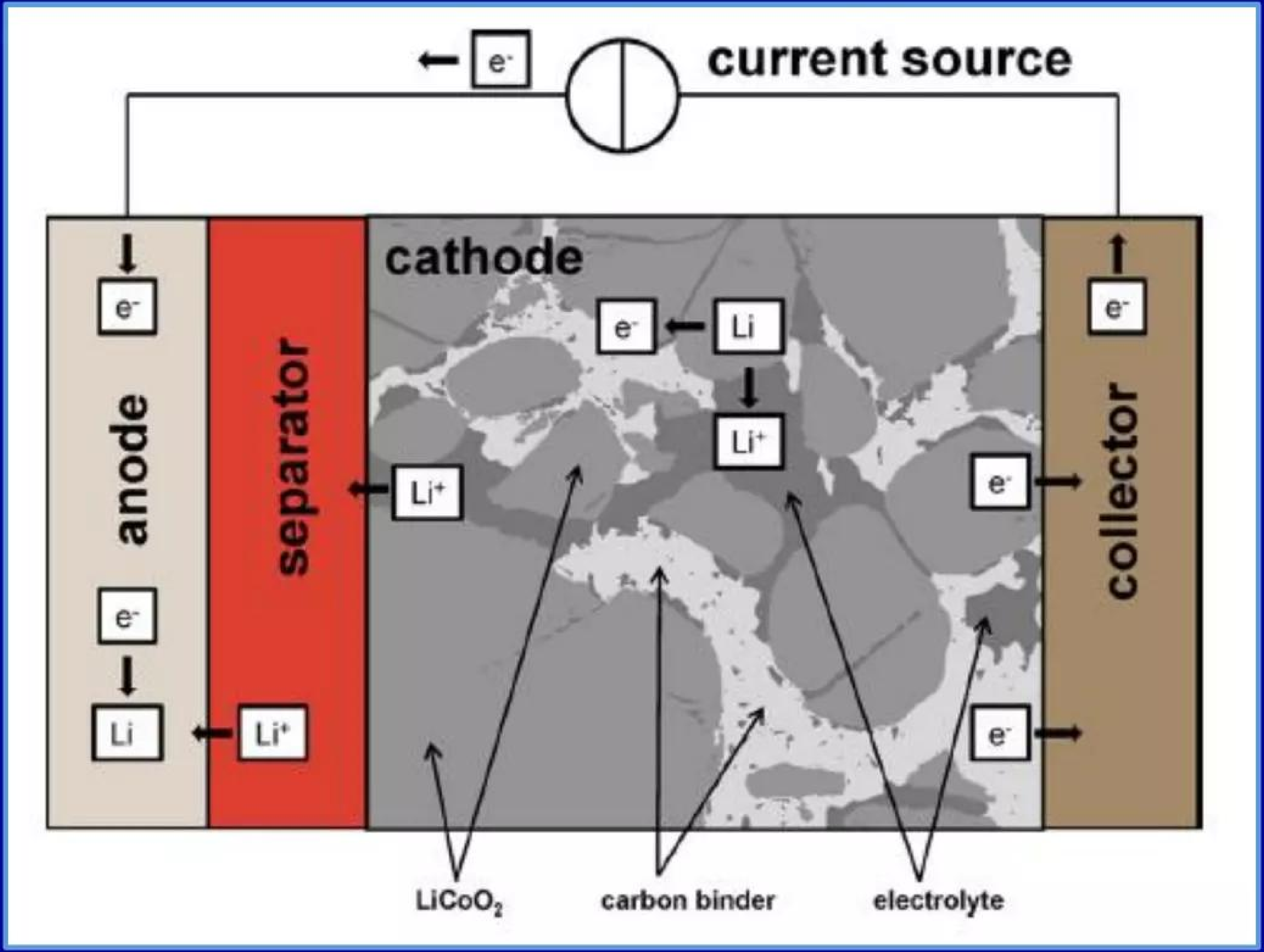
Conceptual overview of a commercial Lithium-ion battery



http://www.evwind.es/2015/12/25/growth-in-lithium-ion-batteries-for-the-vehicle-electrification-and-grid-energy-storage-sectors-was-significant-in-2014/55060

Microscopic overview: selected portion of Lithium-ion battery

Fig. 3. "The basic working principle of the model during charging of the battery. Lithium stored in the active-material domain is split into cations and electrons. The cations are transported through the electrolyte-filled pore space, across the separator and to the anode. Electrons are transported through the active-material domain (low conductivity) and the carbon-binder domain (high conductivity) to the cathode collector. The collector is electrically connected to the anode which allows recombination of cations and electrons at the anode. The relocation of lithium from the cathode to the anode, and thus the charging of the battery, is driven by an external current source."



"Three-dimensional electrochemical Li-ion battery modelling featuring a focused ion-beam/scanning electron microscopy based three-phase reconstruction of a $LiCoO_2$ cathode" T. Hutzenlaub *et al.*, *Electrochimica Acta* 115 pp. 131 - 139 (2014)

Computer CPU clock speeds increased over 475x in 34 years

Enormous decreases in size with vastly greater raw computing power

CPU clock speed of 2016 Apple iPhone 6s$^+$ is 1.9 GHZ or ~475x > Osborne

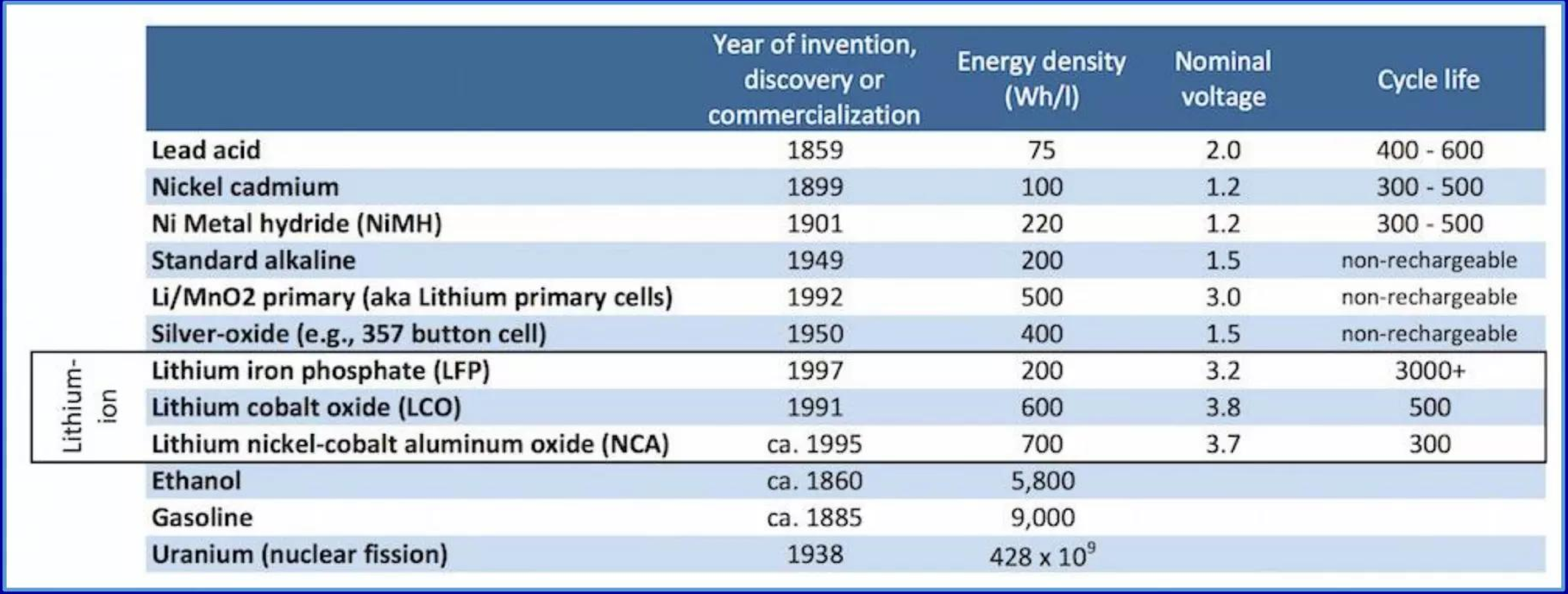
"An Osborne Executive portable computer, from 1982 with a Zilog Z80 4 MHz (0.004 GHZ) CPU, and a 2007 Apple iPhone with a 412 MHz ARM11 CPU; the Executive weighs 100 times as much, has nearly 500 times as much volume, cost ~ 10 times as much (adjusted for inflation), and has ~ 1/100th the clock frequency of the smartphone."

Source: Wikipedia

Energy density of batteries has increased ~10x in 157 years

Nadim Maluf, CEO of Qnovo, comments about battery energy densities

"So by now, you are probably disappointed about the future of batteries! It is true that the progress of batteries over the last 150 years has been slow, and it is true that batteries can't yet compete with carbon-based fuels … Yes, they can be better, but present batteries boasting 700 Wh/l can and are sufficient to provide an electric vehicle with a range of 300 miles. In other words, don't expect miracles in batteries, but do expect that incremental technologies from materials to algorithms and electronics will be sufficient to address a wide range of energy storage needs, including smartphones that can last an honest day to electric vehicles with a range of 200 - 300 miles."



		Year of invention, discovery or commercialization	Energy density (Wh/l)	Nominal voltage	Cycle life
	Lead acid	1859	75	2.0	400 - 600
	Nickel cadmium	1899	100	1.2	300 - 500
	Ni Metal hydride (NiMH)	1901	220	1.2	300 - 500
	Standard alkaline	1949	200	1.5	non-rechargeable
	Li/MnO2 primary (aka Lithium primary cells)	1992	500	3.0	non-rechargeable
	Silver-oxide (e.g., 357 button cell)	1950	400	1.5	non-rechargeable
Lithium-ion	Lithium iron phosphate (LFP)	1997	200	3.2	3000+
	Lithium cobalt oxide (LCO)	1991	600	3.8	500
	Lithium nickel-cobalt aluminum oxide (NCA)	ca. 1995	700	3.7	300
	Ethanol	ca. 1860	5,800		
	Gasoline	ca. 1885	9,000		
	Uranium (nuclear fission)	1938	428×10^9		

http://qnovo.com/category/chemistry/

Energy density of batteries has increased ~10x in 157 years

Nadim Maluf, CEO of Qnovo, comments about battery energy densities

Tesla claims to be able to double (2x) volumetric energy density over 10 years

"The third observation: Energy density increased by a factor of 10X over 150 years! That's not terribly promising unless the future brings forth some serious breakthroughs in materials. Is there anything on the horizon? There is a lot of promising good material research, but when one takes into account cost, cycle life, and other constraints such as manufacturing and capital, it is very hard to point to one particular technology that is likely to be commercialized in the next 5 years. So the wait and the hope continue."

"The fourth observation: Lithium-ion technologies, first commercialized by Sony in 1991, encompass a wide range of energy densities depending on the particular choice of material for the electrodes. Lithium-ion batteries using nickel-cobalt-aluminum oxide (NCA) electrodes --- the type used in the Tesla Model S --- have over 3X the energy density of lithium-ion batteries with lithium iron-phosphate (LFP) electrodes. So why is anyone considering LFP lithium-ion batteries: cycle life! Welcome to the world of compromises."

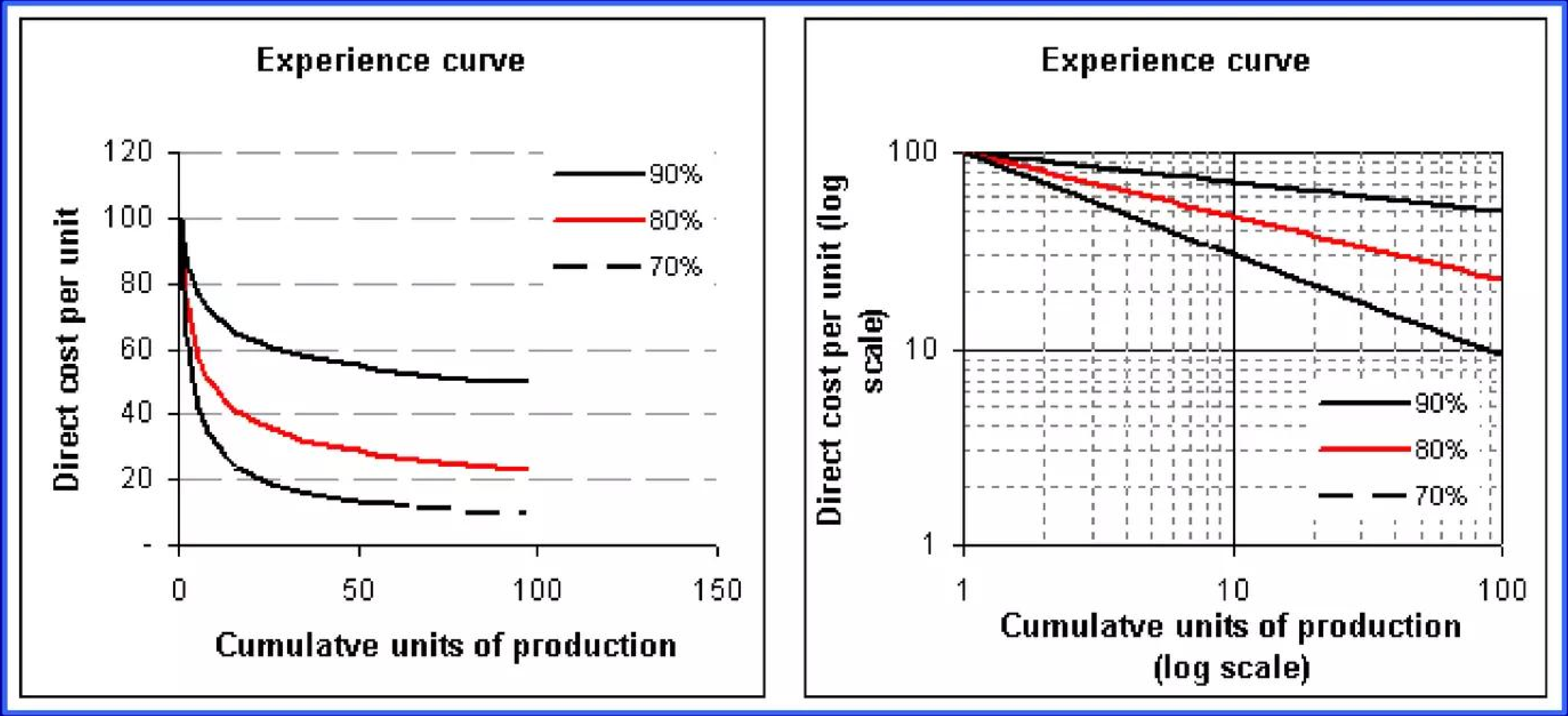
http://qnovo.com/category/chemistry/

Experience curve effect reduces product costs over time

Battery cost/kwh to store electricity have declined greatly over 157 years

An experience curve, which differs somewhat from a so-called "learning curve," is a graphical representation of a price phenomenon that was developed and widely publicized as a corporate strategy tool by Bruce Henderson, founder of the Boston Consulting Group. Concept refers to effect that manufacturers learn from doing, which means that the higher the cumulative volume of production, the lower the direct cost per new unit of produced product. Thus, experience curves are innately convex and have downward slopes, as shown in two graphs below:

Idealized relationship between direct cost/unit and total cumulative unit production



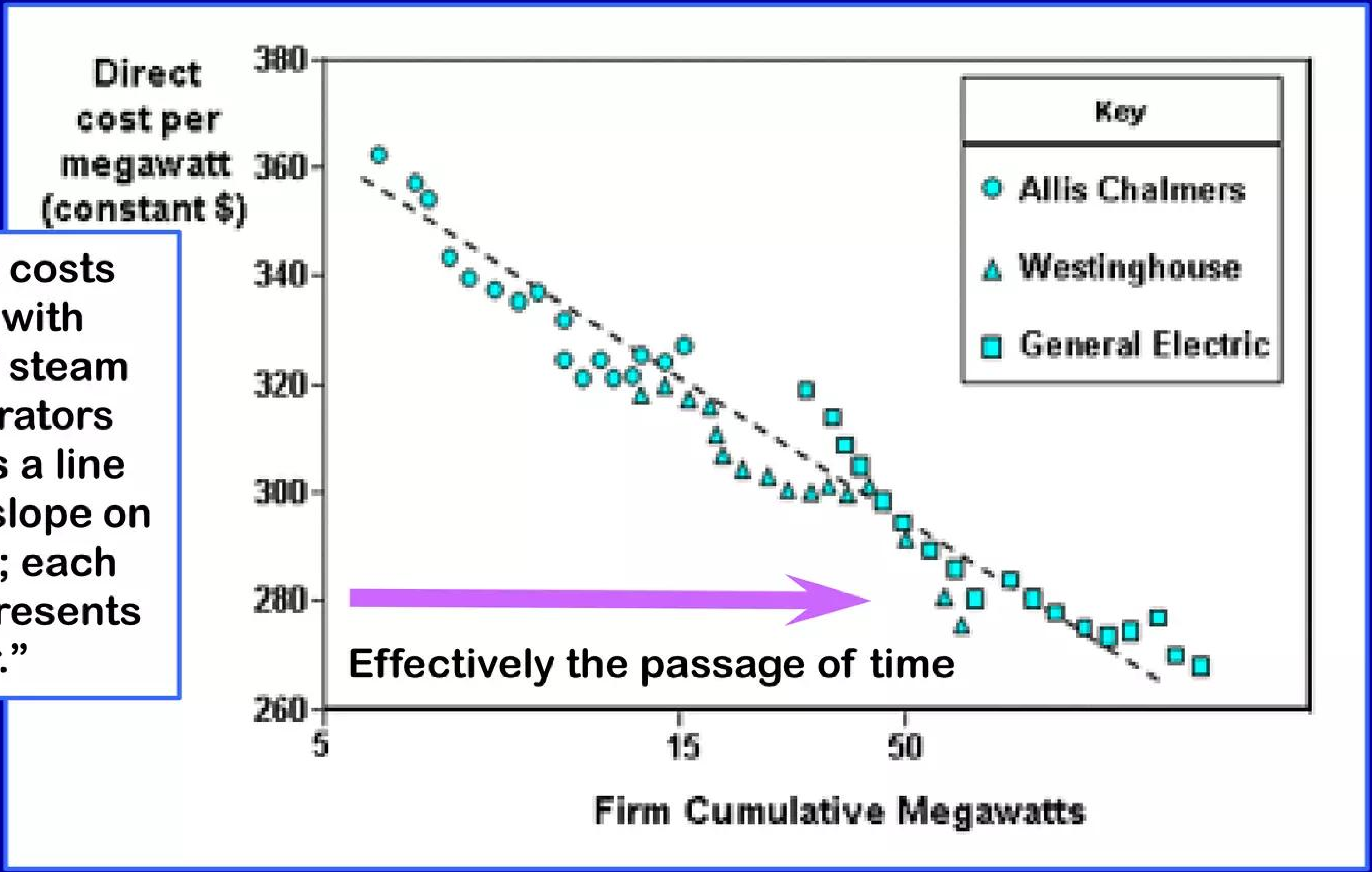
http://en.wikipedia.org/wiki/Experience_curve_effects

Experience curve cut costs of producing & storing electricity

$ cost/megawatt for steam turbines dropped as unit volumes increased

Empirical data shows that it applies to many different manufactured products

Total direct cost per megawatt (constant $) vs. total cumulative megawatts for steam turbines sold and delivered by three major OEM manufacturers



Effectively the passage of time

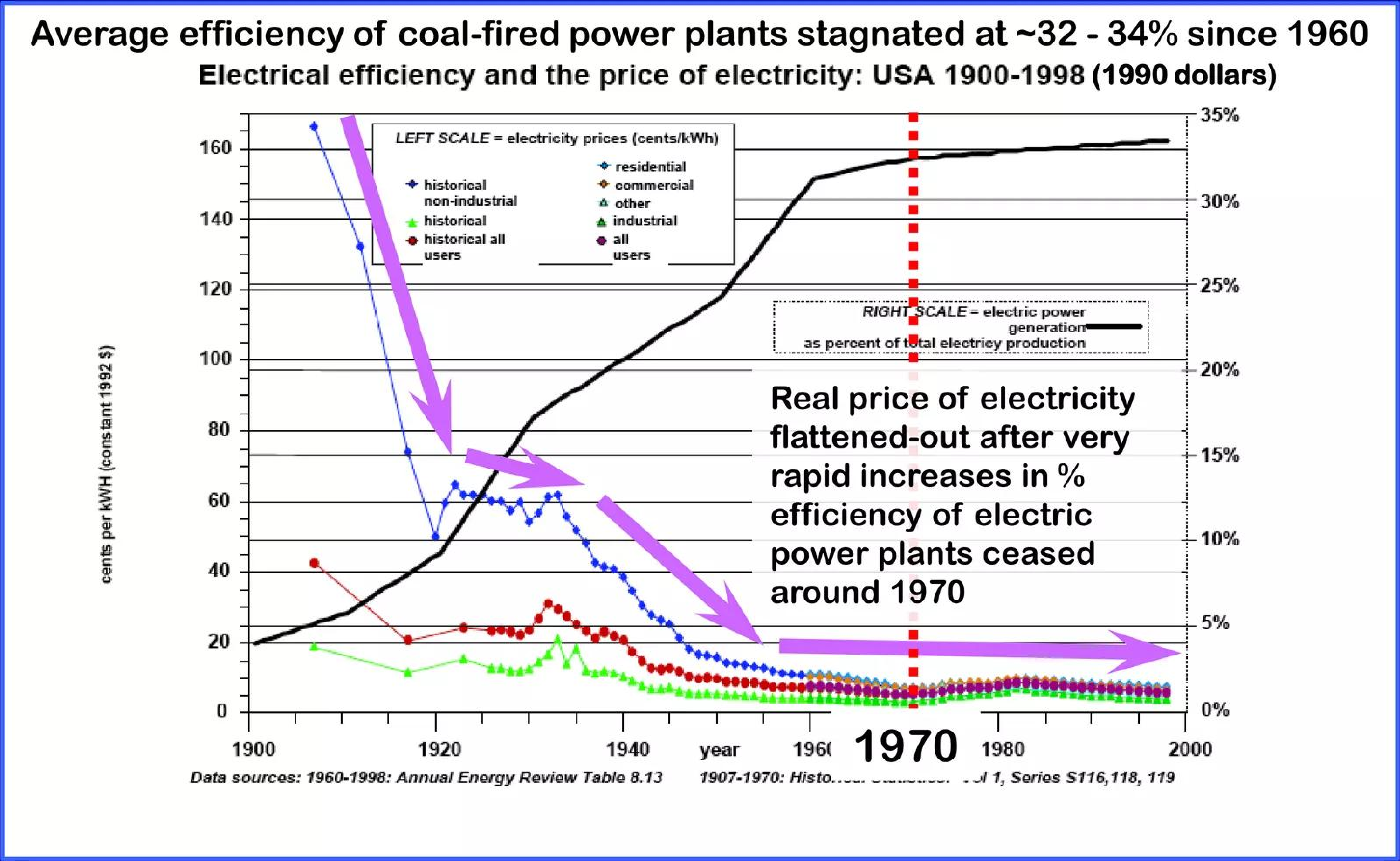
"Decrease in costs associated with production of steam turbine generators trend towards a line with constant slope on a log-log plot; each data point represents one year."

http://vectorstudy.com/management-theories/experience-curve

Cost reductions/time will decrease as a technology matures

Lithium-ion battery chemistry has ridden experience curve for 25 years

By 1910, price of electricity was ~$1.60 per kWh (1990 dollars); from 1920s through mid-1930s It mostly averaged around $0.60 kWh; today, price of electricity ranges from ~ $0.05 to 0.12 kWh



Average efficiency of coal-fired power plants stagnated at ~32 - 34% since 1960

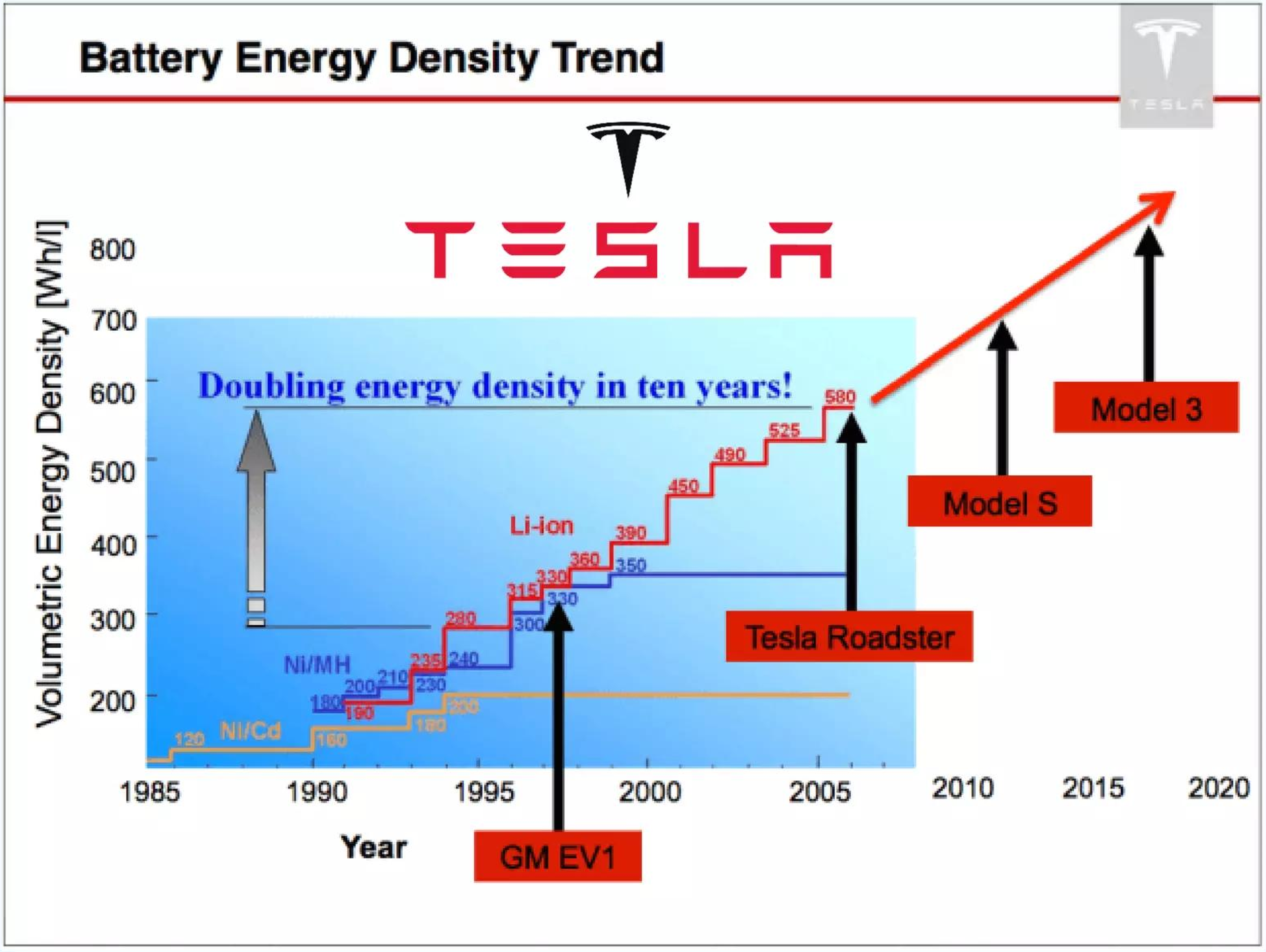
Electrical efficiency and the price of electricity: USA 1900-1998 (1990 dollars)

Real price of electricity flattened-out after very rapid increases in % efficiency of electric power plants ceased around 1970

http://tingilinde.typepad.com/starstuff/2009/05/the-historic-price-of-electricity-in-the-us.html

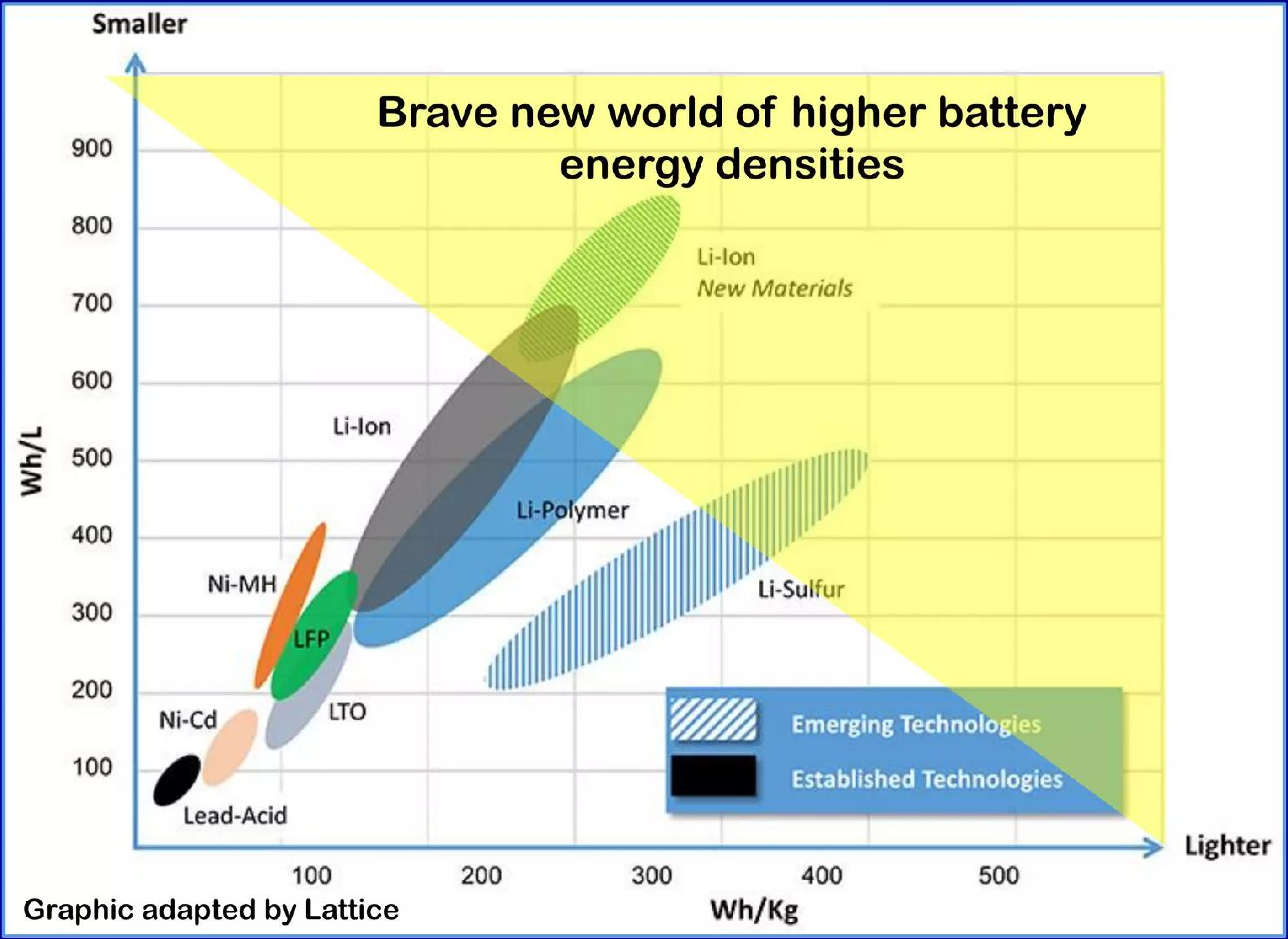
Tesla claims it can double battery energy density in 10 years

e.g. Tesla increased 90D battery's capacity 6% by tweaking cell chemistry



Lithium-sulfur and Lithium-air have higher Wh/kg vs. Li-ion

Battery manufacturers focus R&D on increasing battery energy densities



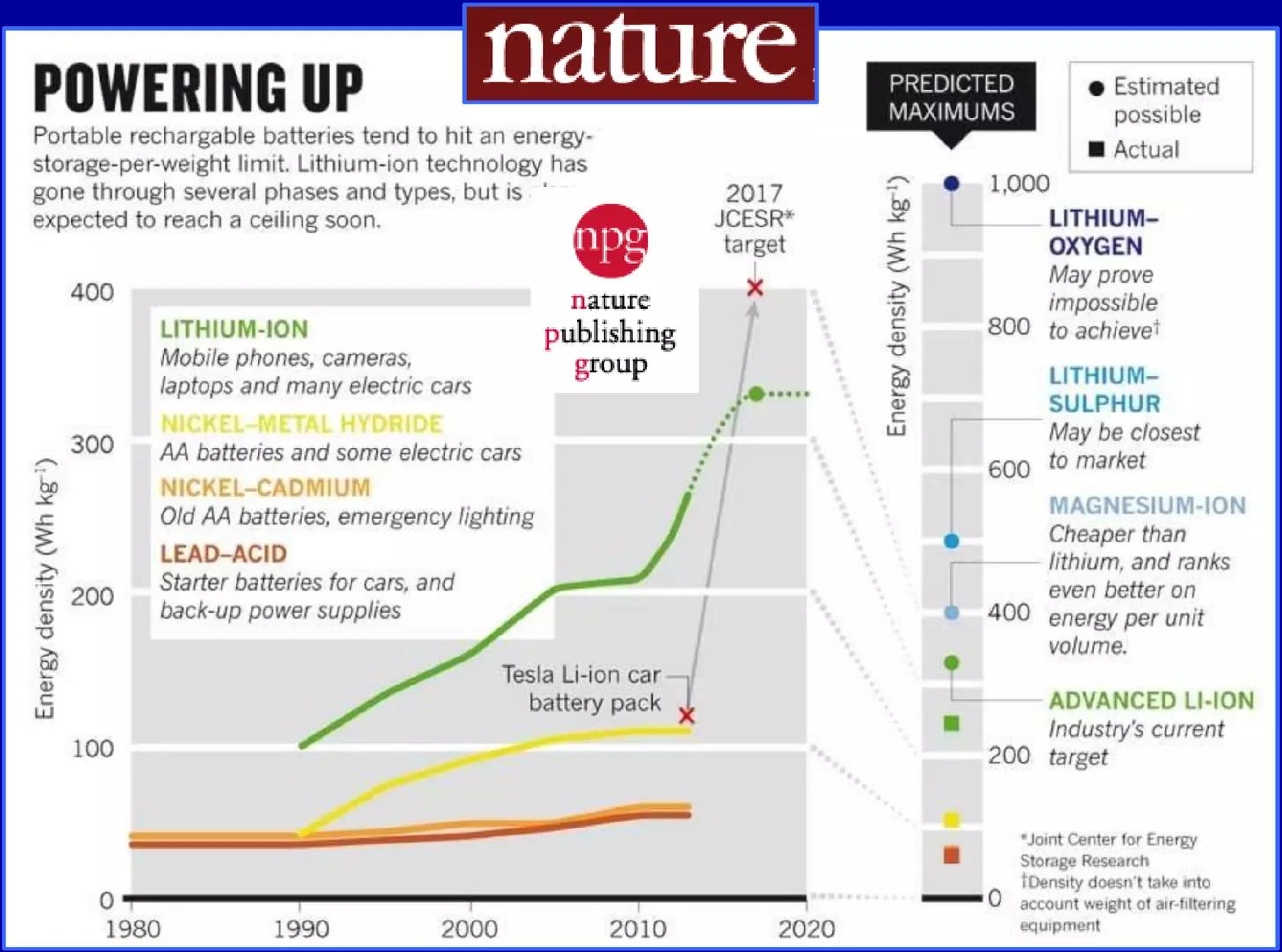
Graphic adapted by Lattice

http://www.datacenterjournal.com/lithiumion-power-data-storage-servers/

Next-generation chemistries: Lithium-sulfur and Lithium-air

Lithium-ion technology is nearing energy-density limits for that chemistry

“A better battery --- Chemists are reinventing rechargeable cells to drive down costs and boost capacity” R. Van Noorden *Nature News* March 5, 2014



POWERING UP

Portable rechargable batteries tend to hit an energy-storage-per-weight limit. Lithium-ion technology has gone through several phases and types, but is expected to reach a ceiling soon.

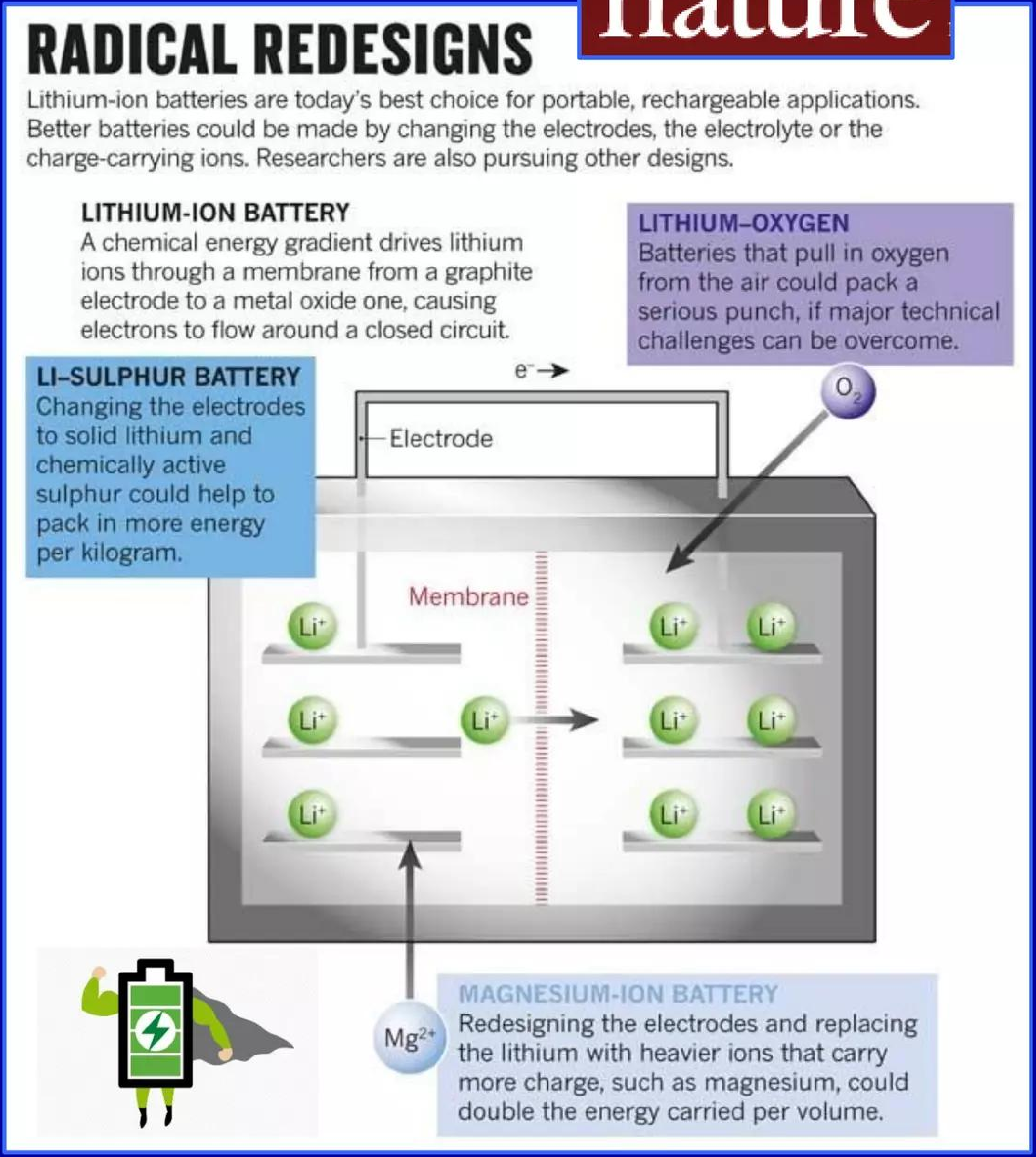
*Joint Center for Energy Storage Research
†Density doesn't take into account weight of air-filtering equipment

http://www.nature.com/polopoly_fs/1.14815!/menu/main/topColumns/topLeftColumn/pdf/507026a.pdf

Next-generation chemistries: Lithium-sulfur and Lithium-air

"A better battery --- Chemists are reinventing rechargeable cells to drive down costs and boost capacity" R. Van Noorden *Nature News* March 5, 2014

nature



RADICAL REDESIGNS

Lithium-ion batteries are today's best choice for portable, rechargeable applications. Better batteries could be made by changing the electrodes, the electrolyte or the charge-carrying ions. Researchers are also pursuing other designs.

LITHIUM-ION BATTERY
A chemical energy gradient drives lithium ions through a membrane from a graphite electrode to a metal oxide one, causing electrons to flow around a closed circuit.

LITHIUM–OXYGEN
Batteries that pull in oxygen from the air could pack a serious punch, if major technical challenges can be overcome.

LI–SULPHUR BATTERY
Changing the electrodes to solid lithium and chemically active sulphur could help to pack in more energy per kilogram.

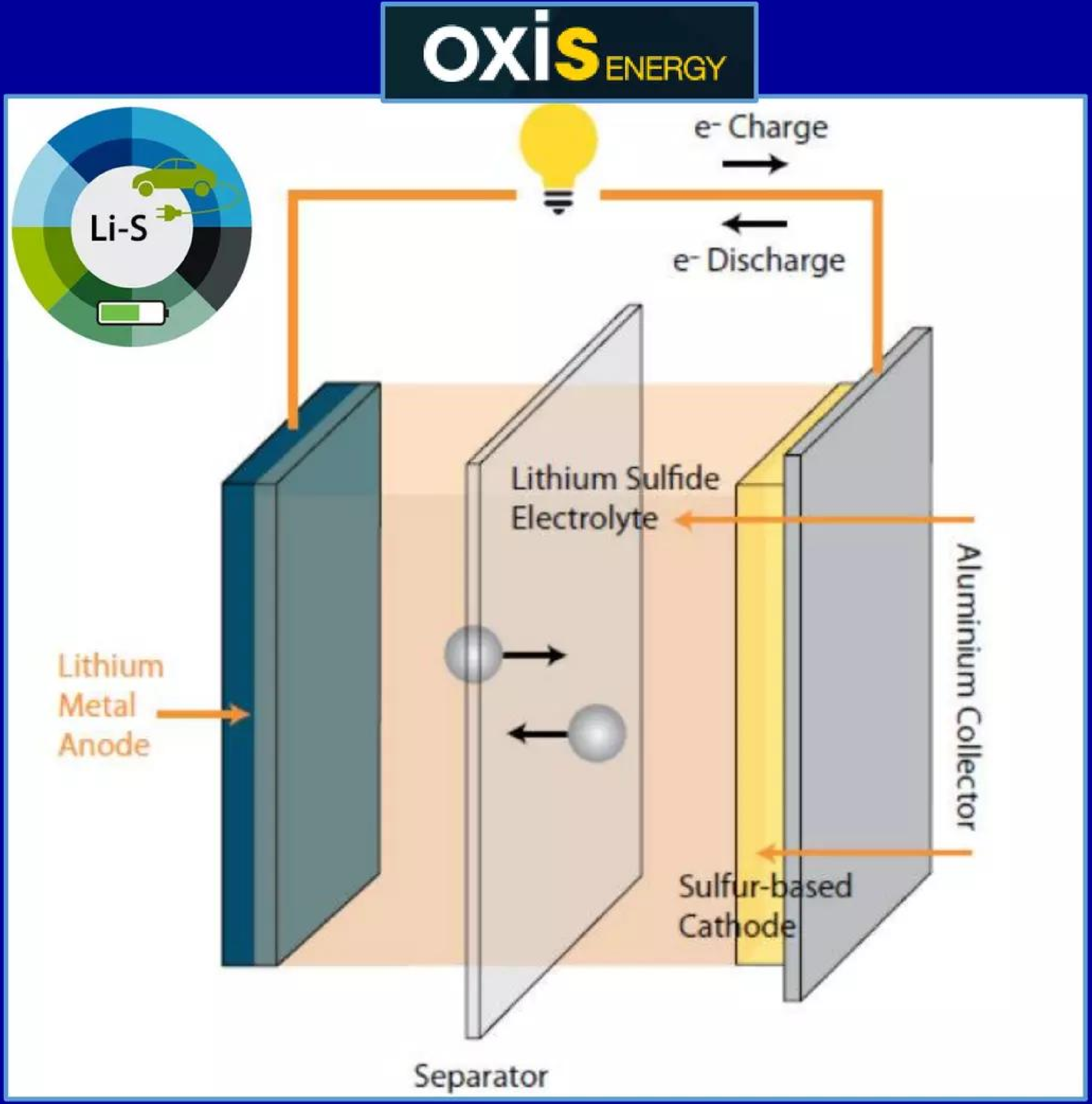
MAGNESIUM-ION BATTERY
Redesigning the electrodes and replacing the lithium with heavier ions that carry more charge, such as magnesium, could double the energy carried per volume.

npg
nature
publishing
group

Lithium-sulfur is possible successor to Li-ion technology

Oxis claims gravimetric energy density of 400 Wh/kg; Li-ion is ~200 Wh/kg

http://cleantechnica.com/2015/07/01/oxis-manufacture-li-s-batteries-achieving-400-whkg/



http://www.hybridcars.com/oxis-jump-starts-first-commercialization-of-lithium-sulfur-batteries/

Lithium-air widely touted as next great thing in batteries

Some have even made claims that it may rival gasoline's energy density

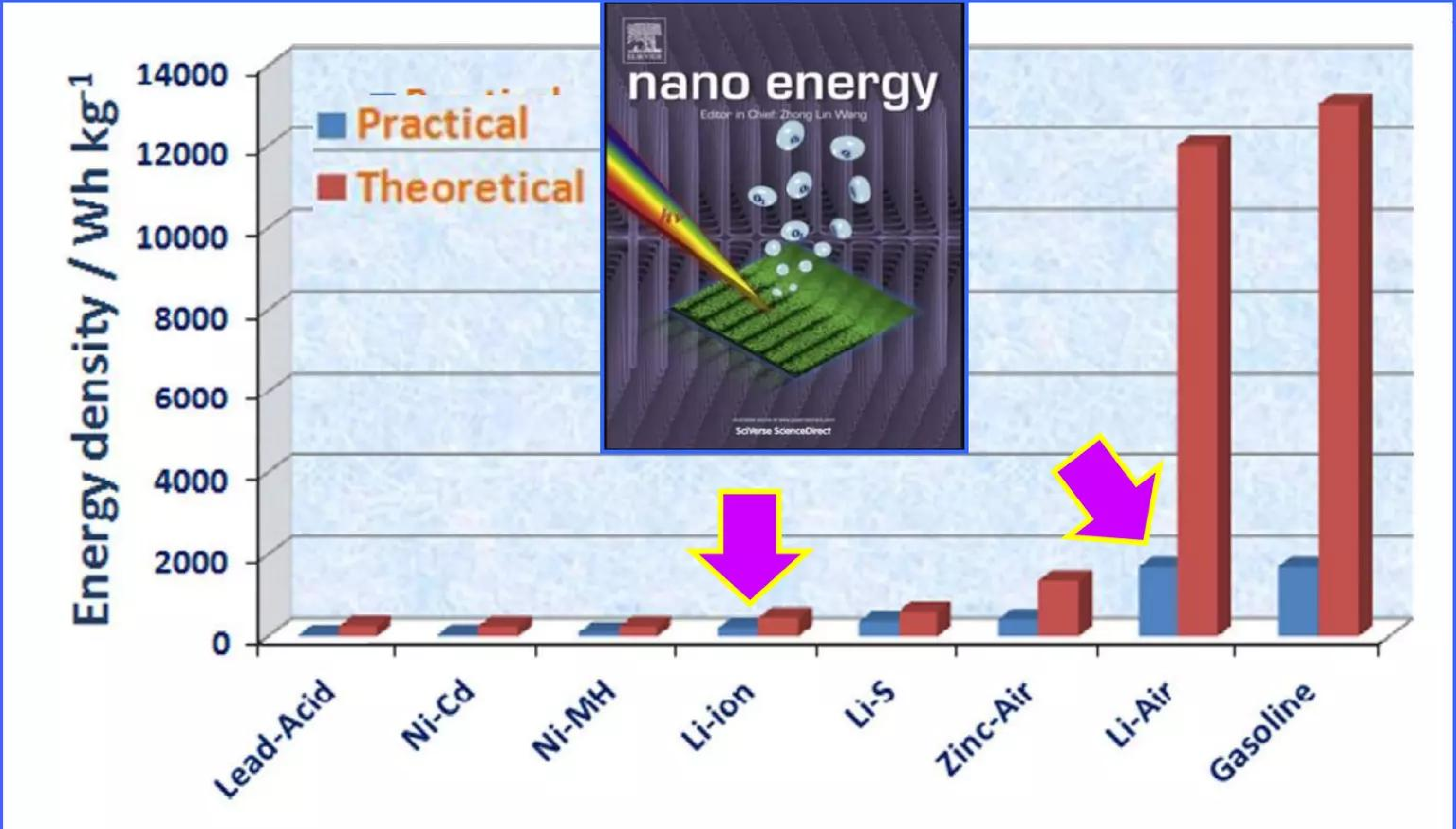


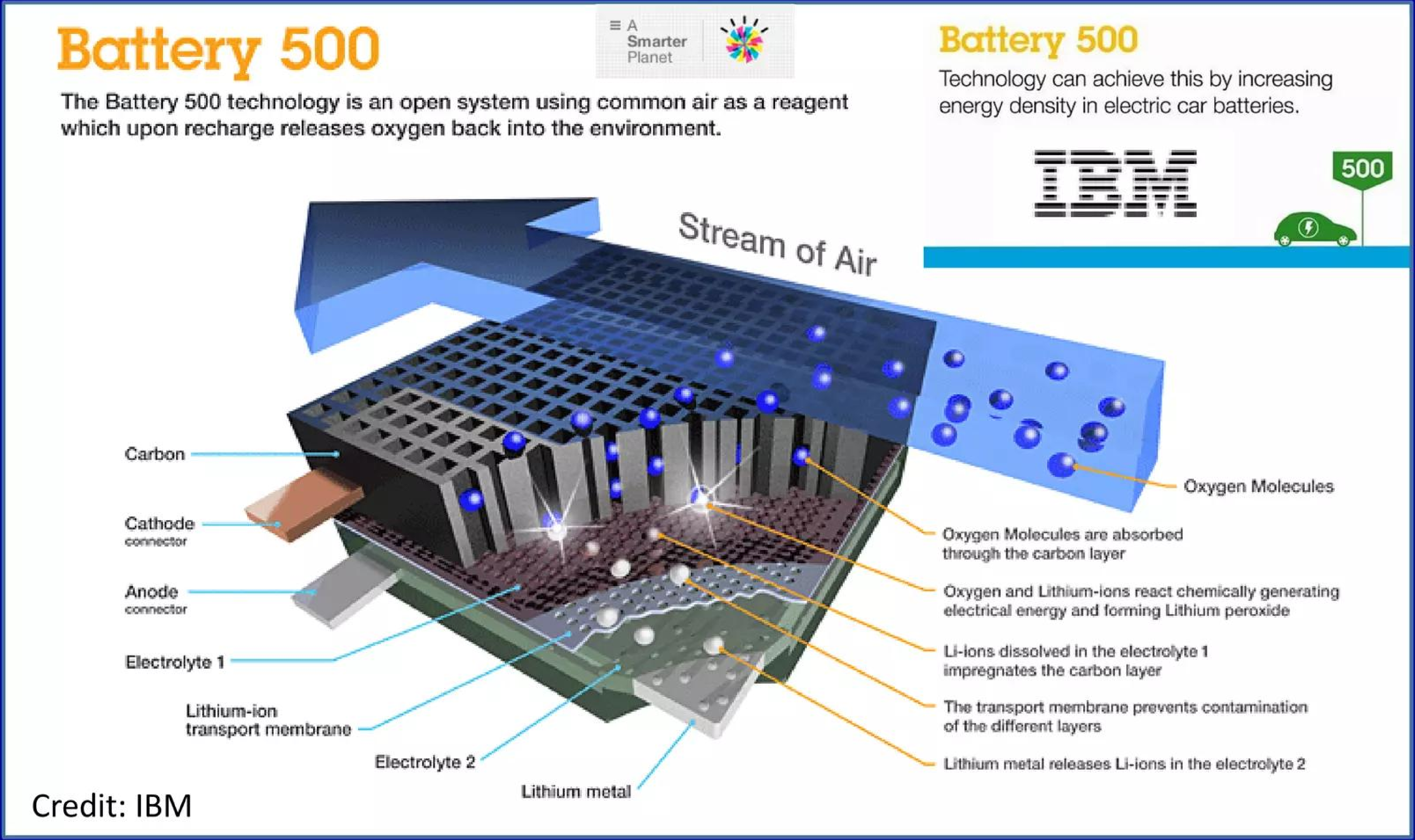
Figure 1 The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline.

Fig. 1 from: "Challenges and opportunities of nanostructured materials for aprotic rechargeable lithium-air batteries" J. Wang, Y. Li, and X. Sun, *Nano Energy* 2 pp. 443 - 467 (2013)

Lithium-air widely touted as next great thing in batteries

Much of IBM's work in Li-air technology conducted in Battery 500 project

Quoting from IBM webpage: "During discharge (driving), oxygen from the air reacts with lithium ions, forming lithium peroxide on a carbon matrix. Upon recharge, the oxygen is given back to the atmosphere and the lithium goes back onto the anode."



Credit: IBM

http://www.ibm.com/smarterplanet/us/en/smart_grid/article/battery500.html

Two major players in Lithium-air batteries curb R&D efforts

IBM and the Joint Center for Energy Storage Research (JCESR)

"Two big labs step back from the most promising next-generation battery"

QUARTZ Steve Levine in *Quartz* May 30, 2014

http://qz.com/214969/two-big-labs-most-promising-next-generation-battery-electric-car/

"In a sign of more gloom in the struggle for a better battery, two major US labs have quietly downgraded research on a technology until now widely believed to be the most promising path to a competitive electric car."

"IBM and the US-funded Joint Center for Energy Storage Research (JCESR) have ratcheted down or outright abandoned their work on the lithium-air battery, a concept in which oxygen would react with lithium to create electricity."

"In a little-remarked-upon article in March, *Nature* magazine reported that IBM's Winfried Wilcke, director of the Battery 500 Project, had a 'change of heart' about lithium-air and had turned his favor to a technology featuring sodium. In an electric car, a sodium-air battery, he said, stood a better chance of meeting the economics needed to compete with conventional cars. It was a dramatic move, with the most bullish player in lithium-air --- Wilcke himself --- calling it a day."

Two major players in Lithium-air batteries curb R&D efforts

IBM and the Joint Center for Energy Storage Research (JCESR)

“Two big labs step back from the most promising next-generation battery”

QUARTZ Steve Levine in *Quartz* May 30, 2014

http://qz.com/214969/two-big-labs-most-promising-next-generation-battery-electric-car/

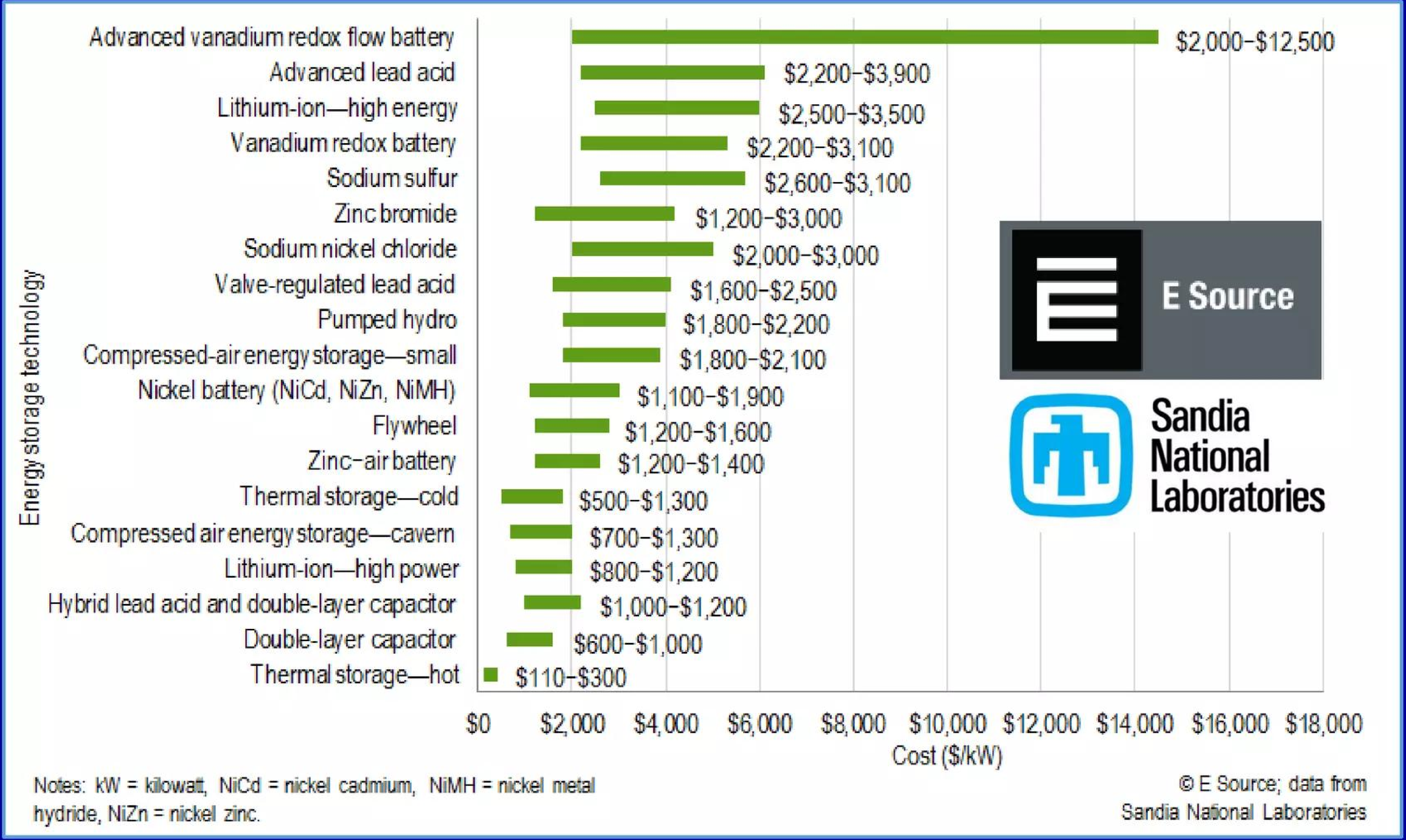
“Wilcke did not respond to emails. An IBM spokesman told Quartz that the *Nature* report is accurate but said that the company is now working on both lithium-air and sodium.”

“About the same time, JCESR dropped its lithium-air project entirely. Like IBM, JCESR did not announce the decision publicly. Kevin Gallagher, a JCESR manager, said it concluded that the challenges were too overwhelming to resolve any time soon. ‘The penalty of using gaseous reactions overwhelmed any advantage,’ he told *Quartz*.”

“Lithium-air is not being abandoned everywhere. At Argonne, Michael Thackeray is directing work on a novel hybrid battery combining lithium-ion *and* lithium-air. The result is the potential for a battery with specific density of 500 watt hours per kilogram, two-and-a-half times greater than today’s best commercial lithium-ion cell.”

Cost of various battery chemistries and other technologies

Vanadium redox flow battery is most expensive; thermal storage cheapest



Notes: kW = kilowatt, NiCd = nickel cadmium, NiMH = nickel metal hydride, NiZn = nickel zinc.

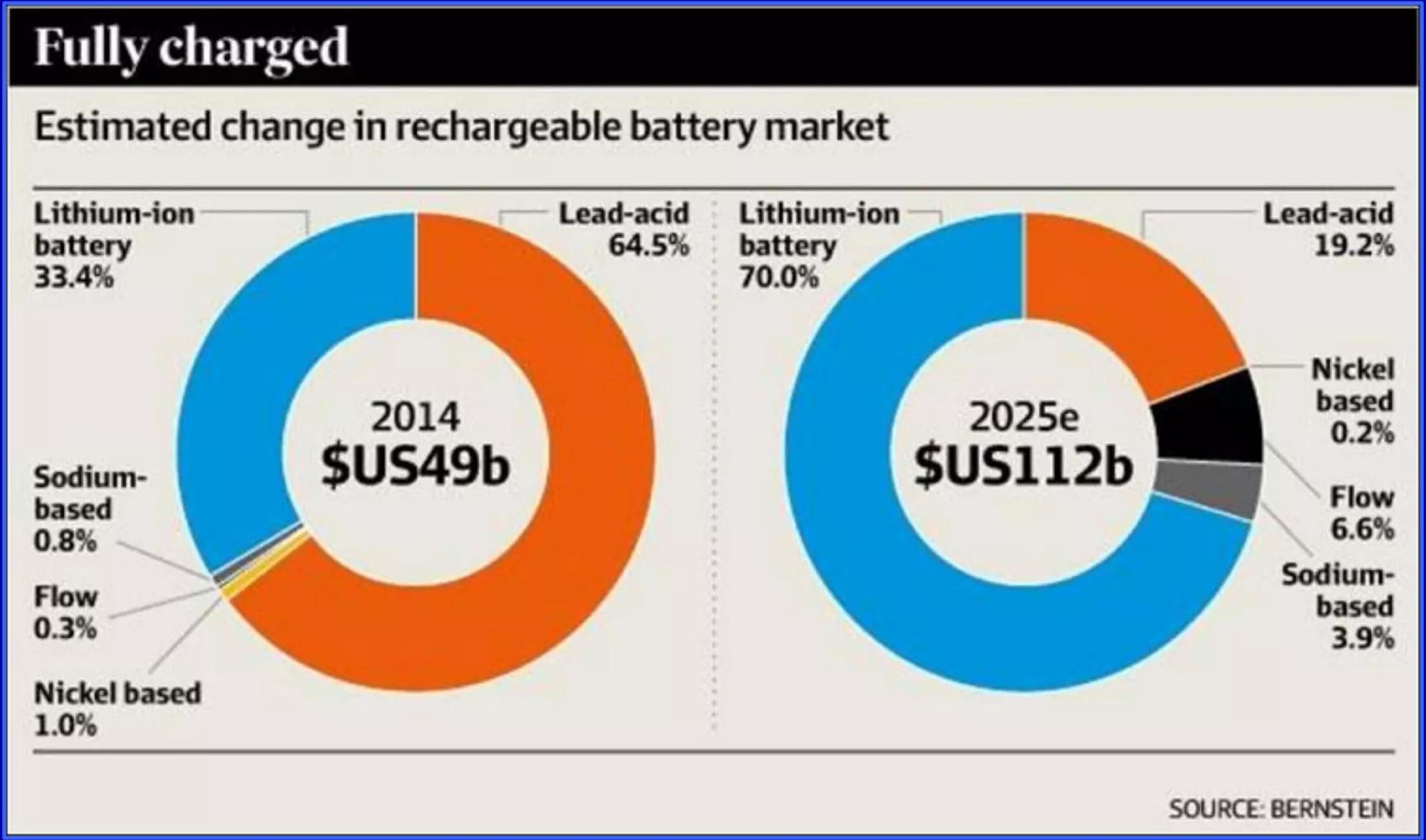
© E Source; data from Sandia National Laboratories

http://www.theenergycollective.com/jayirwinstein/2279921/who-s-reserving-all-those-tesla-batteries-and-what-do-they-plan-using-them

Bernstein projects battery market segments out in 2025

Foresees increased dominance of Lithium-ion chemistry in near-future

Seems to be implying that Li-ion will steal market share from Lead-acid chemistry



What lies for future batteries beyond today's Lithium-ion?

Lithium-ion technology is nearing energy-density limits for the chemistry

"A better battery --- Chemists are reinventing rechargeable cells to drive down costs and boost capacity" R. Van Noorden in *Nature News* March 5, 2014

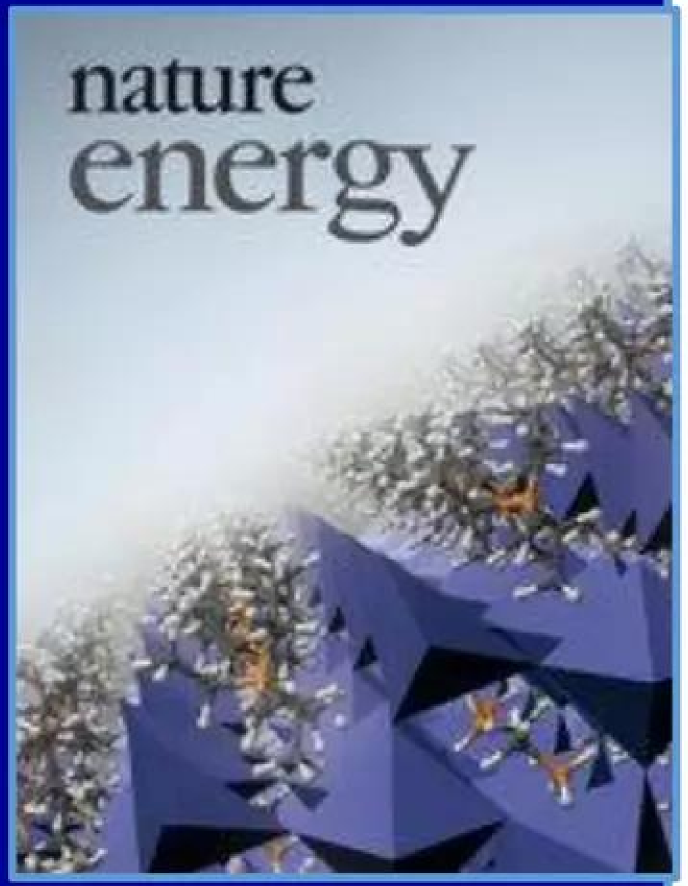
http://www.nature.com/news/the-rechargeable-revolution-a-better-battery-1.14815

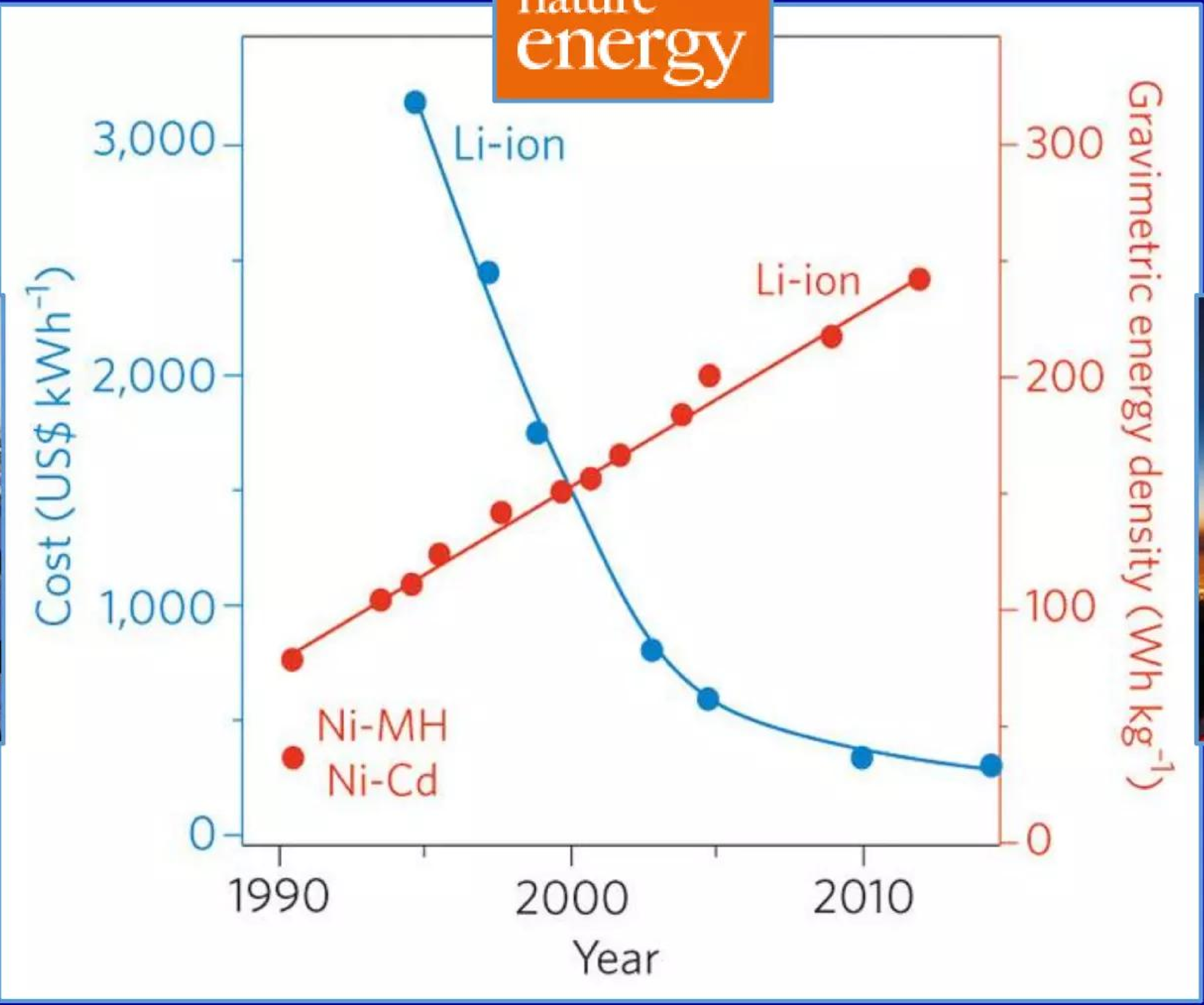
http://www.nature.com/polopoly_fs/1.14815!/menu/main/topColumns/topLeftColumn/pdf/507026a.pdf

"Modern Li-ion batteries hold more than twice as much energy by weight as the first commercial versions sold by Sony in 1991 --- and are ten times cheaper. But they are nearing their limit. Most researchers think that improvements to Li-ion cells can squeeze in at most 30% more energy by weight. That means that Li-ion cells will never give electric cars the 800-kilometre range of a petrol tank, or supply power-hungry smartphones with many days of juice."

Battery cost reduction tied to increases in energy density

If energy density increases slow down then cost reductions will stagnate





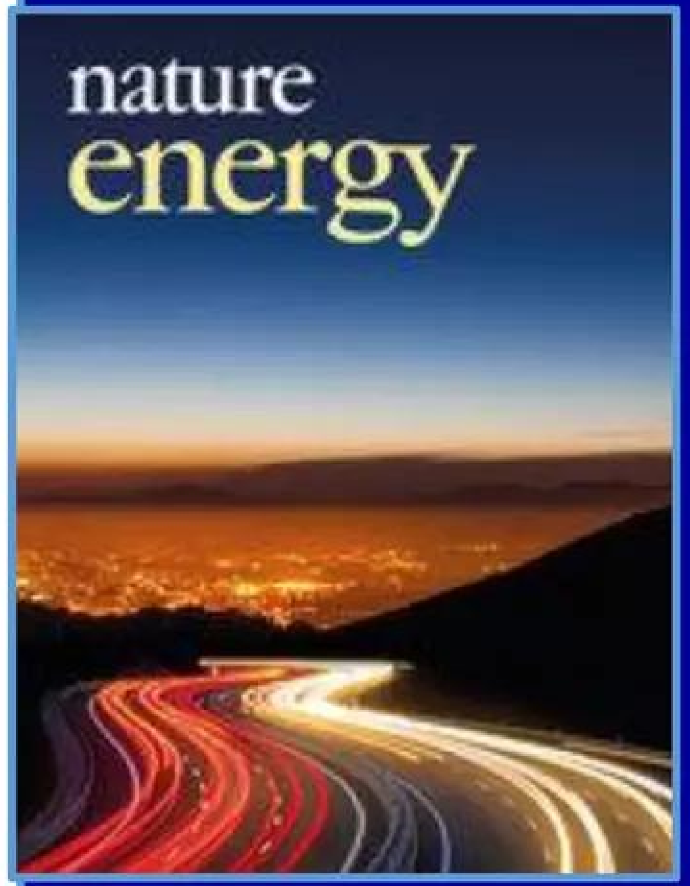
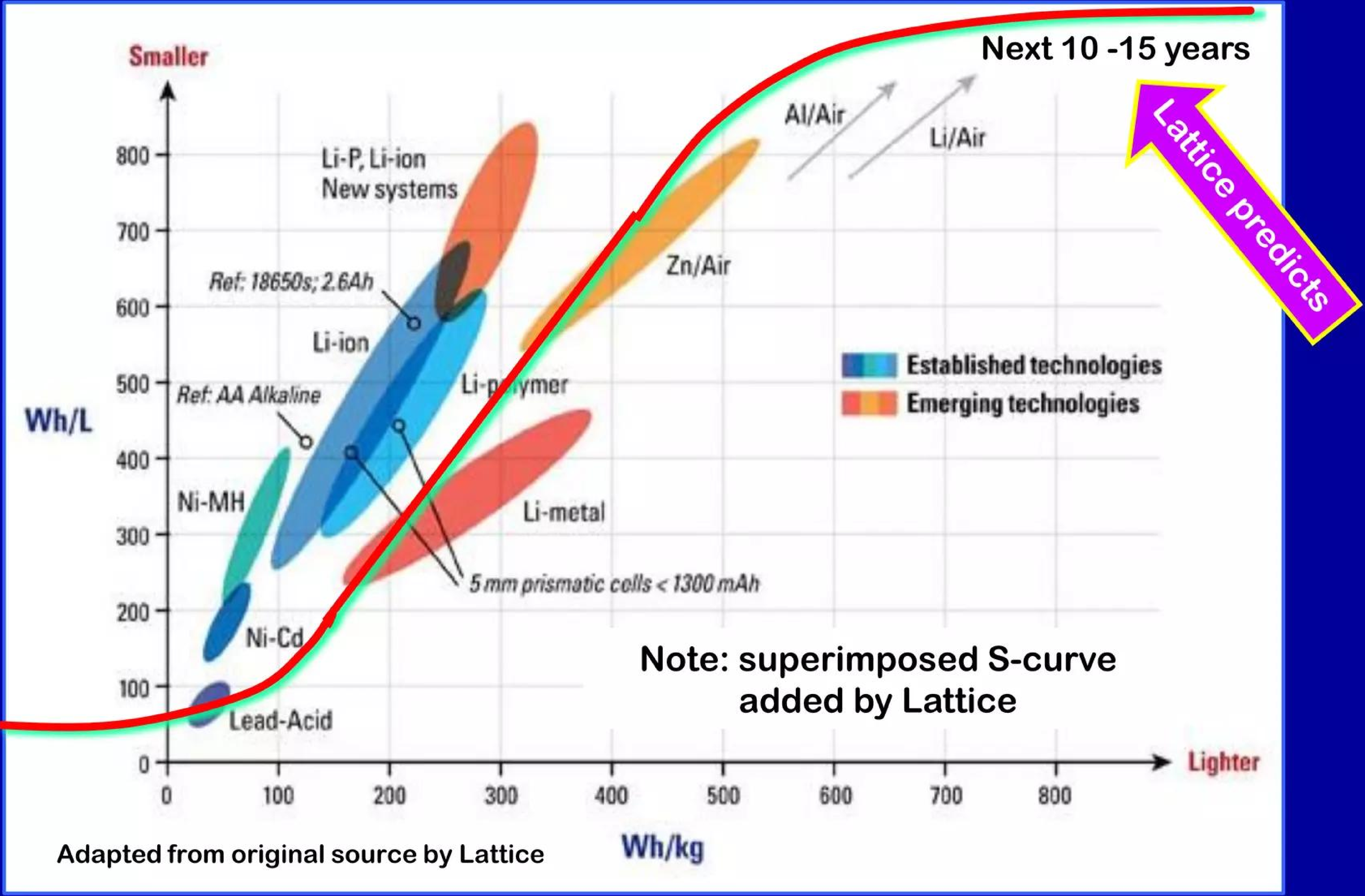


Fig. 3 in "The frontiers of energy" R. Armstrong *et al.* *Nature Energy* 1 Article # 15020 (2016)

http://www.nature.com/articles/nenergy201520

Batteries maturing and approaching technological limits

We predict energy density increases and cost reductions will slow down



Note: superimposed S-curve added by Lattice

Adapted from original source by Lattice

http://www.estquality.com/technology

Downside risk edge of the energy density sword

Caution is merited: battery capacity scale-up can increase safety risks

Runaways in tiny batteries have limited effects; big packs can cause loss-of-life

Risks can increase with scale-up

- ✓ Thermal runaway event inside a single-cell, Lithium-based ‘button’ battery might ruin a small electronic device, but it probably won’t set anything else on fire or hurt any nearby person or persons seriously
- ✓ Runaway inside smartphone’s multi-cell battery might start a woman’s handbag smoking or burn a hole through a man’s pants pocket, or make someone drop it, but it generally would not cause serious skin burns or ignite a large portion of someone’s clothing
- ✓ Catastrophic runaways inside significantly larger, multi-cell laptop computer batteries have inflicted serious burns on people’s legs and in several documented cases, have even burned-down entire homes
- ✓ Runaways involving large to extremely large many-cell secondary batteries on stationary (onsite back-up power) and mobile platforms such as hybrid or all-electric vehicles and passenger or cargo aircraft are very serious matters; can cause multiple fatalities and up to many millions of $ in physical damage to equipment and/or local facilities

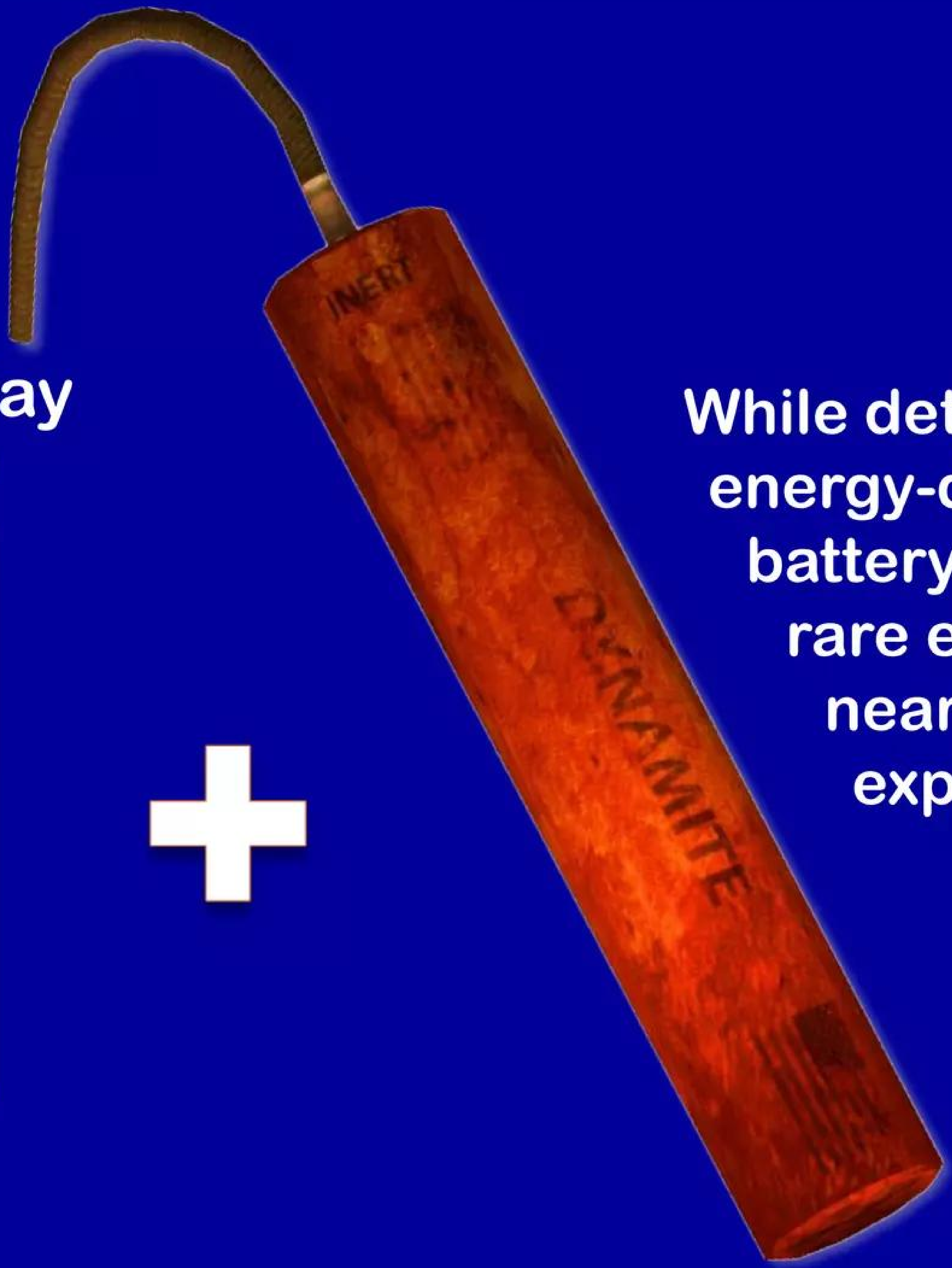
Downside risk edge of the energy density sword

Devices with high chemical or electrical energy densities can be risky

On rare occasions batteries can have problems that create product safety risks

Would you play with this?

+



While detonations of individual energy-dense, Lithium-based battery cells are extremely rare events, they can be nearly as powerful as exploding dynamite

Downside risk edge of the energy density sword

Risks for thermal runaways, hot fires, and catastrophic explosions

Spontaneous Lithium battery fires and explosions have occurred with e-cigarettes

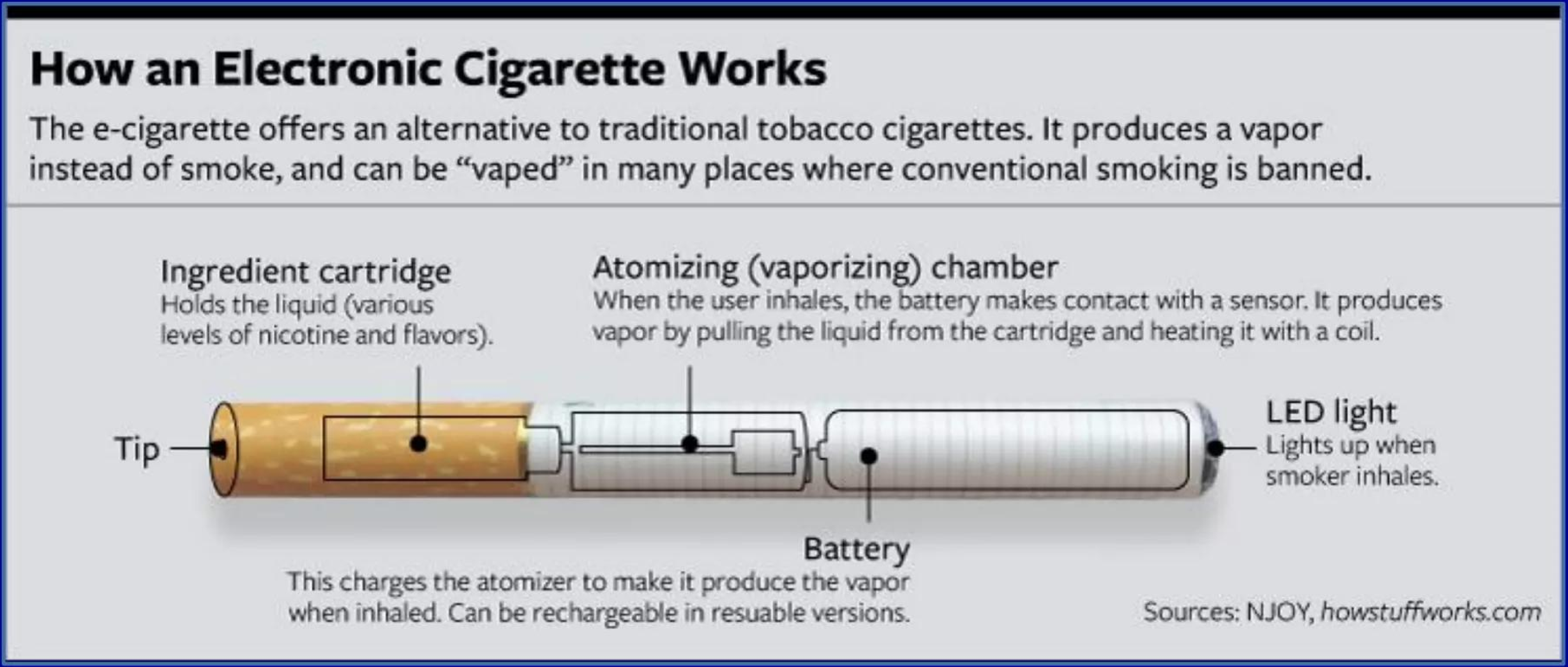
All injuries below occurred recently with e-cigarettes or larger vaping devices

Downside risk edge of the energy density sword

Risks for thermal runaways, hot fires, and catastrophic explosions

Spontaneous Lithium battery fires and explosions have occurred with e-cigarettes

Small Lithium-based batteries in e-cigarettes and vaping devices can cause horrific injuries when they suffer catastrophic spontaneous thermal runaways



How an Electronic Cigarette Works

The e-cigarette offers an alternative to traditional tobacco cigarettes. It produces a vapor instead of smoke, and can be "vaped" in many places where conventional smoking is banned.

Ingredient cartridge
Holds the liquid (various levels of nicotine and flavors).

Atomizing (vaporizing) chamber
When the user inhales, the battery makes contact with a sensor. It produces vapor by pulling the liquid from the cartridge and heating it with a coil.

Tip

LED light
Lights up when smoker inhales.

Battery
This charges the atomizer to make it produce the vapor when inhaled. Can be rechargeable in resuable versions.

Sources: NJOY, *howstuffworks.com*

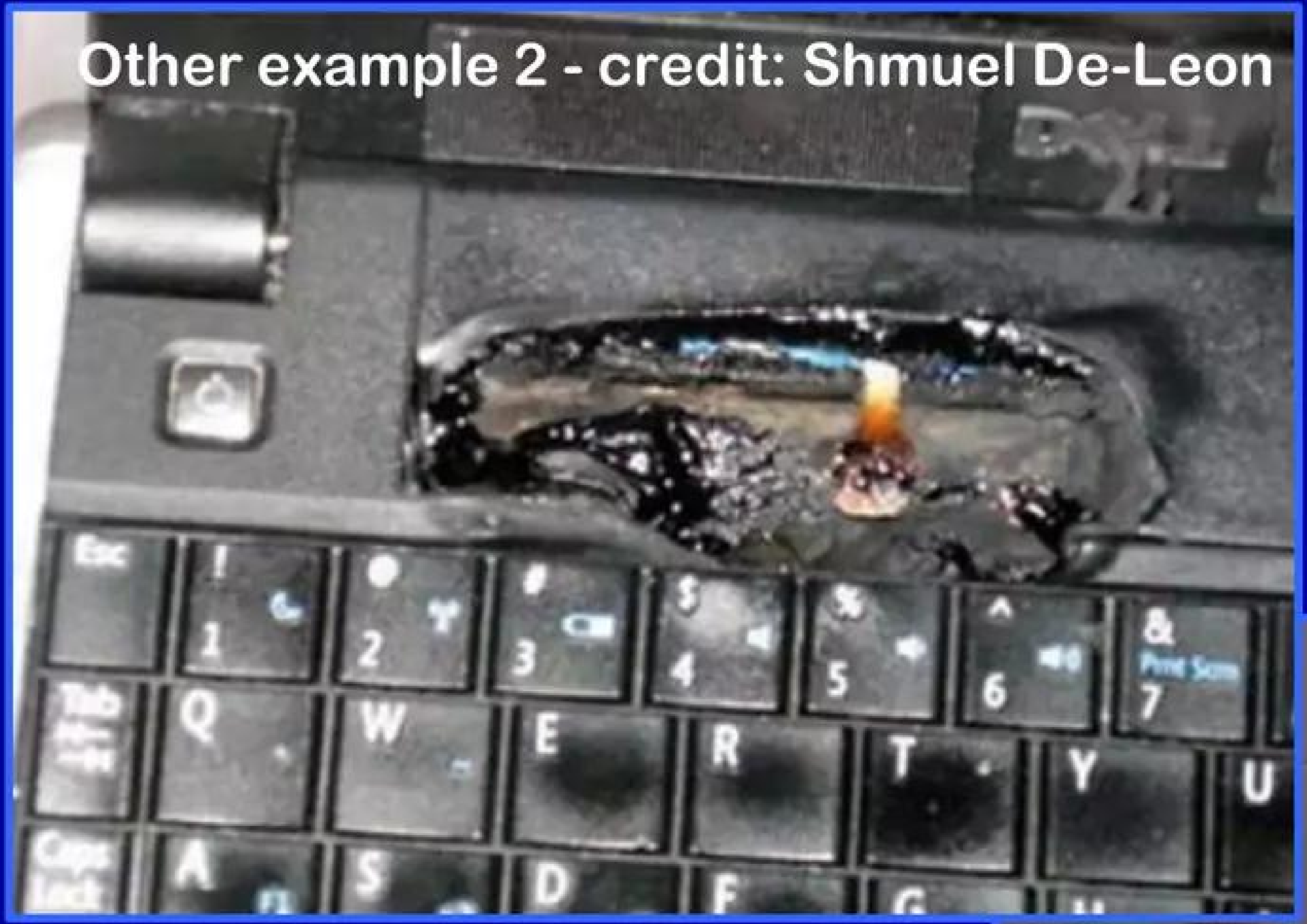
Downside risk edge of the energy density sword

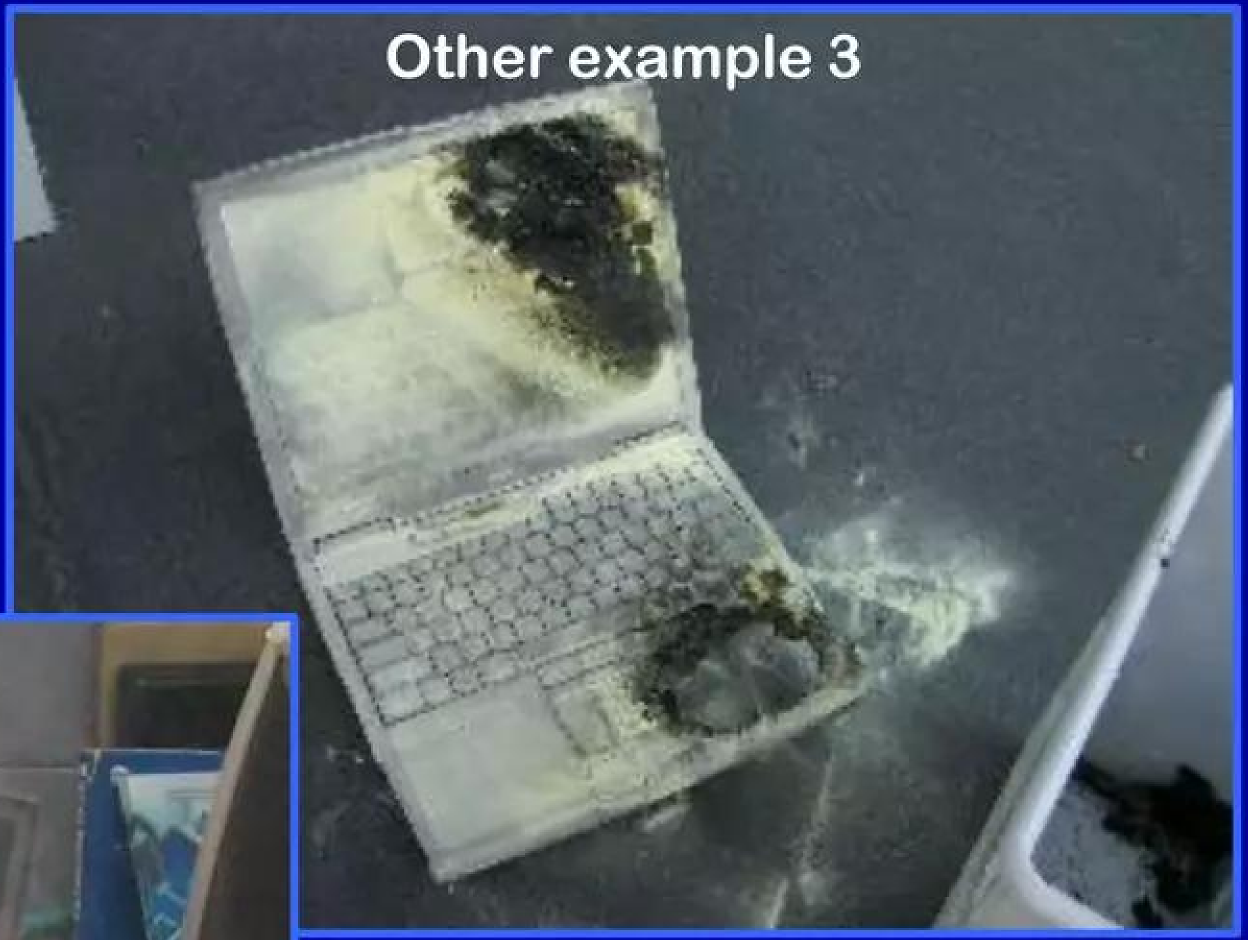
Risks for thermal runaways, hot fires, and catastrophic explosions

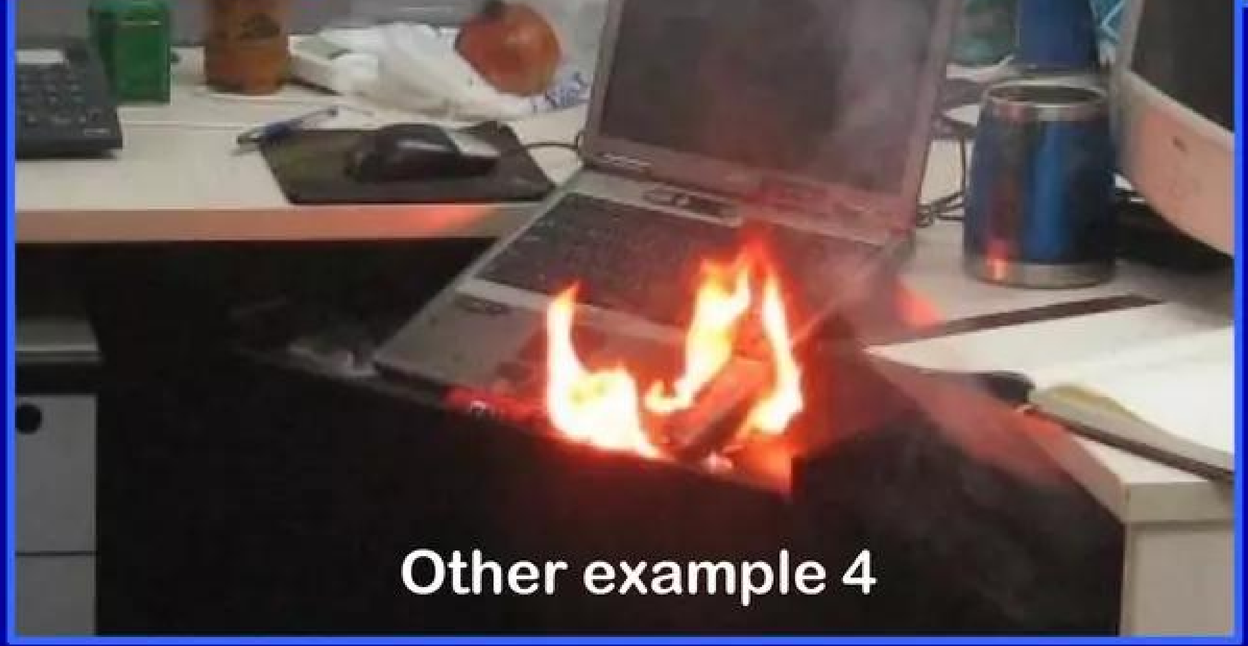
Laptop OEMs have had recalls for battery problems; some houses burned down

"Fire destroys Wilbraham home after laptop battery explosion"
By Maggie Lohmiller and Ryan Trowbridge, *Western Mass News*,
posted: Apr 01, 2016 6:10 PM CDT Updated: Apr 01, 2016 6:10 PM CDT

http://www.westernmassnews.com/story/31624627/fire-destroys-wilbraham-home-after-laptop-battery-explosion


Other example 2 - credit: Shmuel De-Leon


Other example 3


Other example 4

Downside risk edge of the energy density sword

Risks for thermal runaways, hot fires, and catastrophic explosions

Laptop OEMs have had recalls for battery problems; some houses burned down

"Toshiba recalls 100,000 batteries that can melt your laptop"
By Aaron Smith, *CNN*, posted: Apr 01, 2016 6:10 PM CDT

http://money.cnn.com/2016/04/01/technology/toshiba-laptop-battery-recall-panasonic/

"Toshiba is recalling faulty laptop batteries that are too hot to handle. The lithium-ion battery packs, which are made by Panasonic, can overheat, posing burn and fire hazards to consumers, according to the U.S. Consumer Product Safety Commission on Thursday."

"Toshiba received four reports of the battery packs overheating and melting, though the CPSC said no injuries have been reported."

"Toshiba, which first announced the recall in January, said it was recalling the batteries in certain Toshiba Notebook computers sold since June 2011. The Japanese manufacturer said it would replace them for free."

"The CPSC said the recall involves 91,000 laptops sold in the United States and 10,000 sold in Canada. The recall involves 39 models of Portege, Satellite and Tecra laptops."

Downside risk edge of the energy density sword

Risks for thermal runaways, hot fires, and catastrophic explosions

Spontaneous Lithium battery thermal runaways and fires occur in hoverboards

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

Spontaneous Lithium battery thermal runaways have occurred in large systems

"Online internal short circuit detection for a large format lithium ion battery"
X. Feng *et al. Applied Energy* 161 pp. 168 - 180 (2016)

http://www.umich.edu/~racelab/static/Webpublication/2016-ENERGY-XuningF.pdf

"All of the batteries that were involved in the accidents reported in [6–9] have high capacity and large formats in dimension. Large format batteries are favored by manufacturers because they reduce the cell number and pack complexity in battery pack design [10], thereby improving the reliability of a battery pack [11]. However, a large format battery is more vulnerable to safety problems because it contains more stored energy. Cooling is less effective because of the lower surface/volume ratio, which leads to higher non-uniformity in the temperature distribution within the cell [11]. A local hot spot, which may be triggered by an internal short circuit (ISC), can propagate throughout the whole cell, resulting in thermal runaway and fire [11]. An ISC is believed to be the root cause of the large format lithium ion battery fire in a series of accidents of Boeing 787 Dreamliner airplanes [8,9]. In those cases, local heat generation, induced by the ISC, developed into thermal runaway in one of the large format batteries, resulting in cell-to-cell propagation and subsequent failure of the whole battery pack [8,9]."

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

Spontaneous Lithium battery thermal runaways have occurred in large systems

During 2011 several suspicious, rather frightening fires occurred in Renault F1 race cars equipped with Li-ion batteries in the cars' KERS (kinetic energy recovery system); the Saft Li-ion batteries used in the 2011 season's Renault Formula 1 (F1) KERS most likely had Lithium iron phosphate (LIPO) chemistry

http://www.youtube.com/watch?v=TzPv9ptIXNI

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

Spontaneous Lithium battery thermal runaways have occurred in large systems

2013: freeze-frame from amateur video of incident shows entire front-end of Tesla Model S completely engulfed in flames

http://www.youtube.com/watch?feature=player_embedded&v=q0kjI08n4fg

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

Spontaneous Lithium battery thermal runaways have occurred in large systems

2015 Tesla Model S P90D --- MSRP as configured is roughly $121, 950

Model: 2015 Tesla Model S

MSRP: From $105,000

Horsepower: 691 hp

Range: 253 mi battery-only

Engine: Electric

MPGe: 89 city / 98 highway

Battery: 85 kWh lithium-ion

Curb weight: 4,830 lbs

101/102 MPGe
EPA

5.1 sec
0-60

N/A
HP

140 mph
Top Speed

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

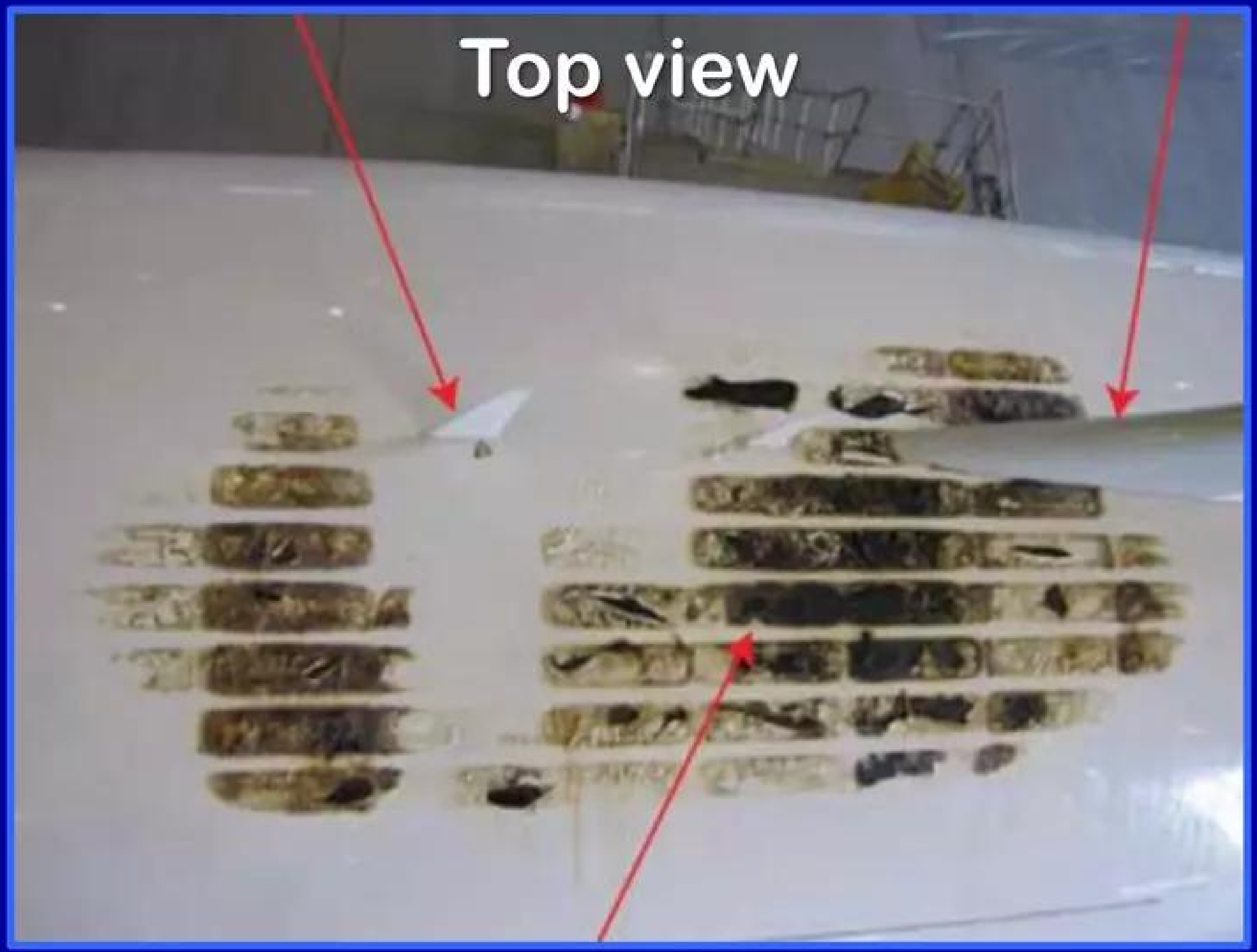
Spontaneous Lithium battery thermal runaways have occurred in large systems

July 12, 2013: battery fire broke out on an empty Ethiopian Airlines 787 sitting on ground

Investigators concluded that this fire was likely caused by Lithium-manganese dioxide primary batteries powering a small Honeywell emergency locator transmitter beacon in the roof area

Side view

Battery fire burned through Carbon-fiber skin



Top view

Some claimed to explain this battery fire was result of “crimped wires” inside Honeywell locator beacon rather than caused by spontaneous internal field-failure of some kind

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

Spontaneous Lithium battery thermal runaways have occurred in large systems

UPS 747-400 Boeing cargo plane caught fire due to Lithium-ion batteries carried in onboard cargo - Dubai Sept. 5, 2010

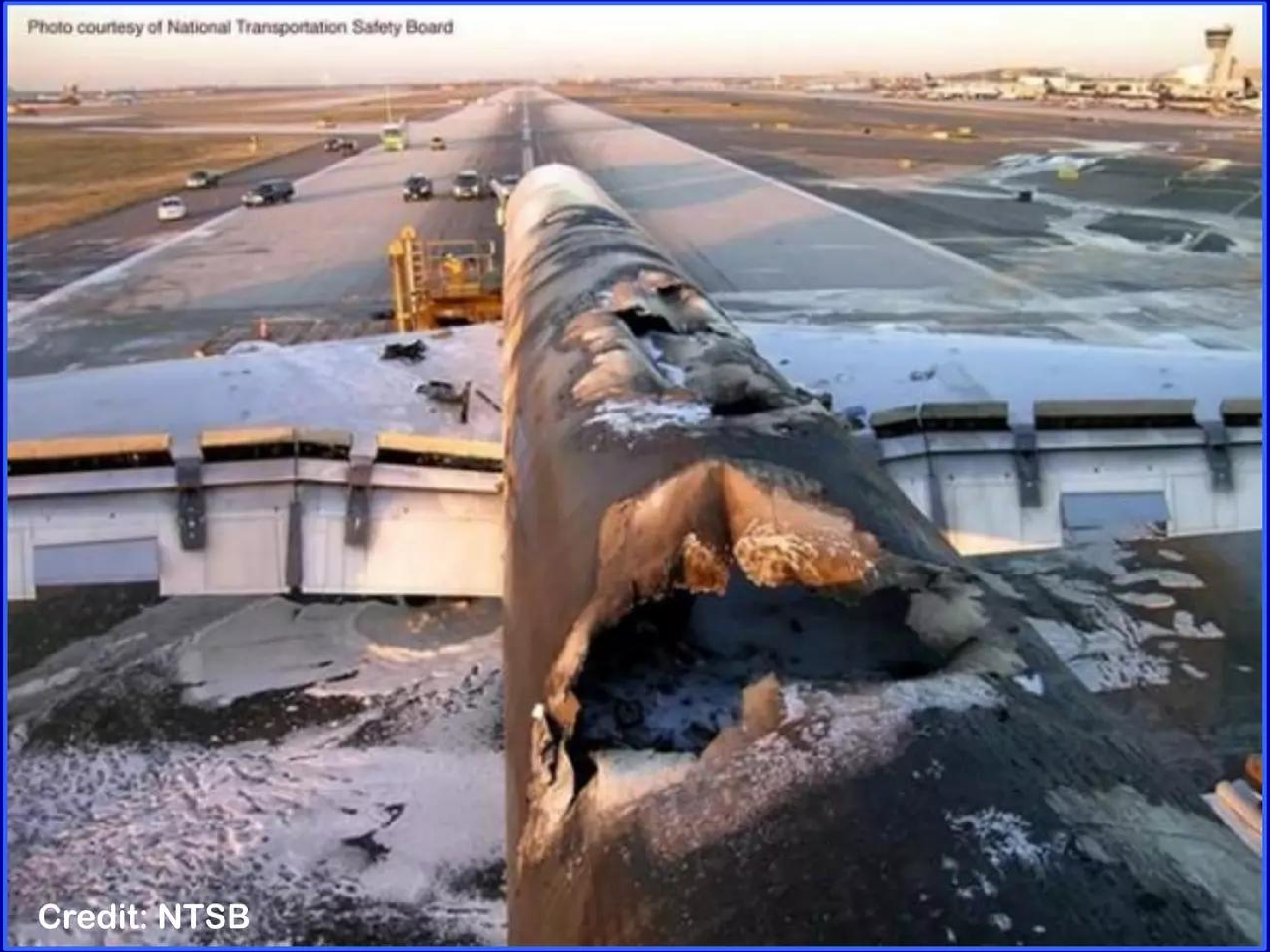
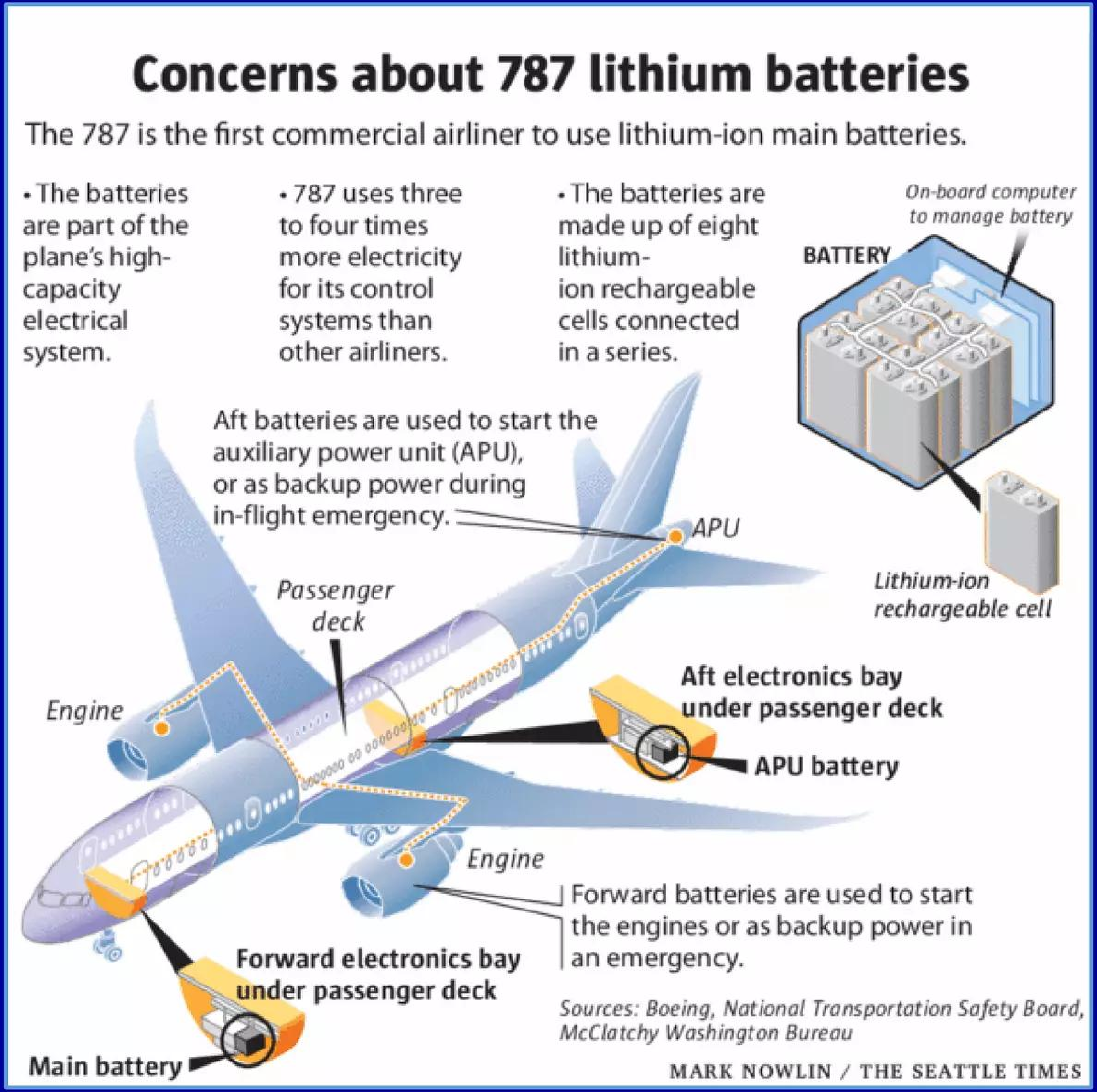


Photo courtesy of National Transportation Safety Board

Credit: NTSB

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions



Concerns about 787 lithium batteries

The 787 is the first commercial airliner to use lithium-ion main batteries.

- The batteries are part of the plane's high-capacity electrical system.
- 787 uses three to four times more electricity for its control systems than other airliners.
- The batteries are made up of eight lithium-ion rechargeable cells connected in a series.

Aft batteries are used to start the auxiliary power unit (APU), or as backup power during in-flight emergency.

Forward batteries are used to start the engines or as backup power in an emergency.

Sources: Boeing, National Transportation Safety Board, McClatchy Washington Bureau

MARK NOWLIN / THE SEATTLE TIMES

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

Spontaneous Lithium battery thermal runaways have occurred in large systems

Since it began flying passengers on Oct. 26, 2011, brand-new Boeing 787 Dreamliners have experienced at least two different thermal runaway incidents involving GS-Yuasa Lithium-ion system backup batteries: first with JAL while on the ground in Boston (Logan) and second with ANA on domestic flight in Japan

Boeing 787 Dreamliner (aft electronics bay)
Boston Logan Airport Lithium-ion battery fire (2013)

Severely fire-damaged aft Boeing787
GS-Yuasa Li-ion backup battery (NTSB)

© Reuters/Sportsfile

Runaways in battery packs or cargo can destroy big systems

Risks for thermal runaways, blazing fires, even catastrophic explosions

At the time of test sea-trials in Hawaii, ASDS had highest-capacity Lithium-based battery pack ever built until then: 1.2 megawatts. In November 2008, while sitting overnight on dry dock being inspected and then recharged, the ASDS minisub was destroyed by a still unexplained battery fire with massive explosions. U.S. Navy cancelled entire ASDS program shortly thereafter without any explanation

Yardney ASDS 1.2 MW battery pack

Advanced seal delivery system (ASDS) all-electric minisub was designed to covertly transport U.S. Navy SEAL teams to land targets from nuclear submarines hidden underwater > 100 miles offshore

Chemical batteries: very safe energy storage technology

In statistical terms, severe thermal runaways are extremely rare events

Nonetheless they must be mitigated as much as possible to prevent human injury

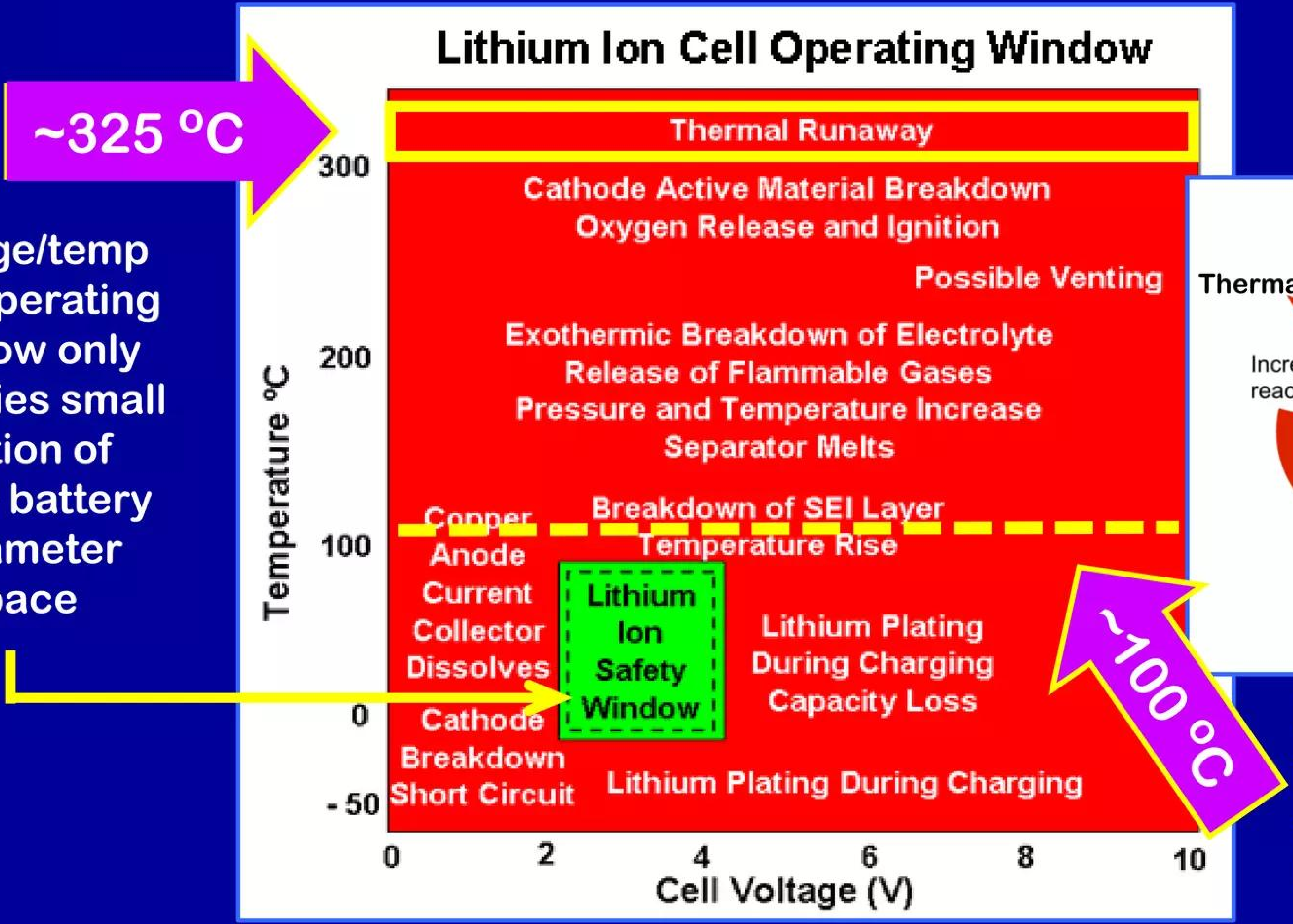
- ✓ By any reasonable standard, Lithium-based batteries are a very safe technology; ‘garden variety’ thermal runaways only occur at frequencies of one failure event per several million battery cells
- ✓ Very worst, often catastrophic, and least understood type of thermal runaway goes under the innocuous-sounding sobriquet of “field-failure.” According to statistics collected over a long time period by a major Japanese manufacturer of Lithium-ion consumer batteries, field-failures seemingly occur at rates of one such event per ~ 4 - 5 million fresh Lithium-based battery cells that come right off the production line, regardless of their chemistry or whether a battery is primary versus secondary
- ✓ One more related issue: although it is admittedly difficult to specify quantitatively, the probability of field-failure thermal runaway events appears to increase significantly as batteries ‘age’ and go thru a great many charge-discharge cycles; however, not all battery chemists agree with that contention

Positive temp feedback loop creates thermal runaways

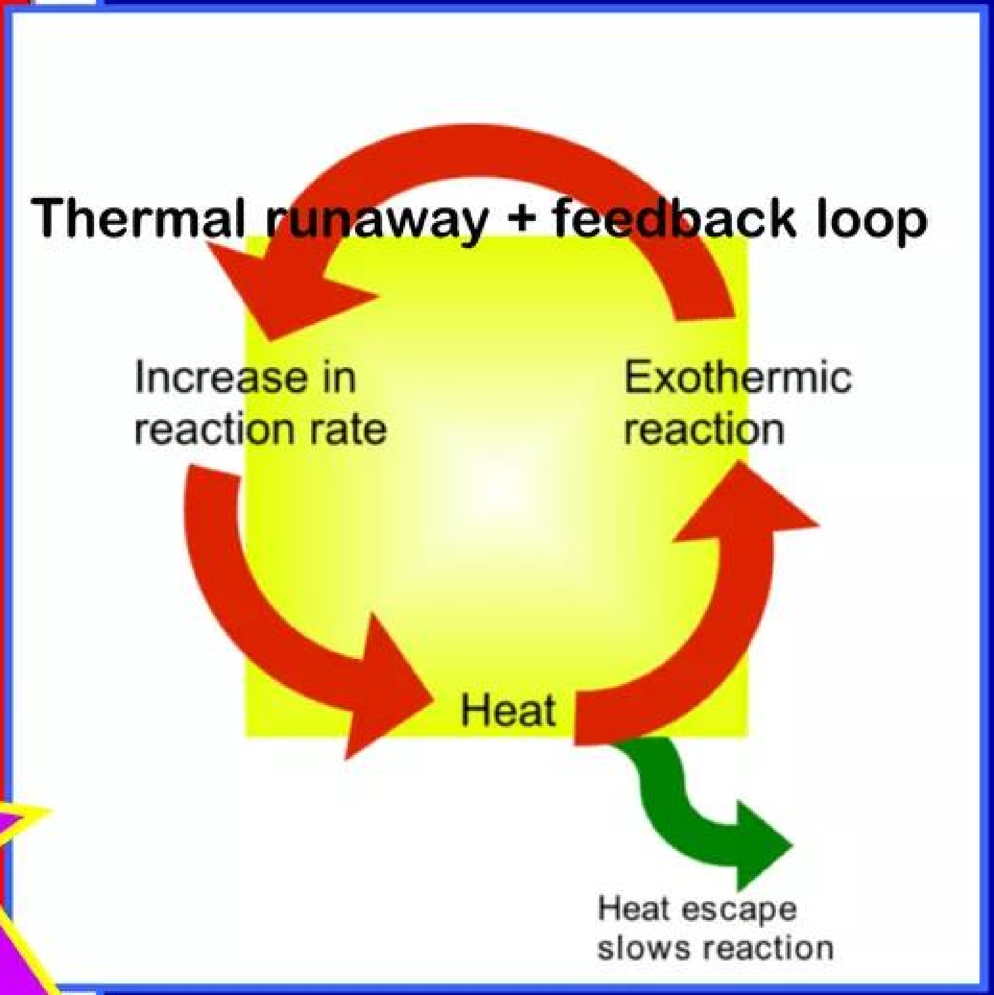
Lithium-ion battery cells have a relatively small safe operating window

Catastrophic thermal runaways can be created by temperatures as low as 325 °C

Voltage/temp safe operating window only occupies small portion of entire battery parameter space



Danger zone starts at ~ 100° C



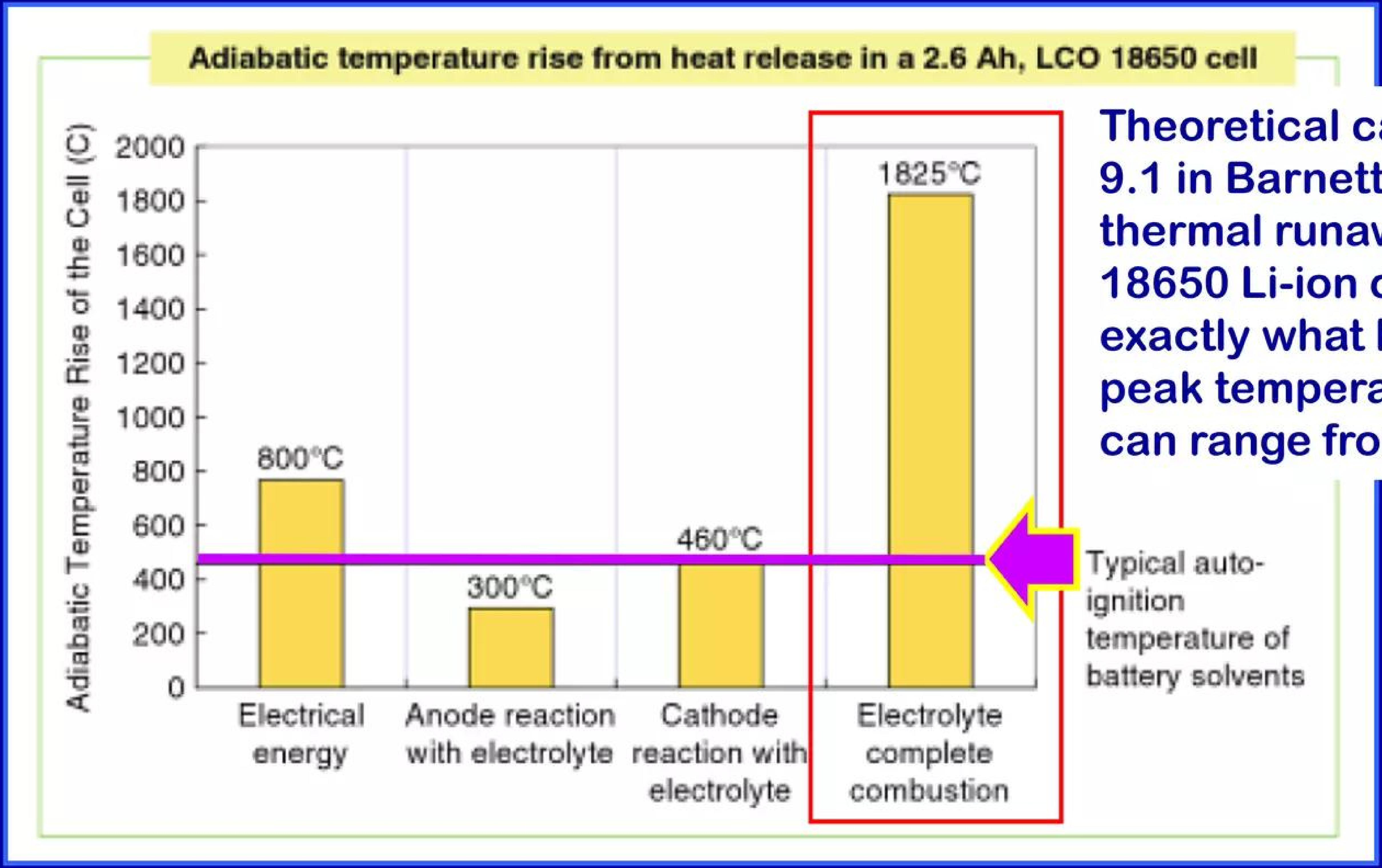
Destabilizing breakdown of crucial SEI layer begins at ~ 100° C

Lattice Energy LLC, Copyright 2016 All rights reserved

Barnett et al: peak temperatures in battery thermal runaways

Different maximums are reached depending on exactly what happens

1825º C for 100% electrolyte combustion; far higher temps with electric arcs



Theoretical calculations from Fig. 9.1 in Barnett *et al*. (2012). With thermal runaway in a commodity 18650 Li-ion cell, and depending on exactly what happens in such a cell, peak temperatures during an event can range from 300 up to 1,825º C

Circa 460º C is a typical value for the auto-ignition temperature of many different battery solvents

"Batteries for Sustainability – Selected Entries from the Encyclopedia of Sustainability in Science and Technology", Ralph J. Brodd, *ed*., Springer ISBN 978-1-4614-5791-6 (eBook) 519 pages (paper); see Chapter 9 by B. Barnett *et al*., "Lithium-ion Batteries, Safety" Springer (New York) 1 edition (2012) US$143.50

Temperatures in some thermal runaways can reach >3,000º C

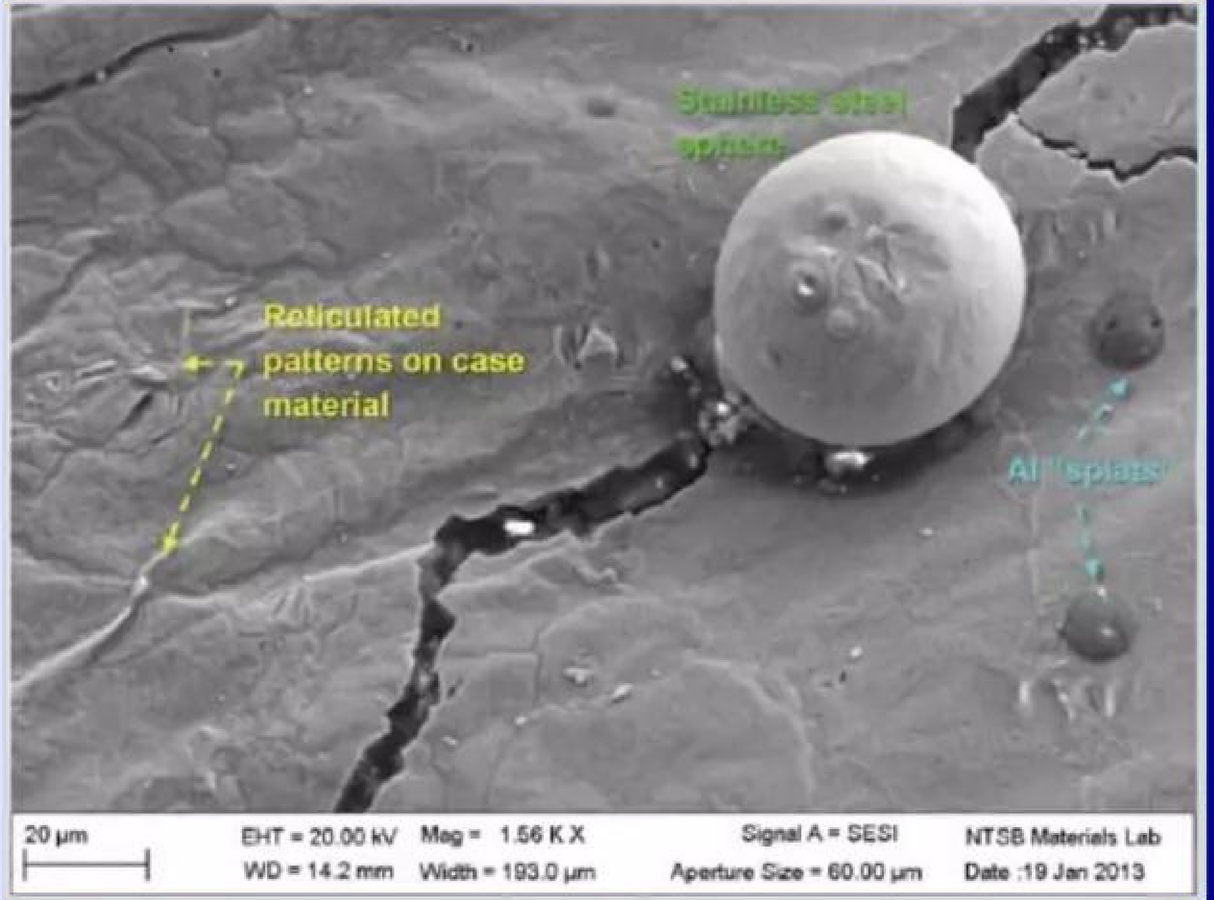
Internal shorts can lead to electric arcs in catastrophic battery failures

Steel microspheres in SEM images of battery debris after thermal runaway

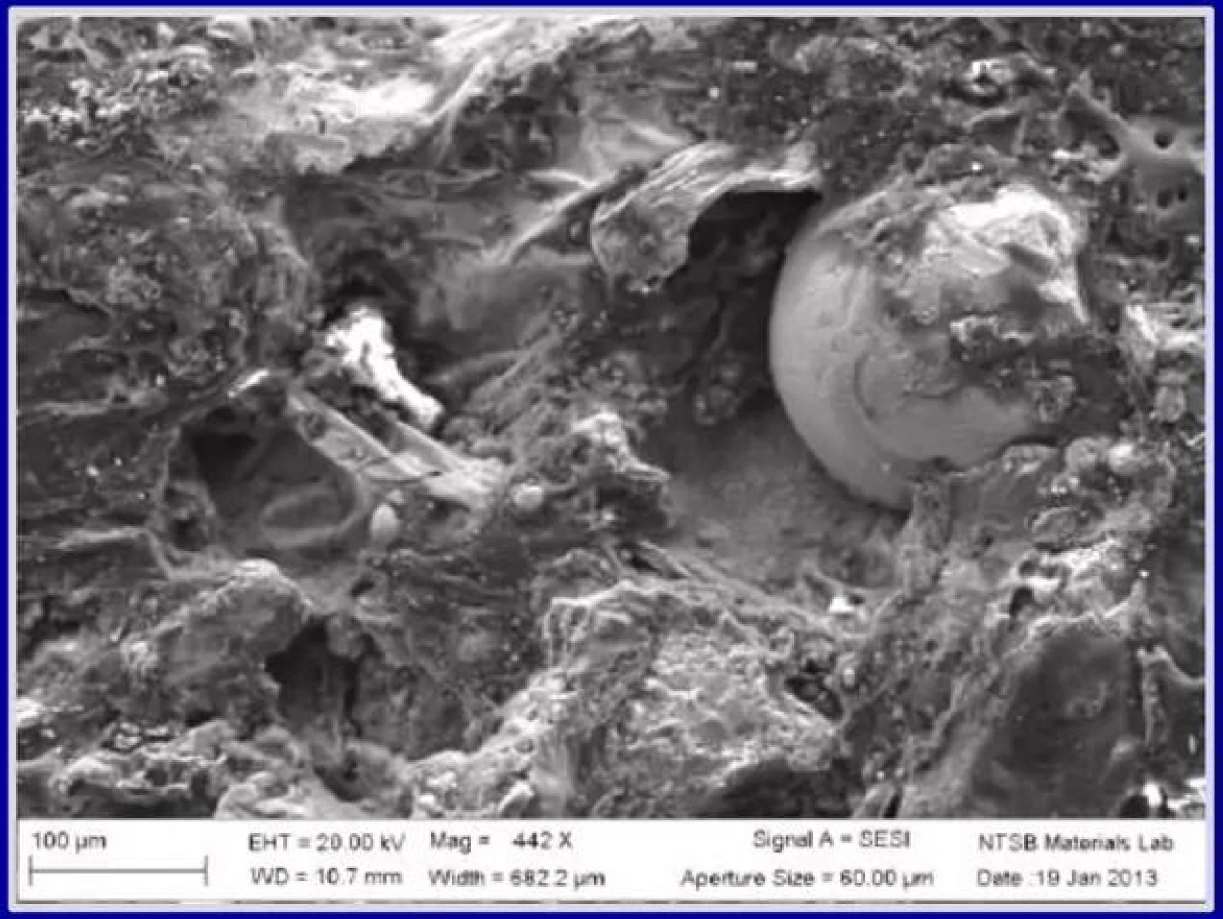
NTSB report indicated extremely high local internal temperatures (2013)

Data suggests that temperatures above 3,000º Centigrade likely occurred at local hotspots created by high-current electric arcs occurring inside a GS Yuasa Lithium battery during Boeing Dreamliner thermal runaway event at Boston Logan airport

NTSB Report No. 13-013



NTSB Report No. 13-013



Lattice has concluded that presence of perfect stainless steel microspheres in debris of the ruined GS Yuasa battery implies local temperatures must have reached > 3,000º C. Such tiny microspheres are created by condensation of droplets from a vapor phase; identical types of microspheres are produced when metals are subjected to high-intensity laser pulse ablation

Inner cores of electric arcs can hit monstrous temperatures

Refractory metals will be melted and other materials will be combusted

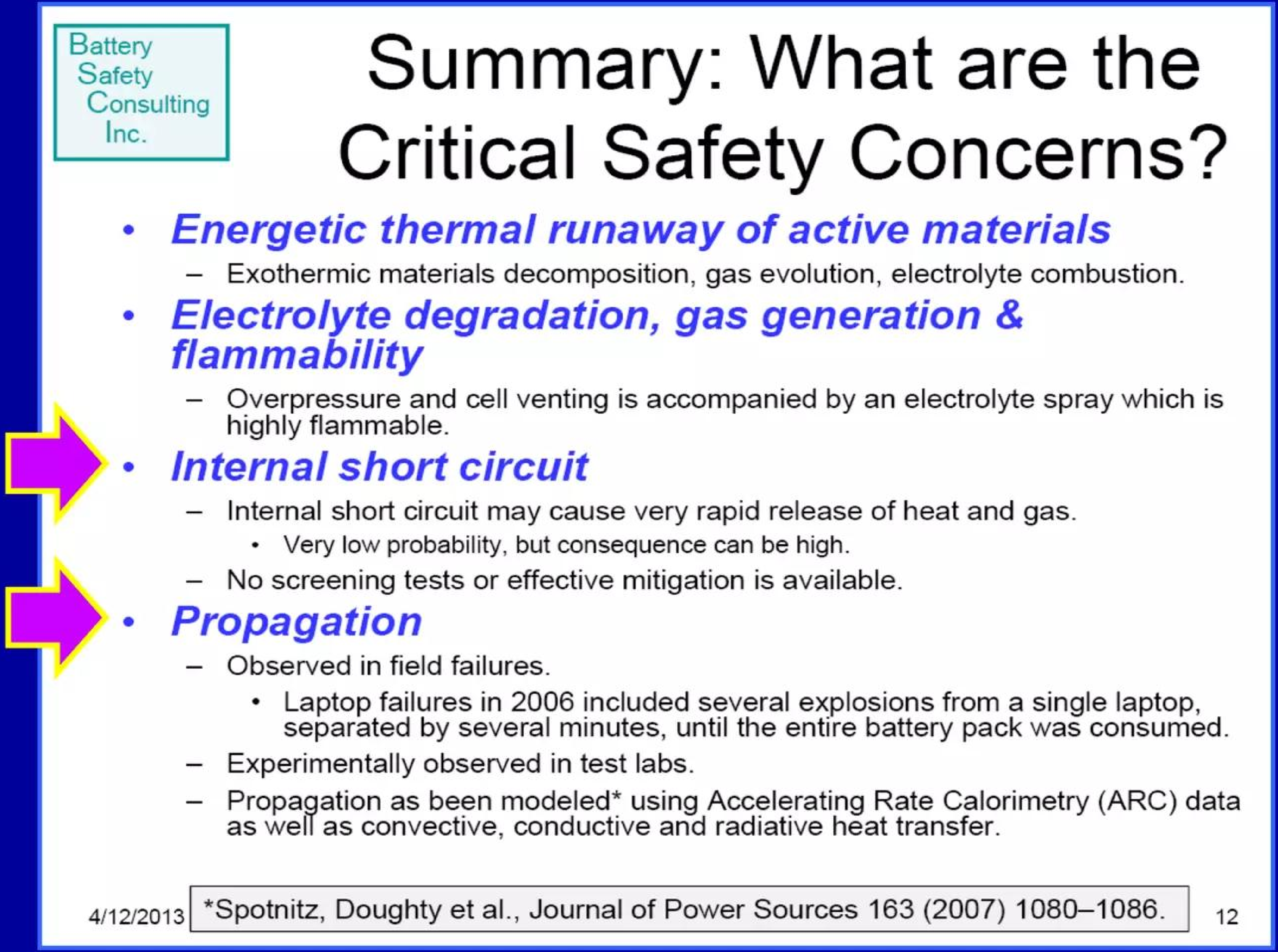
Inner cores of high-current electric arcs can reach peak temperatures of over 20,000° C in just milliseconds

What factors are involved in triggering thermal runaways?

Complex: many different things can contribute to battery thermal failures

“Failure mechanisms of Li-ion batteries”
Dr. Daniel Doughty, Battery Safety Consulting, Inc.
NTSB Battery Forum 12 MS-PowerPoint slides April 11, 2013

http://www.ntsb.gov/news/events/Documents/2013_Lithium_Batteries_FRM-Panel1d-Doughty.pdf



Battery
Safety
Consulting
Inc.

Summary: What are the Critical Safety Concerns?

- ***Energetic thermal runaway of active materials***
  - Exothermic materials decomposition, gas evolution, electrolyte combustion.
- ***Electrolyte degradation, gas generation & flammability***
  - Overpressure and cell venting is accompanied by an electrolyte spray which is highly flammable.
- ***Internal short circuit***
  - Internal short circuit may cause very rapid release of heat and gas.
    - Very low probability, but consequence can be high.
  - No screening tests or effective mitigation is available.
- ***Propagation***
  - Observed in field failures.
    - Laptop failures in 2006 included several explosions from a single laptop, separated by several minutes, until the entire battery pack was consumed.
  - Experimentally observed in test labs.
  - Propagation as been modeled* using Accelerating Rate Calorimetry (ARC) data as well as convective, conductive and radiative heat transfer.

4/12/2013

*Spotnitz, Doughty et al., Journal of Power Sources 163 (2007) 1080–1086.

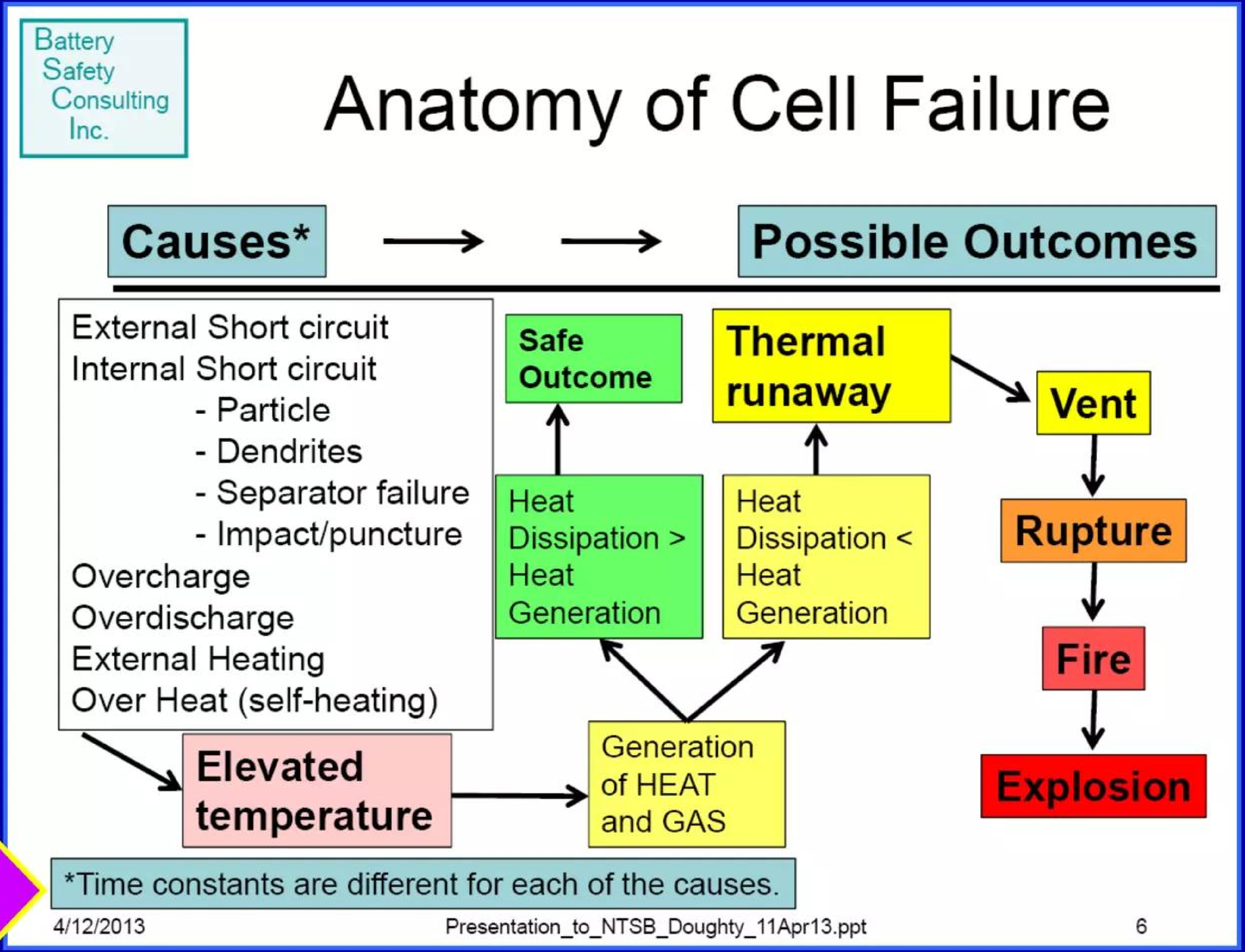
12

Sequence of events associated with thermal runaways

Battery systems design and engineering can steer toward safe outcome

"Failure mechanisms of Li-ion batteries"
Dr. Daniel Doughty, Battery Safety Consulting, Inc.
NTSB Battery Forum 12 MS-PowerPoint slides April 11, 2013

http://www.ntsb.gov/news/events/Documents/2013_Lithium_Batteries_FRM-Panel1d-Doughty.pdf



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Anatomy of Cell Failure

Causes* ⟶ ⟶ **Possible Outcomes**

External Short circuit
Internal Short circuit
  - Particle
  - Dendrites
  - Separator failure
  - Impact/puncture
Overcharge
Overdischarge
External Heating
Over Heat (self-heating)

Elevated temperature → Generation of HEAT and GAS

Heat Dissipation > Heat Generation → **Safe Outcome**

Heat Dissipation < Heat Generation → **Thermal runaway** → **Vent** → **Rupture** → **Fire** → **Explosion**

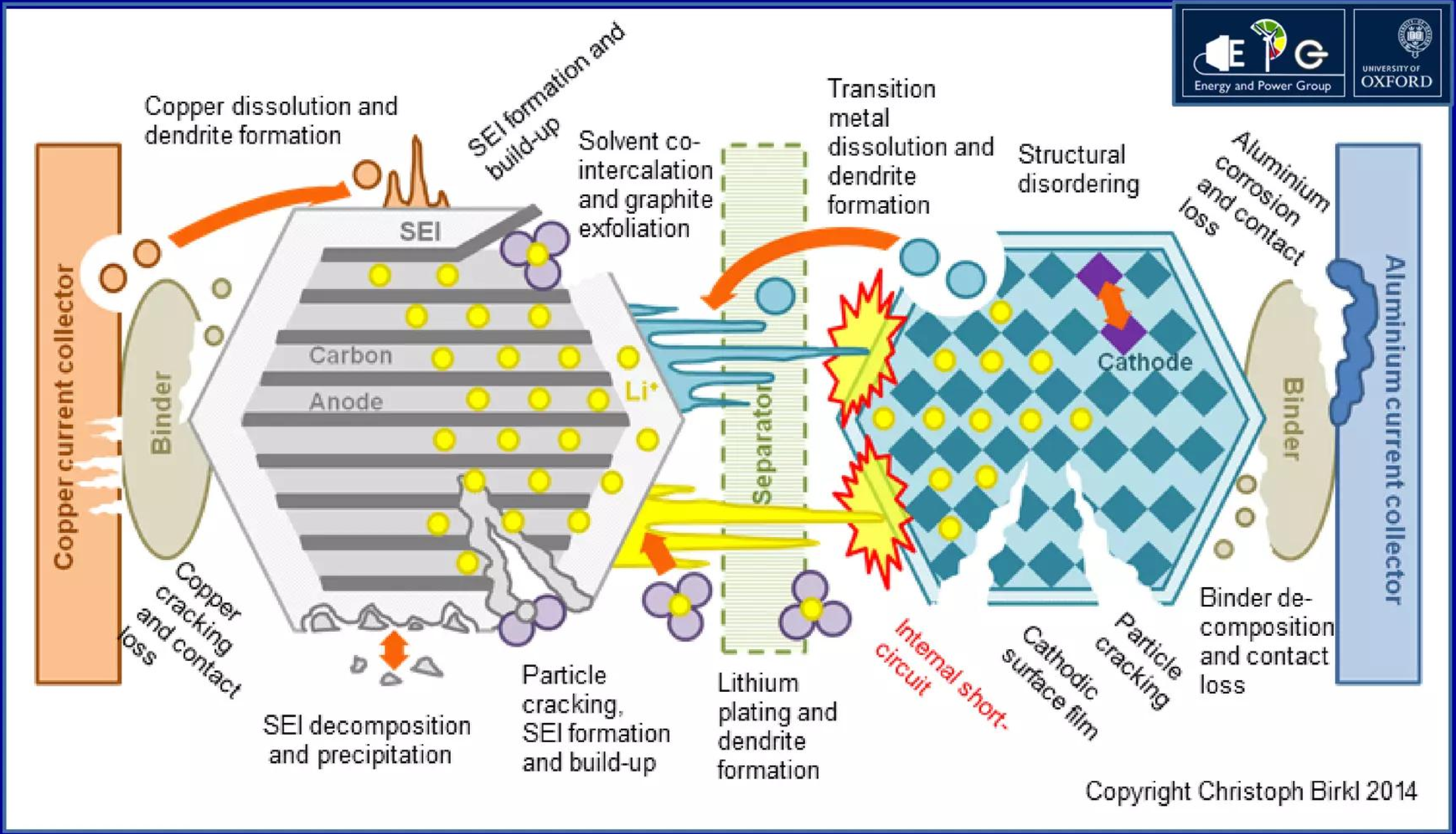
*Time constants are different for each of the causes.

4/12/2013 Presentation_to_NTSB_Doughty_11Apr13.ppt 6

Overview of degradation mechanisms in Lithium batteries

Includes the formation of metallic dendrites and internal short circuits

Fig. 1: “Degradation mechanisms in Li-ion batteries” in Christoph Birkl’s blog article



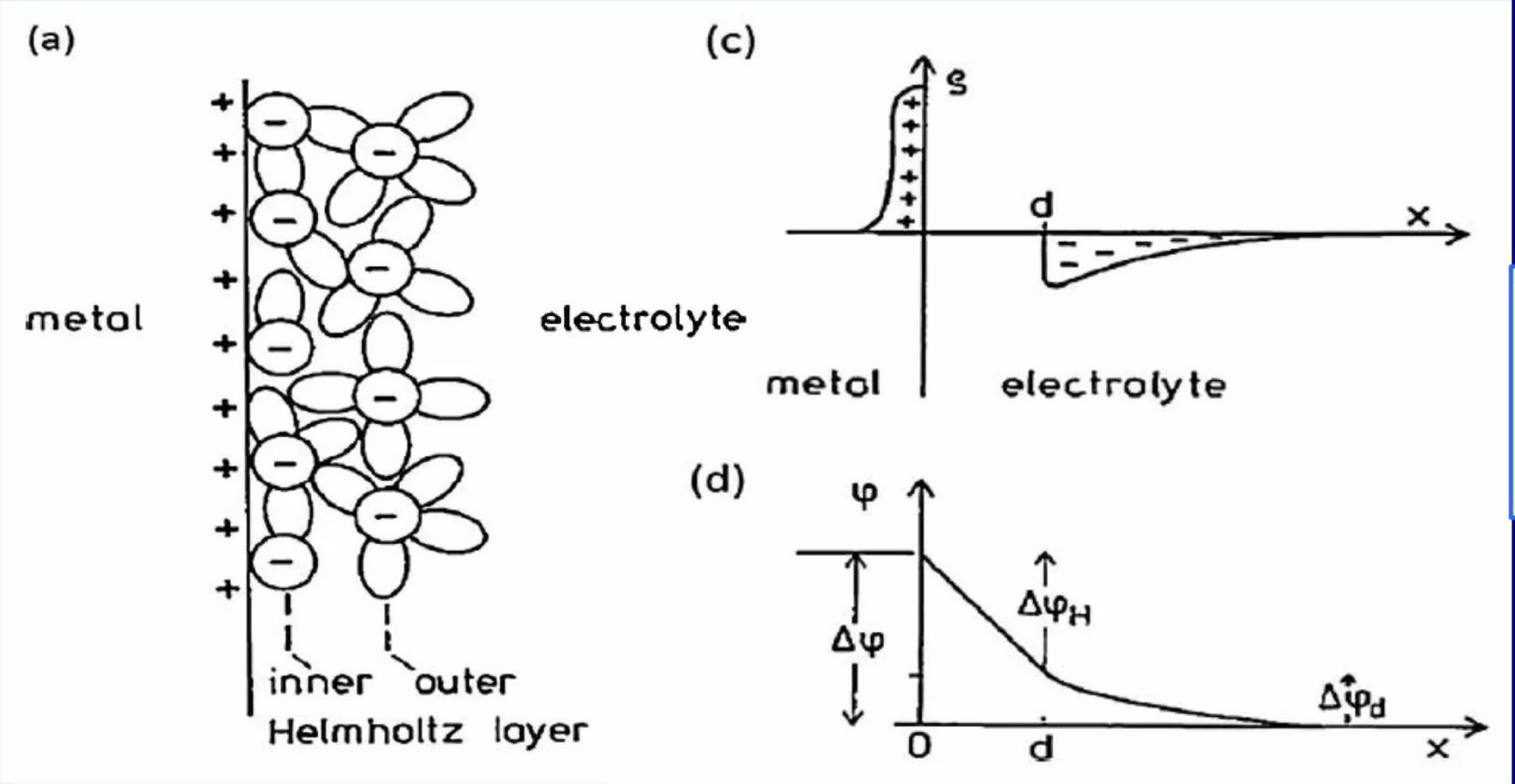
Copyright Christoph Birkl 2014

http://epg.eng.ox.ac.uk/content/degradation-lithium-ion-batteries

High electric field gradients near battery electrode surfaces

Voltage gradient quite high because distance involved is very small

Fig. 8. "(a) The formation of a double layer constituted from an increased concentration of oppositely charged ions on a positive electrode is shown. The spatial extent of the Helmholtz layer is dependent on the character of ions (cations and anions, the degree if solvation). (c) The distribution of the mobile charges in the metal electrode (on the left) and the electrolyte (on the right). (d) Much of the applied voltage on the electrode is dropped across the immobile Helmholtz layer."



"Charge transfer and storage in nanostructures" P. Bandaru *et al.*
Materials Science and Engineering R 96 pp. 1 - 69 (2015)

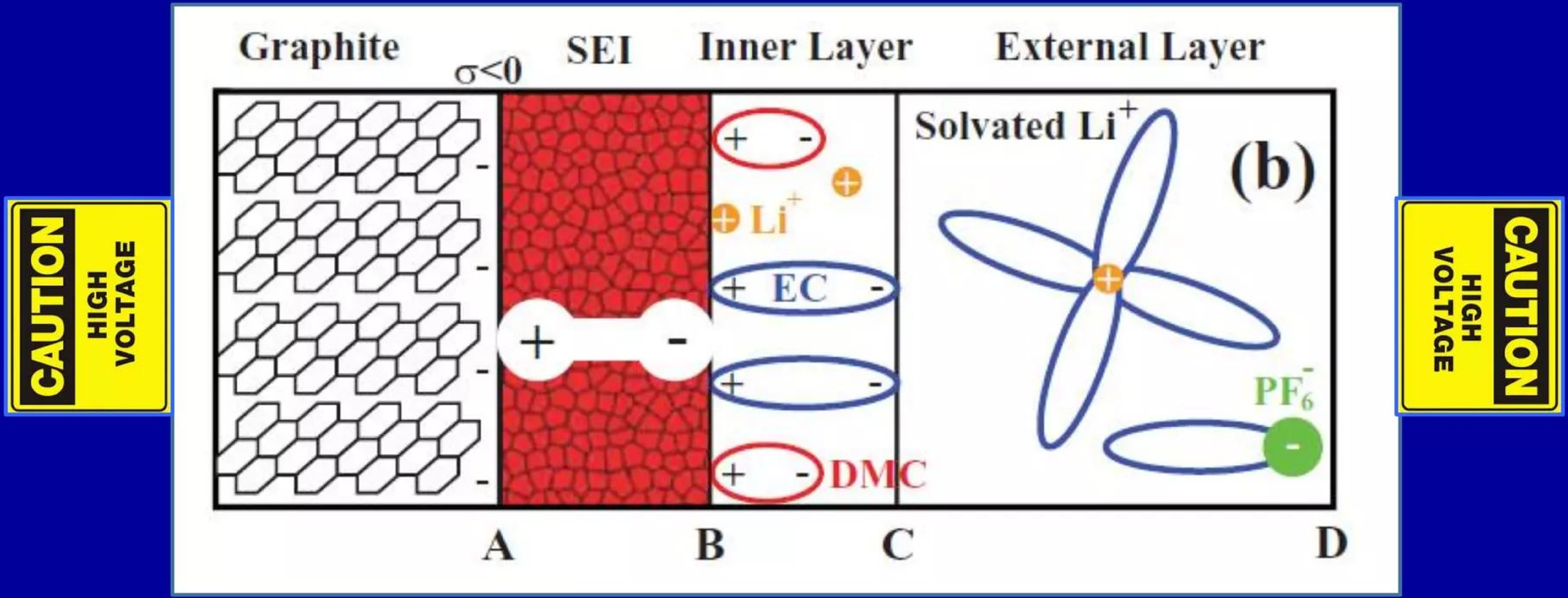
High electric field gradients near battery electrode surfaces

Localized electric field strengths of 10^9 - 10^{10} V/m near electrode surfaces

Inhomogeneities in electric field strengths or current densities are very important

High electric fields occur near battery anode and cathode surfaces. Sudden mechanical changes (fracture) or drastic shifts in electron/ion currents interacting with these fields can boost dendrite growth, cause brief charge separation, destabilize SEIs, and trigger LENRs

Fig. 3 Quiroga *et al.* - Simulated electrode/electrolyte interface in a Lithium-ion battery



"A multiscale model of electrochemical double layers in energy conversion and storage devices" M. Quiroga et al., *Journal of The Electrochemical Society* 161 pp. E3302-E3310 (2014)

Battery electrode double layer has steep E-field gradient

See E. Stuve's article titled "Interfacial chemistry in high electric fields"

Quasi-static electric field strengths of ~ 10^{10} V/m occur very close to double layer

http://faculty.washington.edu/stuve/fi_water.htm

"Density functional theory (DFT) model of Fig. 2, for three water layers and one hydronium ion (dark blue/orange) at a Pt(111) surface, focuses on the adsorbed or near-surface layer. The water molecules alter their orientation in response to the hydronium ion. The red curve shows the potential profile, and the blue curve is the field profile obtained by differentiating the potential profile. The field profile varies from zero in the metal, to a maximum of 1 V/Å near the surface, and to zero into the solution phase. There is an appreciably wide region where the field exceeds 0.3~V/Å, at which water ionization is possible, according to work in our laboratory. Comparison of this experimental result with the computational result shows that ionization would be expected to occur over the range where the field exceeds the ionization threshold, from 1.5 to 3.5 V/Å from the surface.".

High electric fields at cathode surfaces in electrochemical cells; DFT model of double-layer

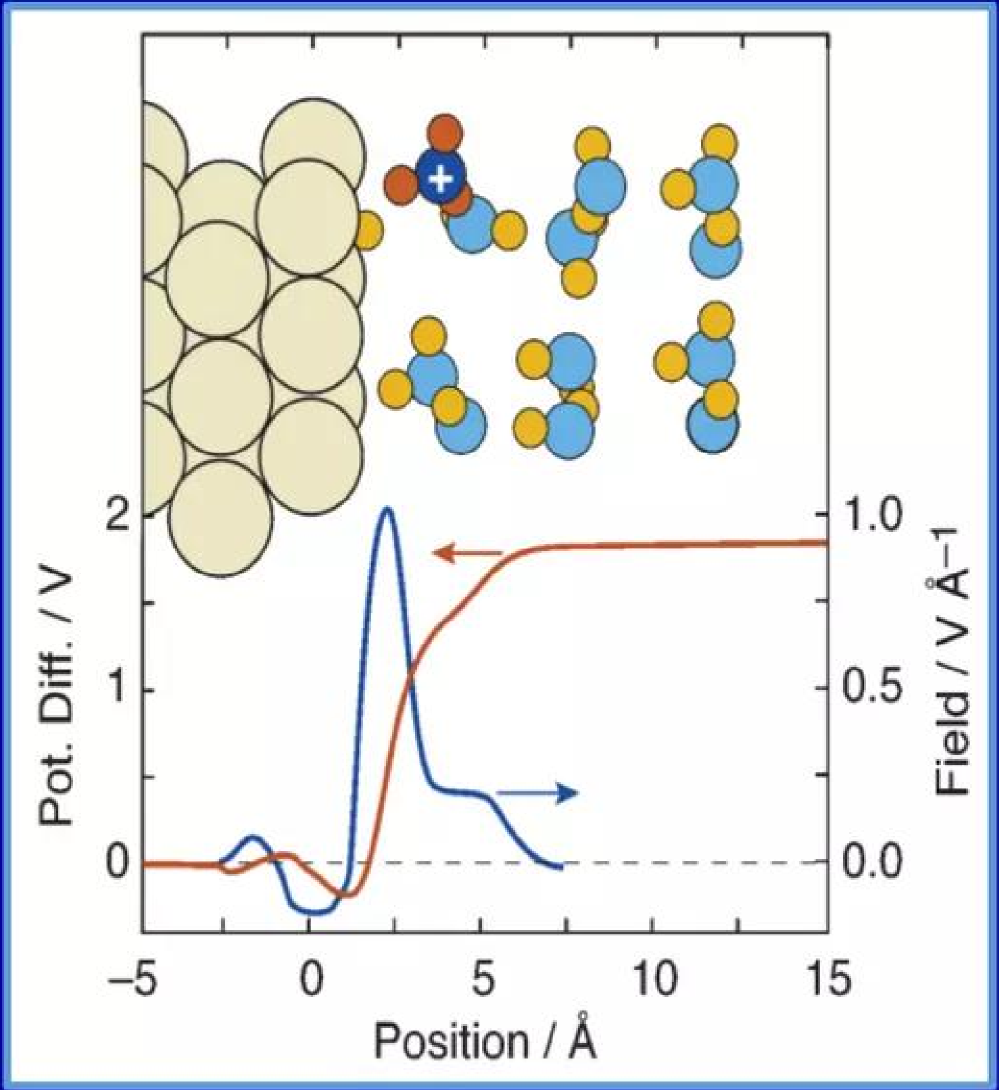


Fig. 2. DFT/molecular dynamics simulation of a charged Pt(111) slab with 3 water layers

Electrode/electrolyte interface is still not well understood

Knowledge about SEI at Li battery anodes is much better than cathodes

Ramifications of very high electric fields in vicinity of EEI are extremely important

The Journal of Physical Chemistry Letters

"Electrode - electrolyte interface in Li-ion batteries: current understanding and new insights"
M. Gauthier *et al. Phys. Chem. Lett.* 6 pp. 4653 - 4672 (2015)

http://pubs.acs.org/doi/abs/10.1021/acs.jpclett.5b01727?journalCode=jpclcd

Abstract: "Understanding reactions at the electrode/electrolyte interface (EEI) is essential to developing strategies to enhance cycle life and safety of lithium batteries. Despite research in the past four decades, there is still limited understanding by what means different components are formed at the EEI and how they influence EEI layer properties. We review findings used to establish the well-known mosaic structure model for the EEI (often referred to as solid electrolyte interphase or SEI) on negative electrodes including lithium, graphite, tin, and silicon. Much less understanding exists for EEI layers for positive electrodes. High-capacity Li-rich layered oxides $y\mathrm{Li}_{2-x}\mathrm{MnO}_3\cdot(1-y)\mathrm{Li}_{1-x}\mathrm{MO}_2$, which can generate highly reactive species toward the electrolyte via oxygen anion redox, highlight the critical need to understand reactions with the electrolyte and EEI layers for advanced positive electrodes. Recent advances in in situ characterization of well-defined electrode surfaces can provide mechanistic insights and strategies to tailor EEI layer composition and properties."

SIMS mass spectroscopy is a very powerful analytical tool

Cameca nanoSIMS-50L is outstanding instrument to look for LENR traces

NANO LETTERS

"In situ mass spectrometric determination of molecular structural evolution at the solid electrolyte interphase in Lithium-ion batteries" Z. Zhu *et al*. *Nano Lett.* 15 pp 6170 - 6176 (2015)

http://pubs.acs.org/doi/abs/10.1021/acs.nanolett.5b02479?src=recsys&journalCode=nalefd

Abstract: "Dynamic structural and chemical evolution at solid-liquid electrolyte interface is always a mystery for a rechargeable battery due to the challenge to directly probe a solid-liquid interface under reaction conditions. We describe the creation and usage of *in situ* liquid secondary ion mass spectroscopy (SIMS) for the first time to directly observe the molecular structural evolution at the solid-liquid electrolyte interface for a Lithium (Li)-ion battery under dynamic operating conditions. We have discovered that the deposition of Li metal on copper electrode leads to the condensation of solvent molecules around the electrode. Chemically, this layer of solvent condensate tends to be depleted of the salt anions and with reduced concentration of Li^+ ions, essentially leading to the formation of a lean electrolyte layer adjacent to the electrode and therefore contributing to the overpotential of the cell. This observation provides unprecedented molecular level dynamic information on the initial formation of the solid electrolyte interphase (SEI) layer. The present work also ultimately opens new avenues for implanting the *in situ* liquid SIMS concept to probe the chemical reaction process that intimately involves solid-liquid interface, such as electrocatalysis, electrodeposition, biofuel conversion, biofilm, and biomineralization."

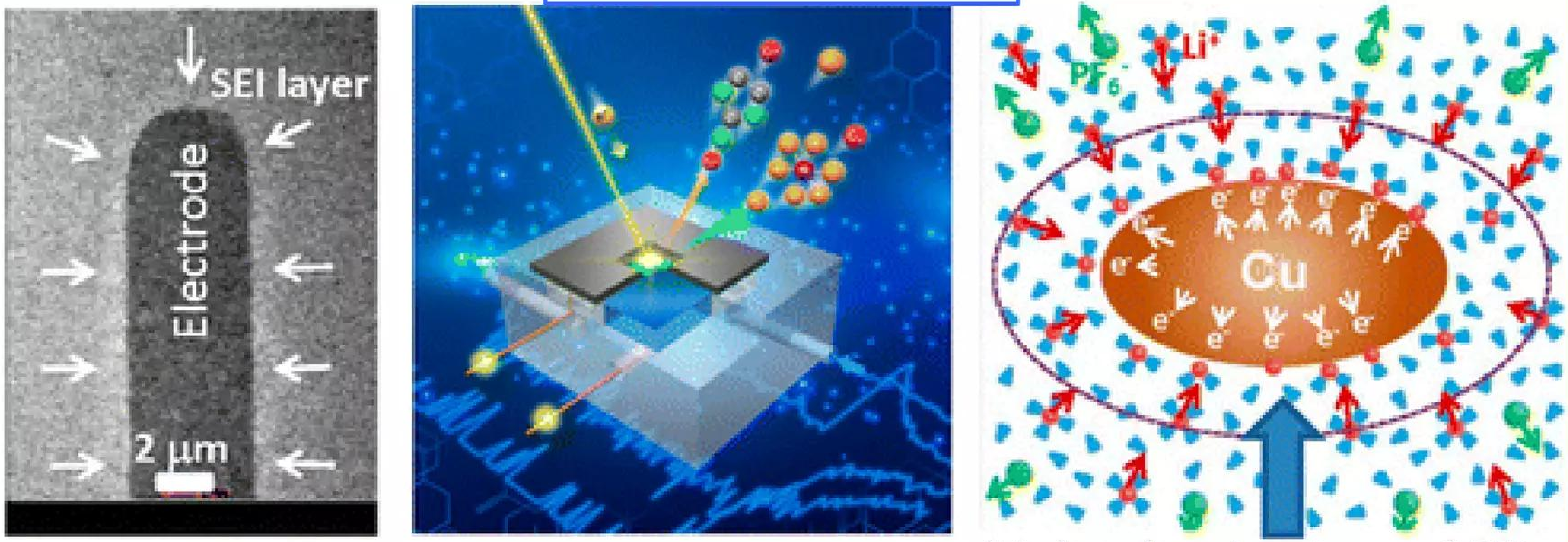
SIMS mass spectroscopy is a very powerful analytical tool

Cameca nanoSIMS-50L is outstanding instrument to look for LENR traces

Note electron-rich (surface plasmon) environment on the surface of Copper (Cu)

http://pubs.acs.org/doi/abs/10.1021/acs.nanolett.5b02479?src=recsys&journalCode=nalefd

NANO LETTERS

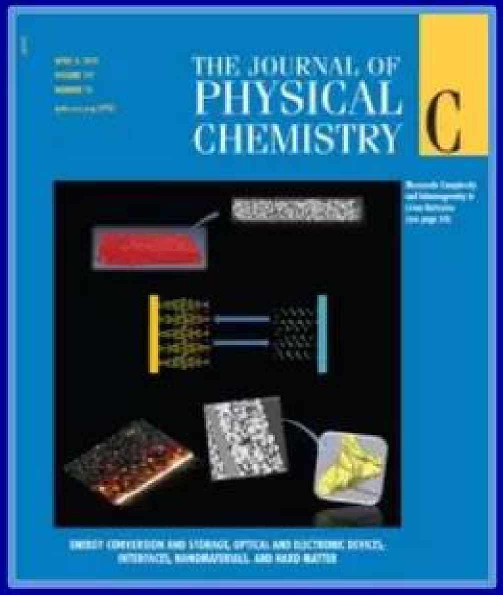


SEI layer morphology by In-situ liquid TEM

In-situ liquid SIMS

Molecular structure of SEI layer by in-situ liquid SIMS

Explains how inhomogenities can impact battery durability



"Effects of inhomogeneities --- nanoscale to mesoscale --- on the durability of Li-ion batteries"
S. Harris (Lawrence Berkeley National Lab) and P. Lu (General Motors)
The Journal of Physical Chemistry C 117 pp. 6481 - 6492 (2013)

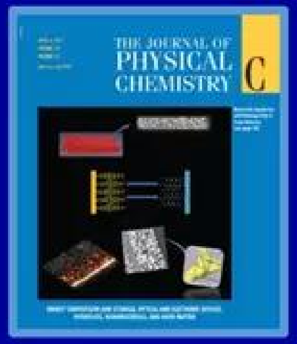
http://lithiumbatteryresearch.com/pdf/Inhomogeneities-and-Durability.pdf

"Inhomogeneities in batteries --- just like inhomogeneities in practically all materials --- are the primary drivers of failure, so that in at least some cases, a purely homogeneous model will not be able to predict durability. Instead, we suggest that a detailed understanding of the electrode structures and inhomogeneities at all scales, from nano- to mesoscale (where inhomogeneities interact), can lead to an improved understanding of durability and failure mechanisms, ultimately leading to longer-lived batteries, with all their attendant advantages."

"Materials do not in general fail homogeneously; instead, nano- and microscale inhomogeneities interact at the mesoscale to cause failure. We hypothesize that battery failure is the result of interactions among local inhomogeneities --- mechanical, electrical, morphological, or chemical. (For the purposes of our work, we define inhomogeneities as regions with sharply varying properties --- which includes interfaces --- whether present by 'accident' or design.)"

Explains how inhomogenities can impact battery durability

State of charge [SOC] is really not homogenous on nanoscales



"Effects of inhomogeneities --- nanoscale to mesoscale --- on the durability of Li-ion batteries", Harris & Lu (2013) continued

"Until recently, there were no in situ Li maps, no *in situ* strain maps, no 3D electrode or particle data, no models dealing with real 3D data, no determinations of how Li transports through the SEI, and in general only a very modest interest in how nano- and microscale inhomogeneities might interact to cause failure at the mesoscale."

"Maire *et al.* showed a graphite electrode that failed heterogeneously, with variations in SOC [state of charge] on a scale of millimeters. Such heterogeneous failure suggests different remediation strategies than would homogeneous failure … The isotropy assumption predicts that the state of charge [SOC] on the surface of a spherical particle must be uniform. That translates to a prediction for spherical graphite particles that their external surfaces are monochromatic (gray/black, blue, red, or gold). Our *in situ* optical images of lithiating ~10 μm spherical mesocarbon microbeads (MCMBs) show instead that particles lithiate gradually from 'hot spots' that expand over the surface until they cover the particle (Figure 3). This observation is readily rationalized using a microstructural model of MCMB particles in which the hot spot location depends on the internal microstructure of the graphite."

Explains how inhomogenities can impact battery durability

"Effects of inhomogeneities --- nanoscale to mesoscale --- on the durability of Li-ion batteries", Harris & Lu (2013) continued

"There is little experimental information about Li transport mechanisms through the SEI --- how the SEI actually functions --- although at least three different mechanisms have been proposed. In addition, we are not aware of any measurements of the electrical conductivity of an SEI film, which ideally should be zero but is clearly not, since SEI films inevitably grow. In fact, while tunneling is commonly invoked as a mechanism for electron transport through the SEI, a thickness of 10 or 20 nm indicates that it must be combined with other mechanisms, as suggested by Qi. To understand battery degradation, we need mechanistic information about how SEI films fail … TOF-SIMS depth profiles show that this outer SEI region is composed largely of polymeric and organic Li salts, chemically distinct from the more inorganic region below it."

"Homogeneous porous electrode models have provided invaluable tools for improving the performance of Li-ion batteries, but the model was not designed to predict durability. We propose that degradation be understood by explicitly considering effects --- beneficial or deleterious --- of local inhomogeneities on Li^+ transport at larger scales. The value of this hypothesis, if true, is that it gives a straightforward prescription for making more durable batteries: control the number and intensity of heterogeneities. While this approach is widely used to make other materials more durable, it is not discussed in the context of Li-ion battery failure."

High electric fields foster Lithium metal dendrite growth

Electric fields are concentrated and much higher on tips of dendrites

Enhancement of electric field strengths also occurs on spherical nanoparticles

- ✓ Role of metallic Lithium dendrites in battery failures is well-known and much R&D has consequently been focused on limiting or eliminating such dendrite growth as batteries age over time; note: as conductive metal, surface plasmon electrons can be present on surfaces of Lithium nanostructures (more later)
- ✓ Besides growing longer and then mechanically puncturing battery separators (causing internal short circuits), Lithium metal dendrites can great amplify local electric field strength on their very tips; this is called the "lightning rod effect." Depending on exactly how high these fields get (determined by local current densities), they can locally break down battery materials and alter rates of nearby chemical redox and also "parasitic" reactions (explained later)
- ✓ Dendrites are not the only type of conductive nanostructure that can cause problems with batteries; as we shall shortly see, even spherical nanoparticles (thought to be relatively safe by many battery technologists since they do not possess sharp asperities) can have very large local inhomogeneities in electric current density and amplification of electric field strengths on their surfaces. This is why metallic nanoparticle battery contaminants can be so troublesome
- ✓ Electric fields close to surfaces of battery electrodes routinely reach static values of 10^9 to 10^{10} V/m; transient dynamic effects can briefly hit > 10x higher

Metallic dendrites can trigger thermal runaways in batteries

Dendrites mechanically penetrate separators causing electrical shorts

See 2015 Ph.D. thesis by Jens Steiger at Karlsruher Institut für Technologie

Above: Lithium dendrites growing from an anode surface. Image from R. Chianelli in *Jour. Cryst. Growth* 34 pp. 239 - 244 (1976)

Lithium needles grow into dendritic Lithium bushes

Credit: Jens Steiger (2015)

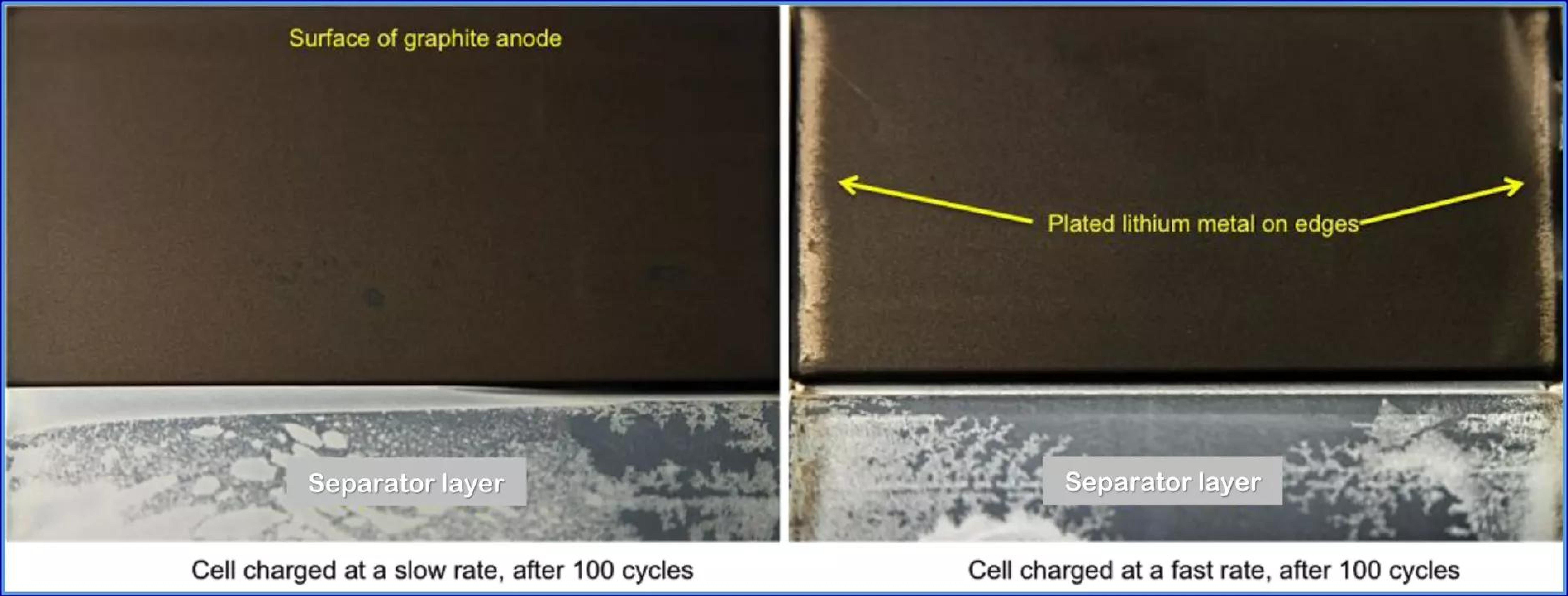
Fig. 4(a). Lithium needles and faceted particles in "Mechanisms of dendrite growth in Lithium metal batteries"

http://d-nb.info/106673691X/34

High local current densities may trigger Lithium plating

Nadim Maluf, CEO of Qnovo, comments about Lithium metal growths

"On the left side, the surface of the graphite anode is pristine. On the right side, bright stripes of lithium metal are apparent on the edges. That's where lithium metal tends to start forming - the current density on the edges tend to be higher (concentrated electric field lines) thus presenting favorable conditions for the formation of lithium metal. Additionally, manufacturing defects are more likely to be present on the edges, also presenting 'seeds' for plating. As the cell is further cycled (and aged), the lithium plating propagates and covers more of the anode surface, creating increased risks of a catastrophic failure."



Cell charged at a slow rate, after 100 cycles

Cell charged at a fast rate, after 100 cycles

http://qnovo.com/category/chemistry/

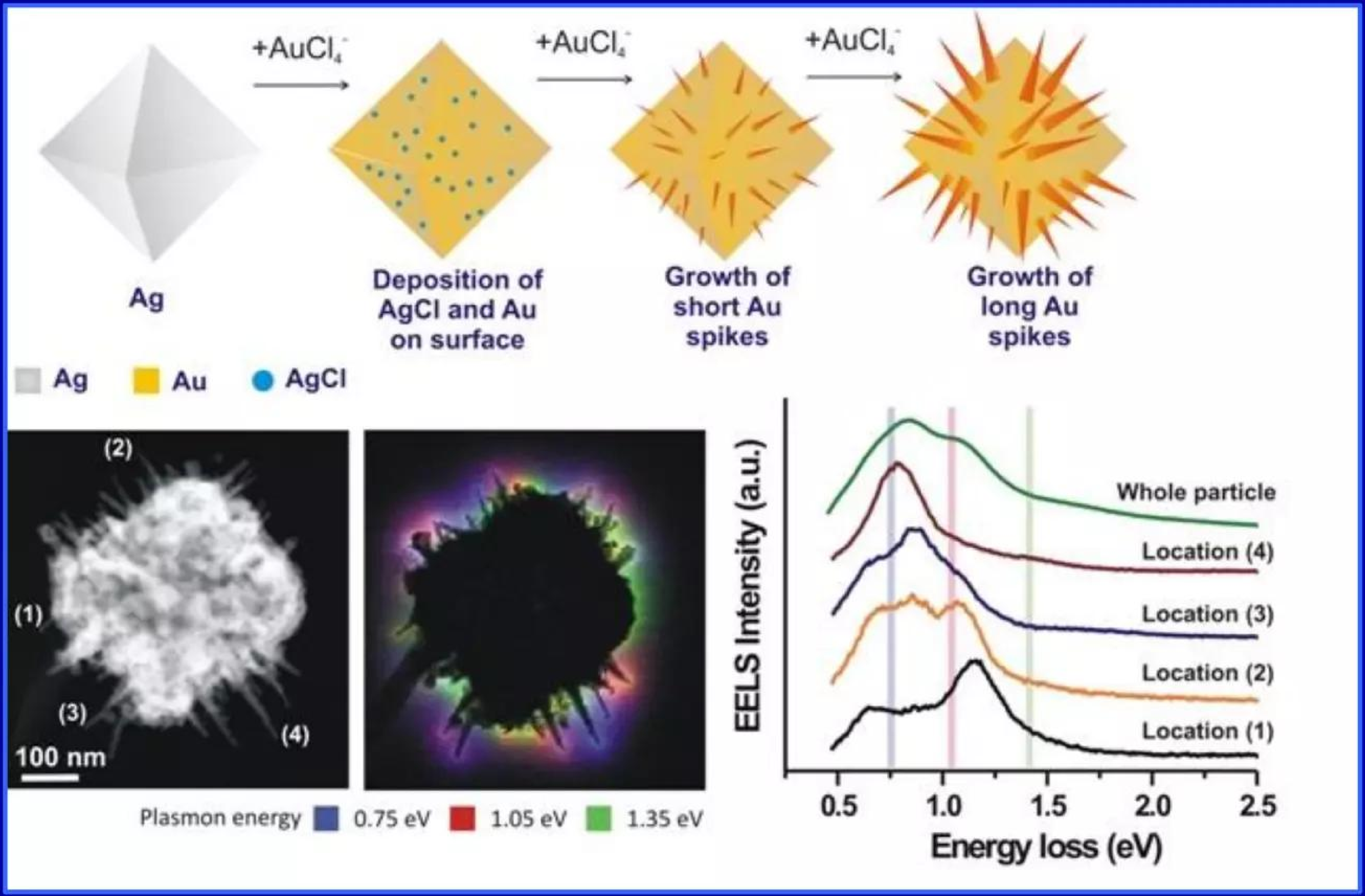
Nanoparticle shapes locally intensify electric fields

May grow inside batteries over time as result of cycling and aging

Surface plasmons are present on surfaces of metallic NPs embedded in oxides

"Synthesis of spiky Ag-Au octahedral nanoparticles and their tunable optical properties" S. Pedireddy *et al.*, *J. Phys. Chem. C* 117 pp. 16640 - 16649 (2013)

http://pubs.acs.org/doi/abs/10.1021/jp4063077

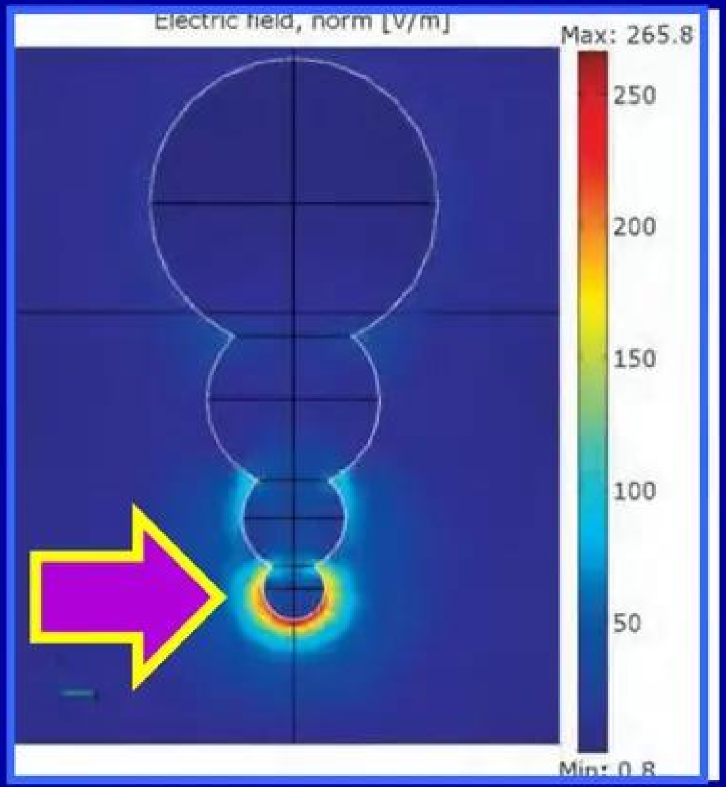


Huge increase in local E-field strengths on nanoscale

Nanostructures of right shapes/compositions amplify electric fields

Details of nanoparticulate features on nm to μ length-scales are key to batteries

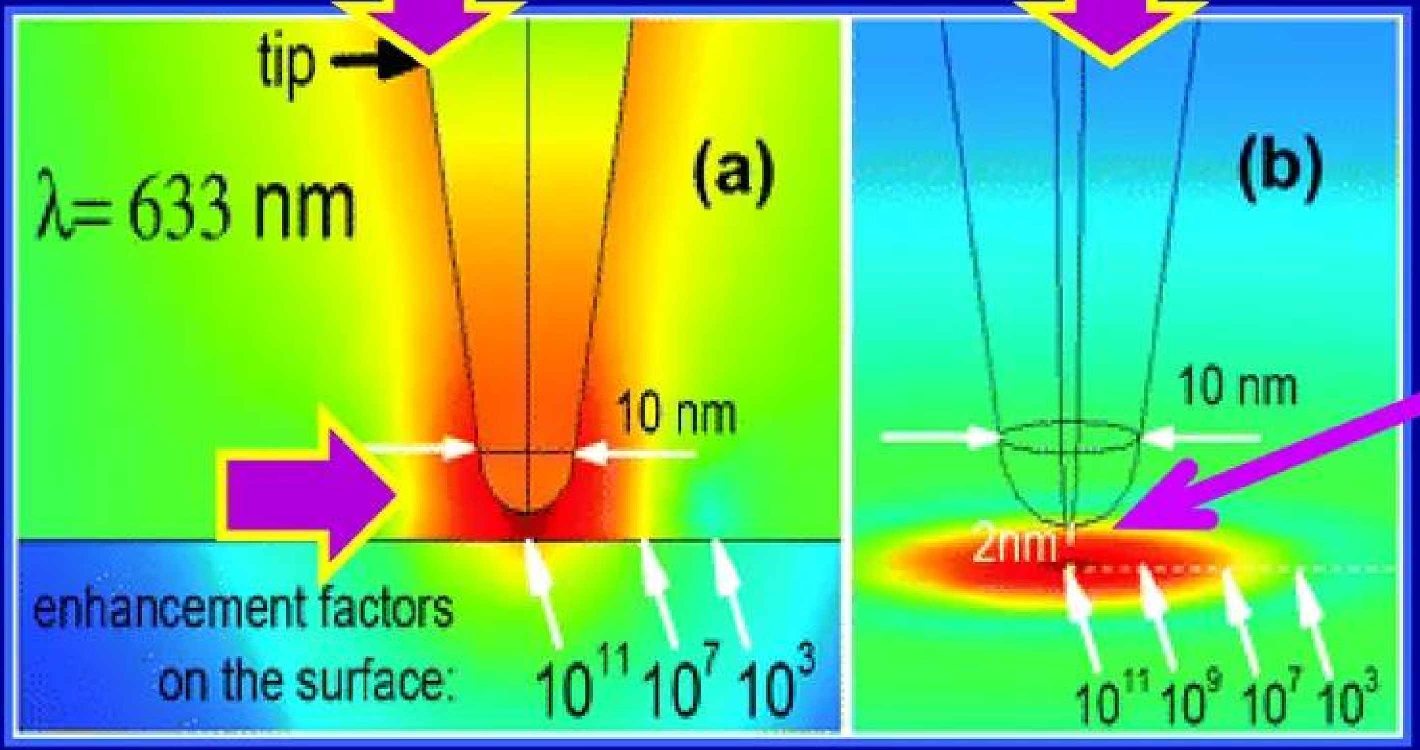
Dendrites are fractal structures




Mandelbrot fractal

Electric field enhancement at nano-antenna tip: R. Kappeler *et al.* (2007)

Electric fields at tips of atomic force microscopes (AFM) often reach 10^{11} V/m

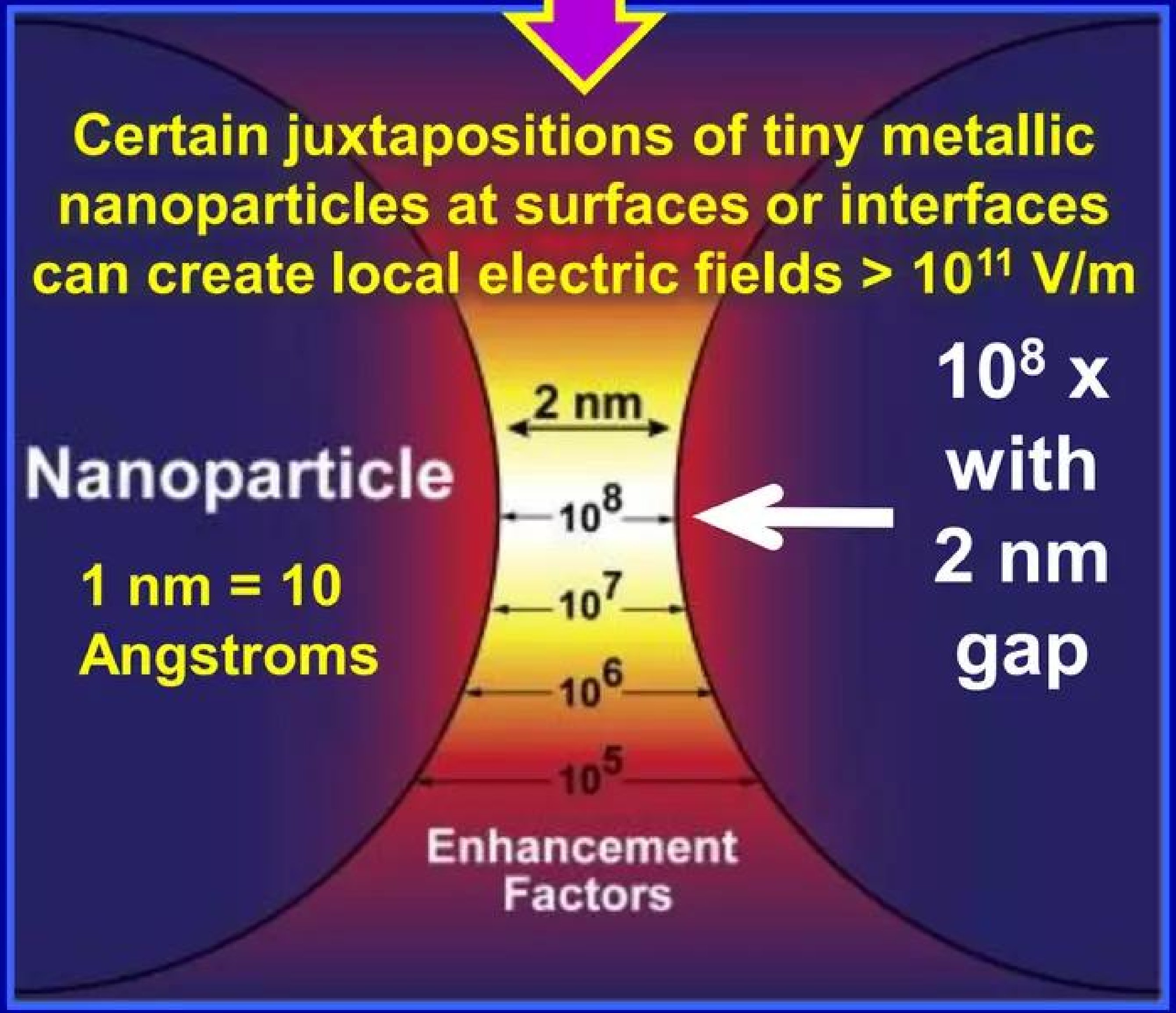


10^{11} x increase

Sharp tips exhibit so-called "lightning rod effect" by creating enormous local enhancement in electric field strengths

Spherically shaped nanoparticles

Shows E-M field strength enhancement as a function of interparticle spacing



Certain juxtapositions of tiny metallic nanoparticles at surfaces or interfaces can create local electric fields > 10^{11} V/m

1 nm = 10 Angstroms

10^{8} x with 2 nm gap

Nanoparticle shapes/positioning redistribute E-fields

E-fields extremely non-uniform across the surfaces of nanoparticles

Nanostructures may be present that briefly create pulsed E-fields > 2 x 10^{11} V/m

"Electromagnetic field redistribution in hybridized plasmonic particle-film system" Y. Fang and Y. Huang
Applied Physics Letters 102 pp. 153108 - 153111 (2013)
http://publications.lib.chalmers.se/records/fulltext/178593/local_178593.pdf

"Combining simulation and experiment, we demonstrate that a metal nanoparticle dimer on a gold film substrate can confine more energy in the particle/film gap because of the hybridization of the dimer resonant lever and the continuous state of the film. The hybridization may even make the electric field enhancement in the dimer/film gap stronger than in the gap between particles. The resonant peak can be tuned by varying the size of the particles and the film thickness."

"By studying the electric field in the gaps A, B, and C (Figures 1(a) and 1(b)), we find that not only is the electric field in the gaps of a dimer-film system much stronger than in a single particle-film system (Figure 1(c)) but also, in a broad wavelength range, the E field in B is even stronger than in C. The maximum enhancement is more than 160 at 680 nm giving a SERS enhancement factor more than 6.5 x 10^8."

"Additional resonant modes are generated in a particle-film system by the hybridization between modes of particles and the continuous surface plasmon state of the film. These hybridized modes, which can be tuned by varying the size of particles and the thickness of the film, will lead to huge electric field enhancements in gaps between particles and film."

Nanoparticle shapes/positioning redistribute E-fields

Fang & Huang's Figs. 1 and 3 show how electric fields are redistributed

Conductive nanostructures can channel currents and amplify local electric fields

Figure 1.

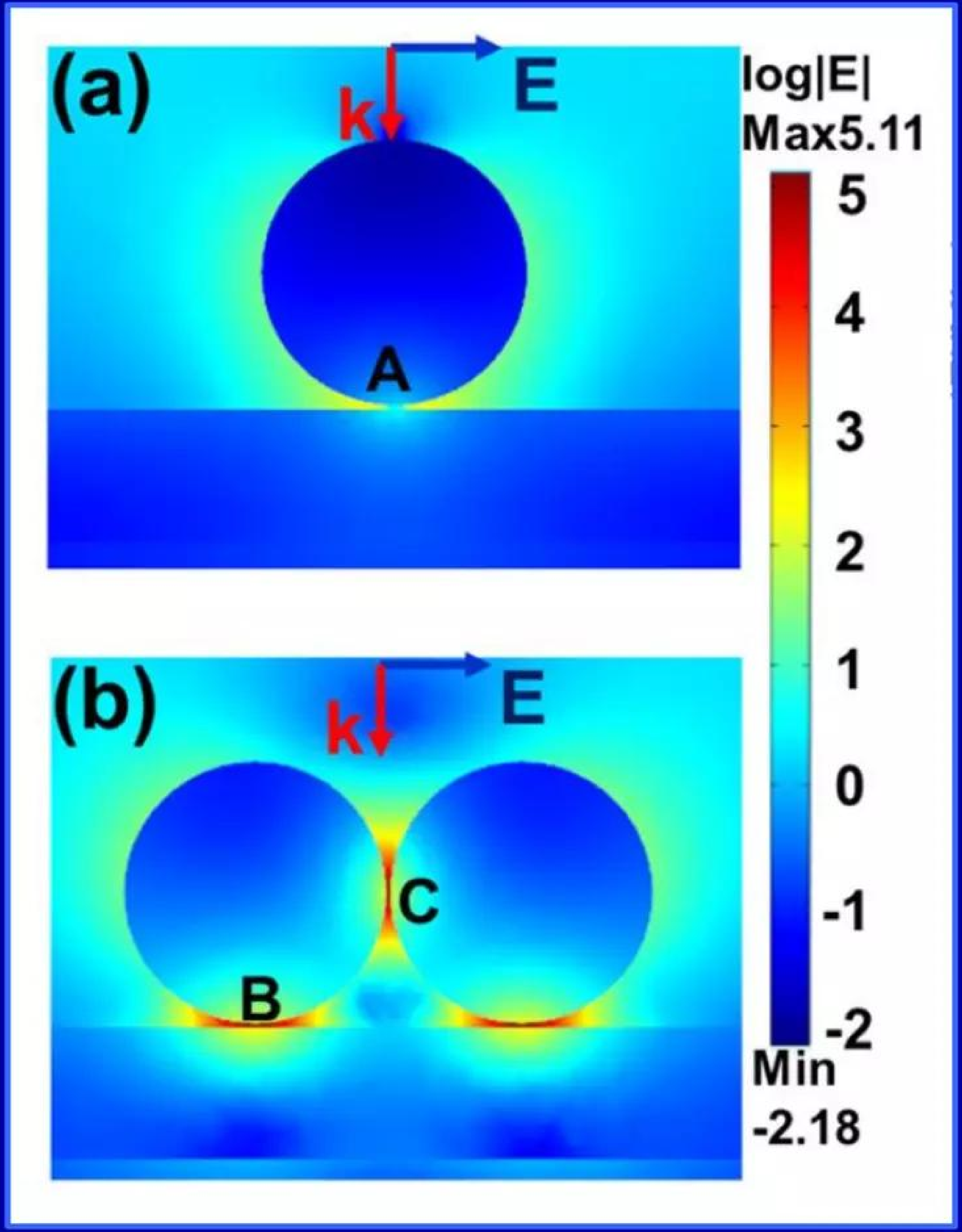
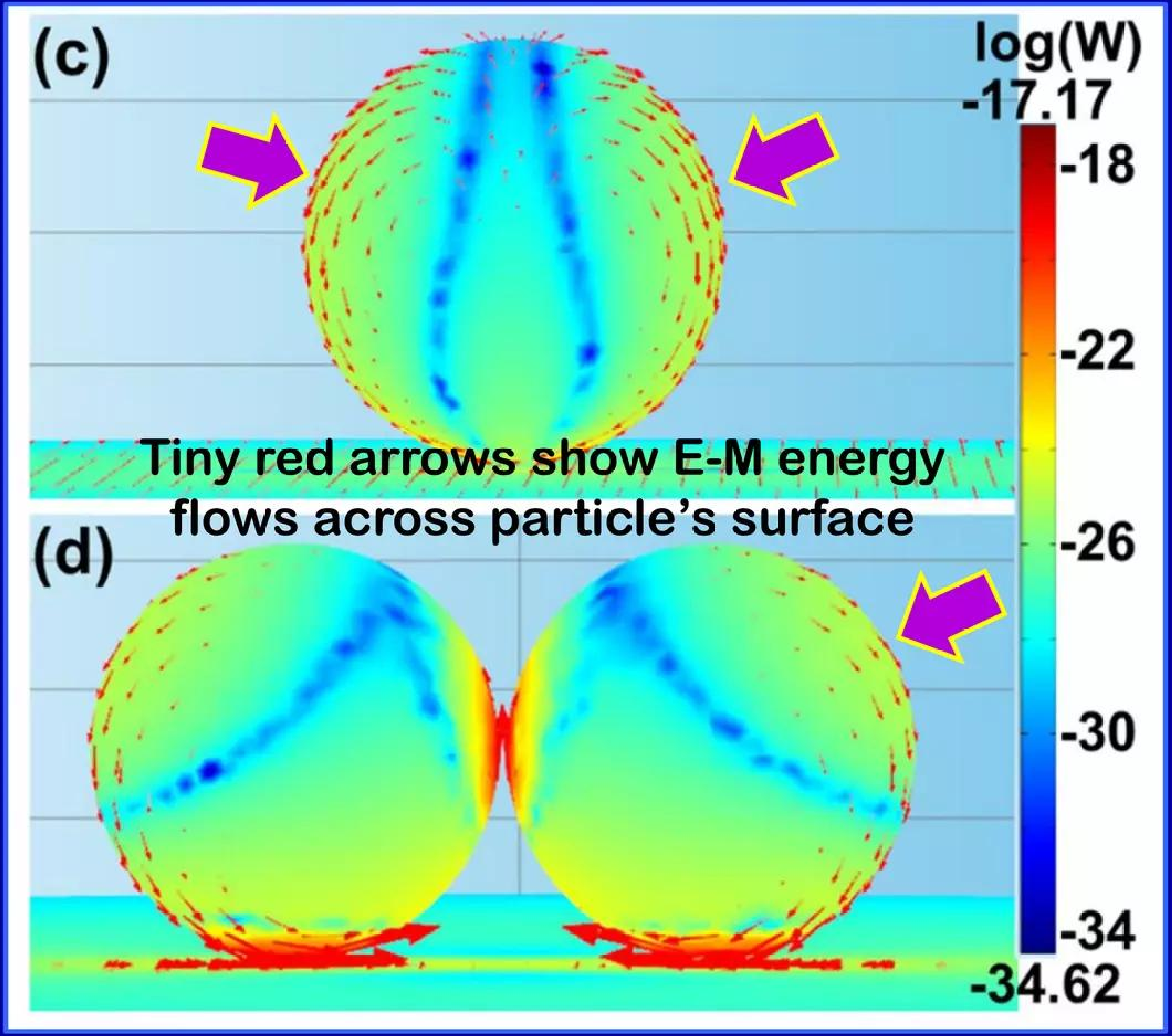


Figure 3.



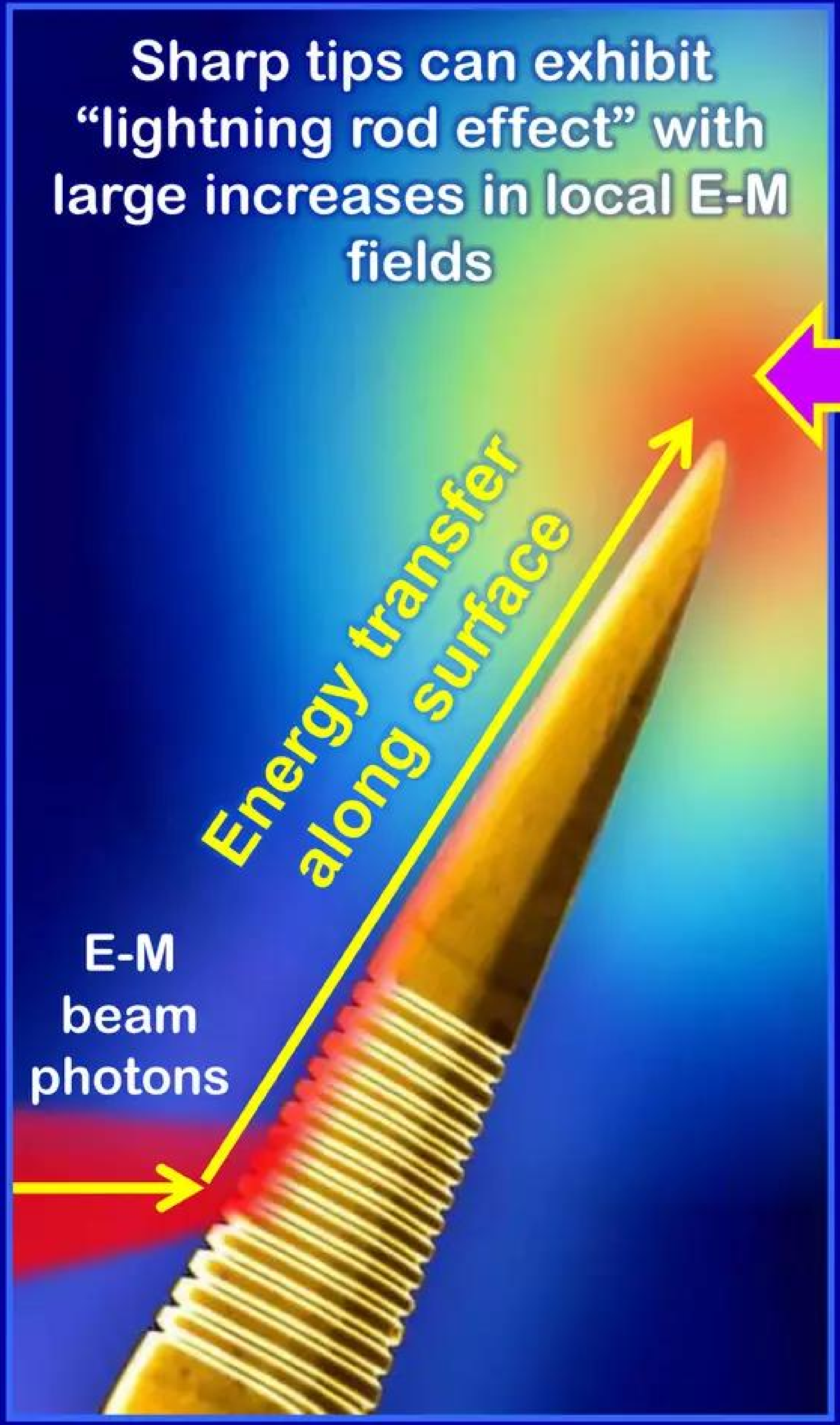
Tiny red arrows show E-M energy flows across particle's surface

Nanostructures can be antennas that absorb E-M energy

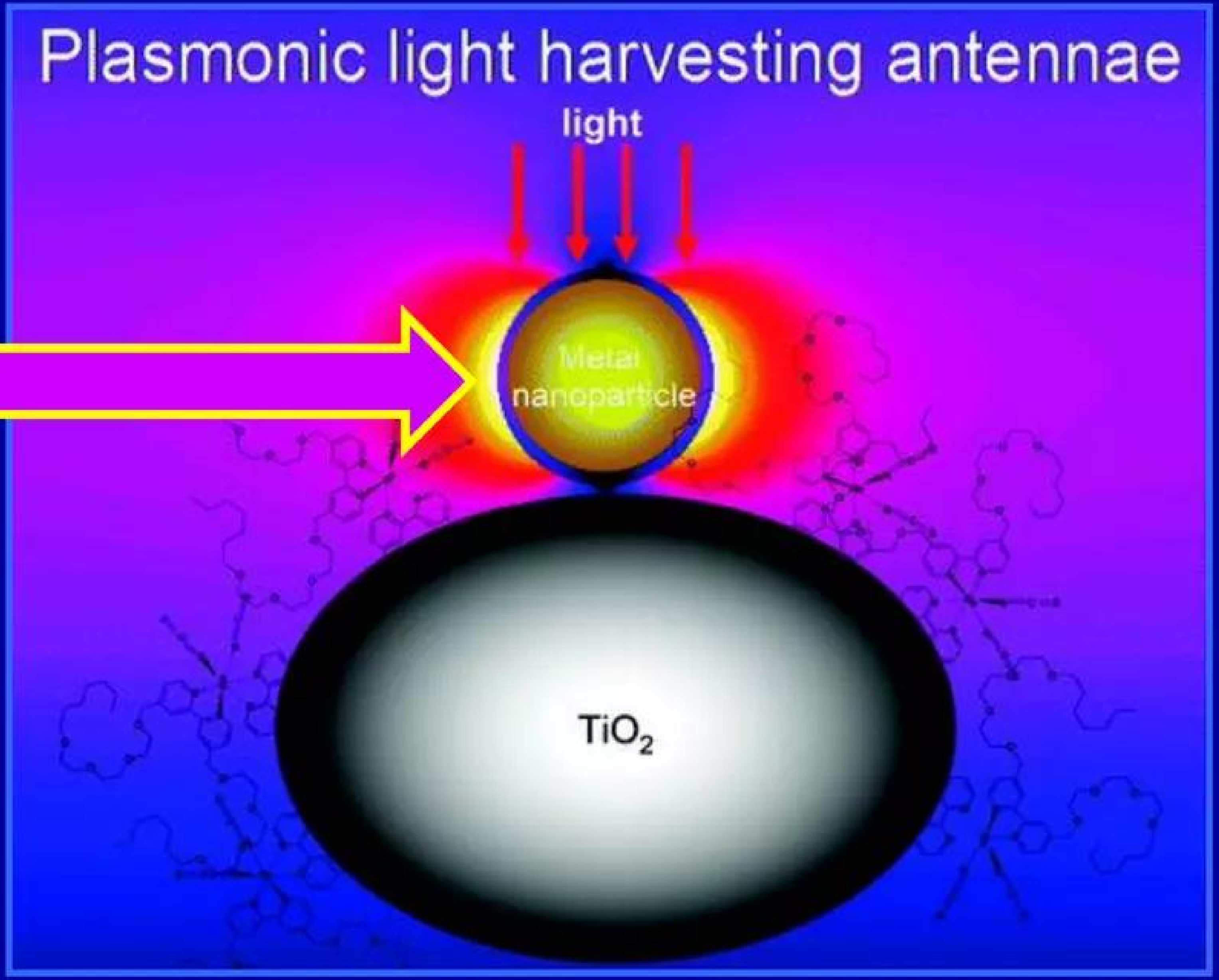
SP electrons on nanoparticles can greatly intensify local electric fields

Current surges can create attosecond E-fields > 2.5 x 10^{11} V/m on nanostructures

Graphics show capture of E-M photons and energy transfer via surface plasmon electrons



Region of enhanced electric fields



http://people.ccmr.cornell.edu/~uli/res_optics.htm

Source of above image is Wiesner Group at Cornell University:

"Plasmonic dye-sensitized solar cells using core-shell metal-insulator nanoparticles" M. Brown *et al.*, *Nano Letters* 11 pp. 438 - 445 (2011) http://pubs.acs.org/doi/abs/10.1021/nl1031106

Surface E-field strength can alter chemical reaction rates

Extremely high electric fields on electrode surfaces impacts chemistry

Time-averaged electric fields inside active sites of enzymes can exceed 10^{10} V/m

- ✓ Recent work has shown that extremely strong electric fields found in active sites of biological enzymes and ordinary chemical catalysis can often play a very important if not pivotal role in accelerating rates of chemical reactions; see selected references below that concern electrostatic catalysis
- ✓ By extension, large upward fluctuations in short-lived transient E-fields (for as little as attoseconds and as long as milliseconds) in nm to micron-scale regions on electrode surfaces in batteries could locally impact redox reaction rates, boost parasitic side-reactions, and on rare occasions, may even trigger LENRs
- ✓ **Key:** evolution of nanostructures on aging electrode surfaces and how they may create inhomogeneities in local current density and electric field strengths

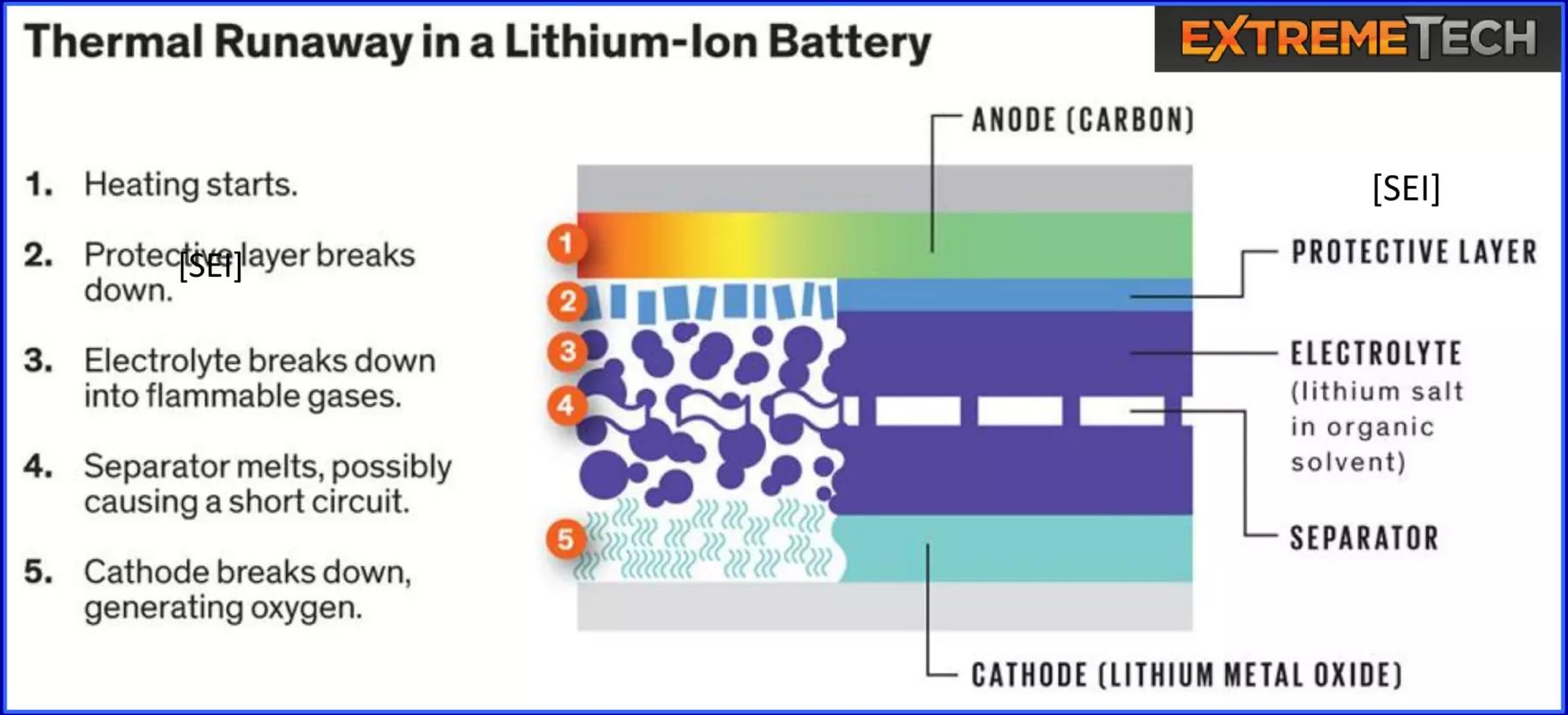
"Electrostatic catalysis of a Diels-Alder reaction"
A. Aragonès *et al. Nature* 531 pp. 88 - 91 (March 3, 2016)
http://www.nature.com/nature/journal/v531/n7592/full/nature16989.html

"Extreme electric fields power catalysis in the active site of ketosteroid isomerase"
S. Fried *et al.*, *Science* 346 pp. 1510 - 1514 (2014)
http://web.stanford.edu/group/boxer/papers/paper303.pdf

Idealized events for thermal runaway in Lithium-ion battery

Local heating starts, breaks down nearby materials, and melts separator

Severity of runaways varies greatly from shutdown of one cell to violent explosion



Thermal Runaway in a Lithium-Ion Battery

1. Heating starts.
2. Protective [SEI] layer breaks down.
3. Electrolyte breaks down into flammable gases.
4. Separator melts, possibly causing a short circuit.
5. Cathode breaks down, generating oxygen.

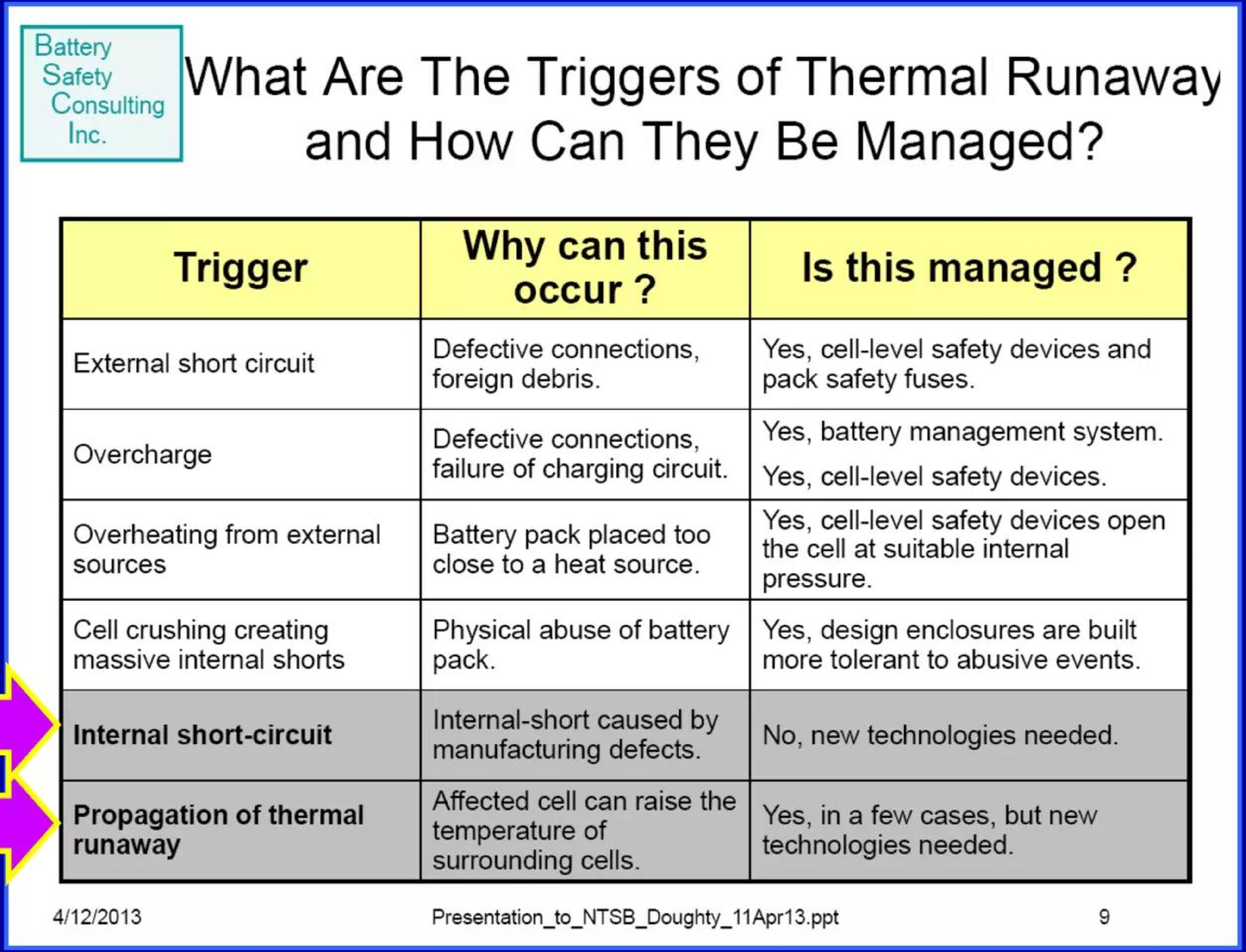
http://www.extremetech.com/extreme/208888-doping-lithium-ion-batteries-could-prevent-overheating-and-explosion

Battery industry recognizes six causes of thermal runaways

Internal shorts and propagation of thermal runaways are safety issues

"Failure mechanisms of Li-ion batteries"
Dr. Daniel Doughty, Battery Safety Consulting, Inc.
NTSB Battery Forum 12 MS-PowerPoint slides April 11, 2013

http://www.ntsb.gov/news/events/Documents/2013_Lithium_Batteries_FRM-Panel1d-Doughty.pdf



Battery
Safety
Consulting
Inc.

What Are The Triggers of Thermal Runaway and How Can They Be Managed?

Trigger	Why can this occur ?	Is this managed ?
External short circuit	Defective connections, foreign debris.	Yes, cell-level safety devices and pack safety fuses.
Overcharge	Defective connections, failure of charging circuit.	Yes, battery management system. Yes, cell-level safety devices.
Overheating from external sources	Battery pack placed too close to a heat source.	Yes, cell-level safety devices open the cell at suitable internal pressure.
Cell crushing creating massive internal shorts	Physical abuse of battery pack.	Yes, design enclosures are built more tolerant to abusive events.
Internal short-circuit	Internal-short caused by manufacturing defects.	No, new technologies needed.
Propagation of thermal runaway	Affected cell can raise the temperature of surrounding cells.	Yes, in a few cases, but new technologies needed.

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Battery industry definition of severe type of thermal runaway

Field-failures appear to be spontaneous internal events inside batteries

Not preceded by external abuse and no warning signs; violent with high temps

> "Safety concerns have been heightened by highly publicized safety incidents and ensuing widespread recalls of Lithium-ion batteries used in laptop computers and cell phones. When these rare safety incidents occur, Lithium-ion batteries operating under otherwise normal conditions undergo what appear to be spontaneous [internal] thermal runaway events, often with violent flaming and extremely high temperatures. Moreover, these failures usually involve cells and cell designs that have passed extensive abuse testing, including the standardized abuse safety tests. Most such Li-ion safety incidents are not preceded by an obvious external abuse. We refer to these spontaneous safety incidents as field-failures'."

Quoted from: "Batteries for Sustainability - Selected Entries from the Encyclopedia of Sustainability in Science and Technology" Ralph J. Brodd, ed., Chapter 9 by B. Barnett *et al*. "Lithium-ion Batteries, Safety" Springer ISBN 978-1-4614-5791-6 (2012)

Huge electric field gradients near battery electrode surfaces

Fast surface physical changes can trigger charge separation / imbalances

Large fluctuations of local E-field strength/current density in microscopic regions

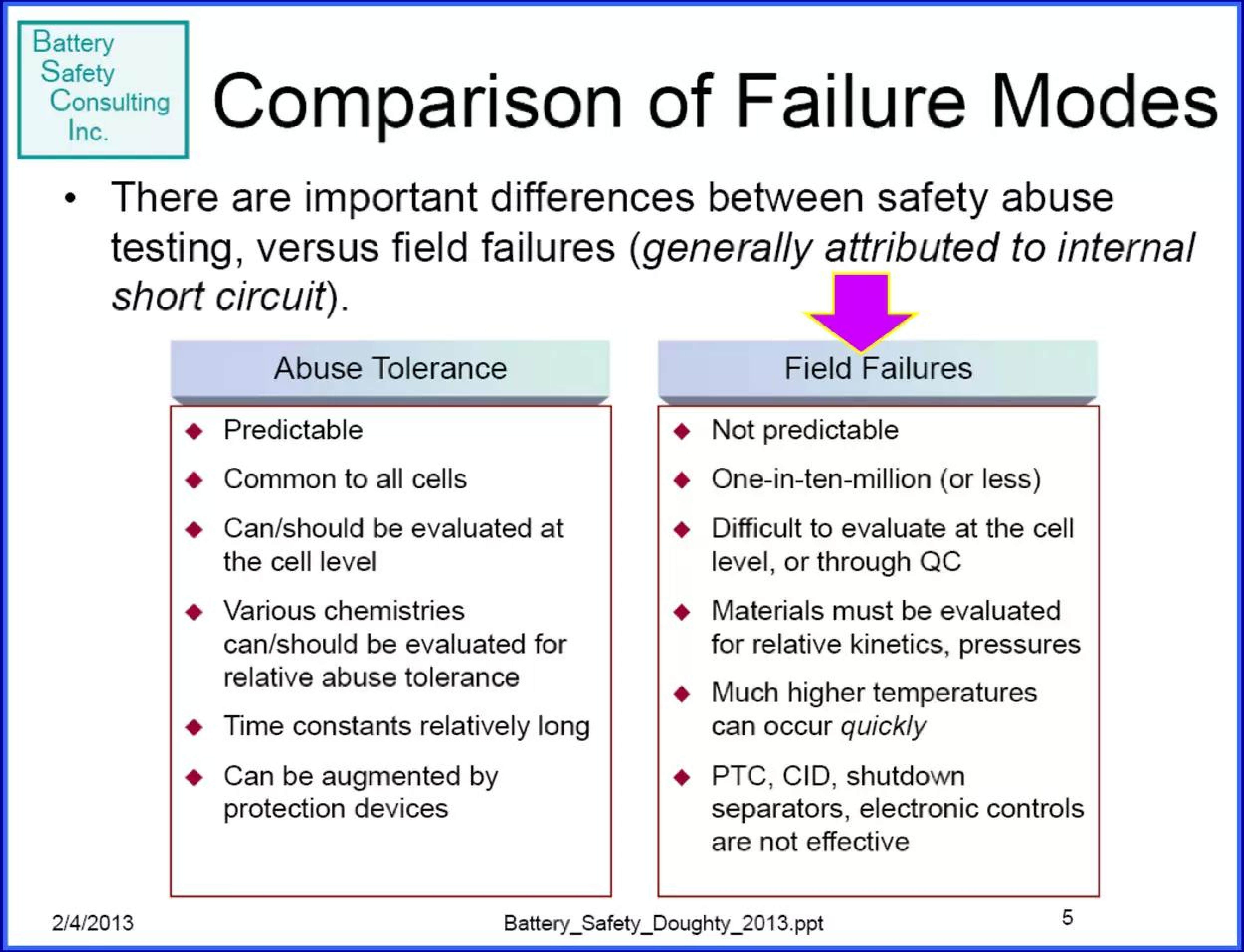
- ✓ Lattice strongly agrees with S. Harris & P. Lu's (2013) insightful suggestion to battery technologists; namely that: "A detailed understanding of the electrode structures and inhomogeneities at all scales, from nano- to mesoscale (where inhomogeneities interact), can lead to an improved understanding of durability and failure mechanisms, ultimately leading to longer-lived batteries, with all their attendant advantages."
- ✓ Extremely high local electric fields - that is, from 1×10^{10} to $> 2.5 \times 10^{11}$ V/m for periods ranging from milliseconds down to attoseconds can cause a variety of problems inside batteries. Among other things, these vexing problems include exceeding electrical breakdown voltage of local materials, thus compromising the integrity of protective SEI layers and separators, triggering internal shorts
- ✓ Lattice therefore believes that long-mysterious spontaneous internal electrical short circuits inside batteries that are widely thought to be one important cause of spontaneous field-failure thermal runaway events are likely to be rooted in transient inhomogeneities in local state of charge (SOC), dynamic charge distribution, current density, and/or electric field strength that can occur in nm to micron-scale regions on various types of nanostructures located in close physical proximity to surfaces of battery anodes or cathodes

Today's safety abuse testing will not predict any field-failures

So-called "field-failures" are often attributed to internal short circuits

"Failure mechanisms of Li-ion batteries"
Dr. Daniel Doughty, Battery Safety Consulting, Inc.
NTSB Battery Forum 12 MS-PowerPoint slides April 11, 2013

http://www.ntsb.gov/news/events/Documents/2013_Lithium_Batteries_FRM-Panel1d-Doughty.pdf



Battery
Safety
Consulting
Inc.

Comparison of Failure Modes

- There are important differences between safety abuse testing, versus field failures (*generally attributed to internal short circuit*).

Abuse Tolerance	Field Failures
◆ Predictable	◆ Not predictable
◆ Common to all cells	◆ One-in-ten-million (or less)
◆ Can/should be evaluated at the cell level	◆ Difficult to evaluate at the cell level, or through QC
◆ Various chemistries can/should be evaluated for relative abuse tolerance	◆ Materials must be evaluated for relative kinetics, pressures
◆ Time constants relatively long	◆ Much higher temperatures can occur *quickly*
◆ Can be augmented by protection devices	◆ PTC, CID, shutdown separators, electronic controls are not effective

2/4/2013 Battery_Safety_Doughty_2013.ppt 5

Tamer ‘garden variety’ of thermal runaways vs. field-failures

Less extreme runaways well-understood; field-failures quite enigmatic

Causes of less severe thermal runaways vs. field-failures not 100% identical

‘Garden variety’ thermal runaways:

- ✓ Reasonably well understood
- ✓ Triggered by substantial over-charging or excessively deep discharges; or,
- ✓ Triggered by external mechanical damage to battery cells, e.g., crushing, punctures; internal dendrites can damage separators

Field-failure thermal runaways:

- ✓ Much rarer and comparatively poorly understood
- ✓ Believed to be triggered by electrical arc discharges (internal shorts); but what causes initial nano-arcs?
- ✓ Much higher peak temps versus ‘garden variety’ events
- ✓ In addition to internal shorts, ultralow energy neutron reactions (LENRs) may be causative for an unknown %

Feng et al. aim for early detection of thermal runaways

Mention “instantaneously triggered ISC” which occurs without warning

“Online internal short circuit [ISC] detection for a large format lithium ion battery”
X. Feng *et al. Applied Energy* 161 pp. 168 - 180 (2016)

http://www.umich.edu/~racelab/static/Webpublication/2016-ENERGY-XuningF.pdf

“It is identified that the abnormal depletion in the state-of-charge (SOC) and excessive heat generation associated with ISC affect the voltage and temperature responses … It is shown that the estimation algorithm can track the parameter variations in real-time, thereby making it feasible to track ISC incubation status or to detect [an] instantaneously triggered ISC.”

“Although there is no clear explanation on what has led to ISC in [8,9], an abundance of evidences and field experiences indicate that it takes a long incubation time before an ISC strikes [12,13]. The ISC develops slowly during the incubation period as cycling continues [13]. The ISC-induced Joule heat will not develop into thermal runaway until the equivalent ISC resistance decreases to a substantially low level [13]. Before an ISC develops into a safety threat, it must be detected effectively to prevent the ensuing thermal runaway. The long time incubation makes it possible to perform early detection of ISC.”

Technology domains converging at nanometer length-scales

Being driven to nm length-scales in a quest for higher energy density

Technology domain	Main purpose	Source of energy	Energy-scale	Typical rates of reactions	Temps in Centigrade	Representative examples
Electro-chemical batteries	Store electrical energy reversibly in chemical bonds	Chemical bonds	Electron Volts (eV)	Slow to moderate; typically diffusion rate-limited at various types of interfaces found inside batteries	Li batteries can generally be operated safely only at temperatures <<< 100^{o} C	Large variety of different chemistries: lead-acid, alkaline, NiMH, Nickel-cadmium, Lithium-ion, $LiFePO_4$, Lithium-oxygen, etc.
Energetic materials	Thermal igniters, explosives, propellants	Chemical bonds	eVs	Fast combustion processes w. O_2, e.g., deflagration and detonation	Macroscopic peak temps max-out at ~5,000º C	Thermite reactions (burning of metals), dinitro-chloro-azido benzene, RDX, etc.
Ultralow energy neutron reactions (LENRs)	Produce large amounts of CO_2-free thermal energy from decay particles' kinetic energies and gamma conversion to infrared	Nuclear binding energy stored inside atomic nuclei	Mega-electron Volts (MeVs) one MeV is equal to a million eVs	Nuclear reactions themselves are super-fast, i.e., picosecond and faster; decays of any resulting unstable isotopes can range from very slow on order of millions of years to fast, i.e., nanoseconds	Peak temperatures in micron-scale, short-lived LENR hotspot regions on surfaces and at interfaces typically reach ~4,000º to 6,000º C	Neutron captures on various elements and isotopes; for example, LENR neutron capture processes starting with Lithium as base fuel target can release ~27 MeV in short sequence of nuclear reactions that do not release any energetic neutron or gamma radiation

Comparison of LENRs to fission and fusion power sources

Fission, fusion, and LENRs all involve controlled release of nuclear binding energy (heat) for power generation: no CO_2 emissions; scale of energy release is MeVs (nuclear regime) > 1,000,000x energy density of chemical energy power sources

Heavy element fission: involves shattering heavy nuclei to release stored nuclear binding energy; requires massive shielding and containment structures to handle radiation; major radioactive waste clean-up issues and costs; limited sources of fuel: today, almost entirely Uranium; Thorium-based fuel cycles now under development; heavy element U-235 (fissile isotope fuel) + neutrons → complex array of lower-mass fission products (some are very long-lived radioisotopes) + energetic gamma radiation + energetic neutron radiation + heat

Fusion of light nuclei: involves smashing light nuclei together to release stored nuclear binding energy; present multi-billion $ development efforts (e.g., ITER, NIF, other Tokamaks) focusing mainly on D+T fusion reaction; requires massive shielding/containment structures to handle 14 MeV neutron radiation; minor radioactive waste clean-up $ costs vs. fission

Two key sources of fuel: Deuterium and Tritium (both are heavy isotopes of Hydrogen)

Most likely to be developed commercial fusion reaction involves:

D + T → He-4 (helium) + neutron + heat (total energy yield 17.6 MeV; ~14.1 MeV in neutron)

Ultralow energy neutron reactions (LENRs): distinguishing feature is neutron production via electroweak reaction; neutron capture on fuel + gamma conversion to IR + decays [β , α] releases nuclear binding energy: early-stage technology; no emission of energetic neutron or gamma radiation and no long lived rad-waste products; LENR systems do not require massive and expensive radiation shielding and containment structures → much lower $$$ cost; many possible fuels: any element/isotope that can capture LENR neutrons; involves neutron-catalyzed transmutations of fuels into heavier stable elements that release heat

Lattice Energy LLC

> “There are known knowns; there are things we
> know that we know. There are known unknowns;
> that is to say, there are things that
> we now know we don't know.
> But there are also unknown unknowns –
> there are things we do not know we don't know.”

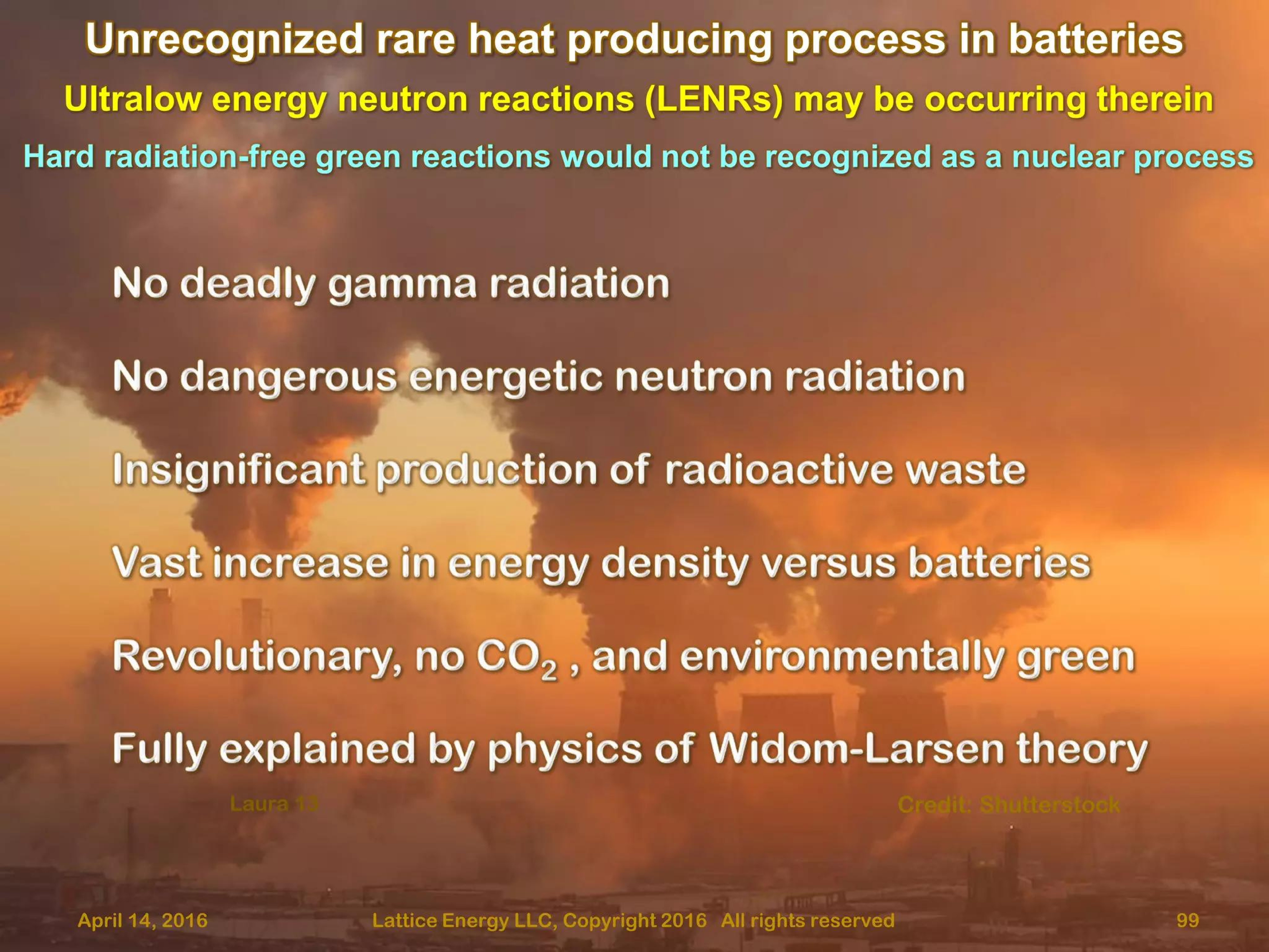
Donald Rumsfeld

U.S. Secretary of Defense
Press conference (2002)

Unrecognized rare heat producing process in batteries

Ultralow energy neutron reactions (LENRs) may be occurring therein

Hard radiation-free green reactions would not be recognized as a nuclear process



No deadly gamma radiation

No dangerous energetic neutron radiation

Insignificant production of radioactive waste

Vast increase in energy density versus batteries

Revolutionary, no CO_2 , and environmentally green

Fully explained by physics of Widom-Larsen theory

Laura 13

Credit: Shutterstock

Widom-Larsen theory of ultralow energy neutron reactions

Three key publications that begin in March of 2006 referenced below

Many-body collective effects enable radiation-free green nuclear power

"Ultra low momentum neutron catalyzed nuclear reactions on metallic hydride surfaces"
A. Widom and L. Larsen
***European Physical Journal C - Particles and Fields* 46 pp. 107 - 112 (2006)**

http://www.slideshare.net/lewisglarsen/widom-and-larsen-ulm-neutron-catalyzed-lenrs-on-metallic-hydride-surfacesepjc-march-2006

"Nuclear abundances in metallic hydride electrodes of electrolytic chemical cells"
A. Widom and L. Larsen
***Cornell physics preprint* arXiv:cond-mat/0602472v1 (2006)**

http://arxiv.org/PS_cache/cond-mat/pdf/0602/0602472v1.pdf

"A primer for electro-weak induced low energy nuclear reactions"
Y. Srivastava, A. Widom, and L. Larsen
***Pramana - Journal of Physics* 75 pp. 617 - 637 (2010)**

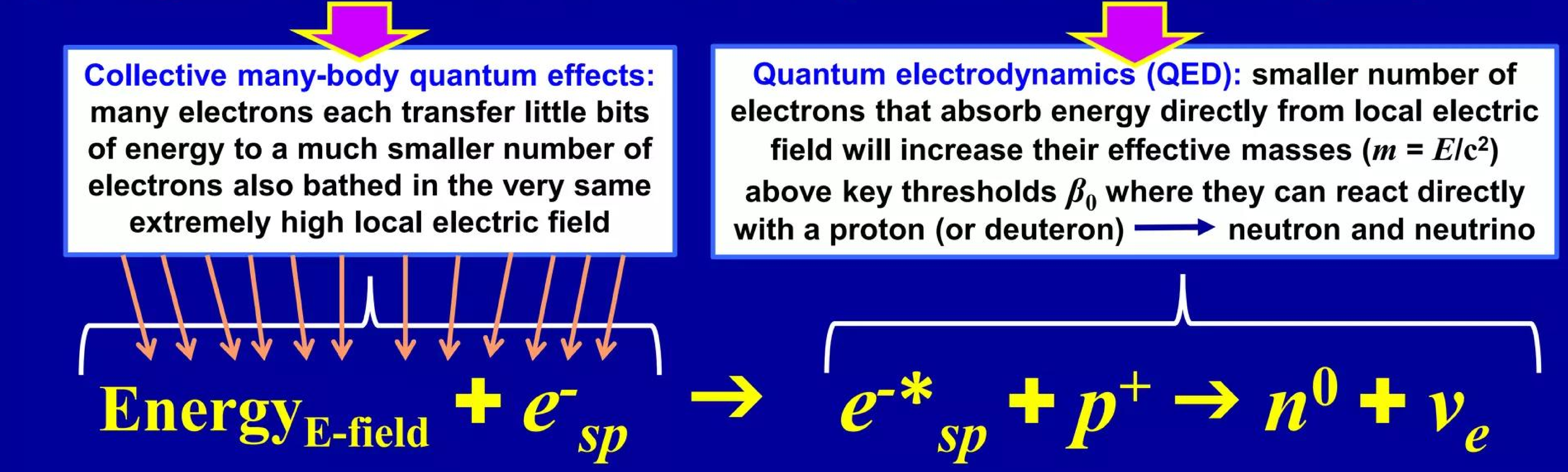
http://www.slideshare.net/lewisglarsen/srivastava-widom-and-larsenprimer-for-electroweak-induced-low-energy-nuclear-reactionspramana-oct-2010

Electroweak reaction in Widom-Larsen theory is simple

Protons or deuterons react directly with electrons to make neutrons

Need input energy source such as electricity to drive LENR neutron production

electrons + protons (Hydrogen) → neutrons + neutrinos (benign photons, fly into space)



Require source(s) of input energy

Input energy creates electric fields > 2.5 x10^{11} V/m

Collective many-body quantum effects: many electrons each transfer little bits of energy to a much smaller number of electrons also bathed in the very same extremely high local electric field

Many-body collective electroweak neutron production

Heavy-mass e^{-*} electrons react directly with protons

Quantum electrodynamics (QED): smaller number of electrons that absorb energy directly from local electric field will increase their effective masses ($m = E/c^2$) above key thresholds β_0 where they can react directly with a proton (or deuteron) ⟶ neutron and neutrino

$$\text{Energy}_{\text{E-field}} + e^{-}_{sp} \rightarrow e^{-*}_{sp} + p^{+} \rightarrow n^{0} + v_{e}$$

v_e neutrinos: ghostly unreactive photons that fly-off into space; n^0 neutrons capture on nearby atoms

Radiation-free LENR transmutation

Neutrons + capture targets ⟶ heavier elements + decay products

Neutrons induce nuclear transmutations that release enormous amounts of clean, CO_2-free heat

Widom-Larsen theory of ultralow energy neutron reactions

Many-body collective effects and quantum entanglement key to LENRs

- ✓ Protons found within a wide variety of many-body condensed matter molecular systems spontaneously oscillate coherently and collectively; their quantum mechanical (Q-M) wave functions are thus effectively entangled with each other and also with nearby collectively oscillating, Q-M entangled surface plasmon or delocalized π electrons on aromatic rings and graphene; amazingly, this Q-M behavior occurs even in comparatively much smaller, simpler molecular systems, e.g. $(NH_4)_2PdCl_6$, ammonium hexaclorometallate (see Krzystyniak *et al.*, 2007 and Abdul-Redah & Dreismann, 2006)

- ✓ While the $e + p$ reaction is written *on paper* as a 2-body charged particle reaction, in condensed matter LENR active sites with entangled protons and electrons it is in fact a many-body reaction involving large numbers of charged particles. Absent many-body collective effects and quantum entanglement, it would take a temperature of ~10 billion degrees inside a collapsing star to drive the $e + p$ reaction forward at substantial rates

- ✓ Term $(\beta - \beta_0)^2$ in Widom & Larsen's $e + p$ reaction rate equation reflects the degree to which heavy-mass (renormalized) e^{-*} electrons in a given LENR active site exceed the minimum threshold effective mass required for neutron production β_0. Details are explained in our first principles ULE neutron production rates calculation preprint found on the Cornell arXiv: http://arxiv.org/PS_cache/nucl-th/pdf/0608/0608059v2.pdf

- ✓ All other things being equal, the higher the μ-scale local density of $e^{-*}p^{+}$ reactants and the greater the rate and quantity of appropriate forms of nonequilibrium energy input, the higher will be the rate of ULE neutron production in nm- to μm-scale LENR-active sites found in failing batteries or in future LENR thermal power generation systems

Appropriate input energy is required to produce neutrons

Electron or ion currents; E-M photon fluxes; organized magnetic fields

Input energy is required to trigger LENRs: to create non-equilibrium conditions that enable nuclear-strength local E-fields which produce populations of heavy-mass $e^{-}*$ electrons that react with many-body surface patches of p^{+}, d^{+}, or t^{+} to produce neutrons via $e^{-}* + p^{+} \rightarrow 1\ n$ or $e^{-}* + d^{+} \rightarrow 2\ n$, $e^{-}* + t^{+} \rightarrow 3\ n$ (energy cost = 0.78 MeV/neutron for H; 0.39 for D; 0.26 for T); includes (can combine sources):

- ✓ **Electrical currents** - i.e., an electron 'beam' of one sort or another can serve as a source of input energy for producing neutrons via $e + p$ electroweak reaction
- ✓ **Ion currents -** passing across a surface or an interface where SP electrons reside (i.e., an ion beam that can be comprised of protons, deuterons, tritons, and/or other types of charged ions); one method used for inputting energy is an ion flux caused by imposing a modest pressure gradient (Iwamura *et al.* 2002)
- ✓ **Incoherent and coherent electromagnetic (E-M) photon fluxes -** can be incoherent E-M radiation found in resonant electromagnetic cavities; with proper momentum coupling, SP electrons can also be directly energized with coherent laser beams emitting photons at appropriate resonant wavelengths
- ✓ **Organized magnetic fields with cylindrical geometries -** many-body collective magnetic LENR regime with direct acceleration of particles operates at very high electron/proton currents; includes organized and so-called dusty plasmas; scales-up to stellar flux tubes on stars with dimensions measured in kilometers

Summary of steps in Widom-Larsen theory of LENRs

5-step green process in sites occurs in 300 - 400 nanoseconds or less

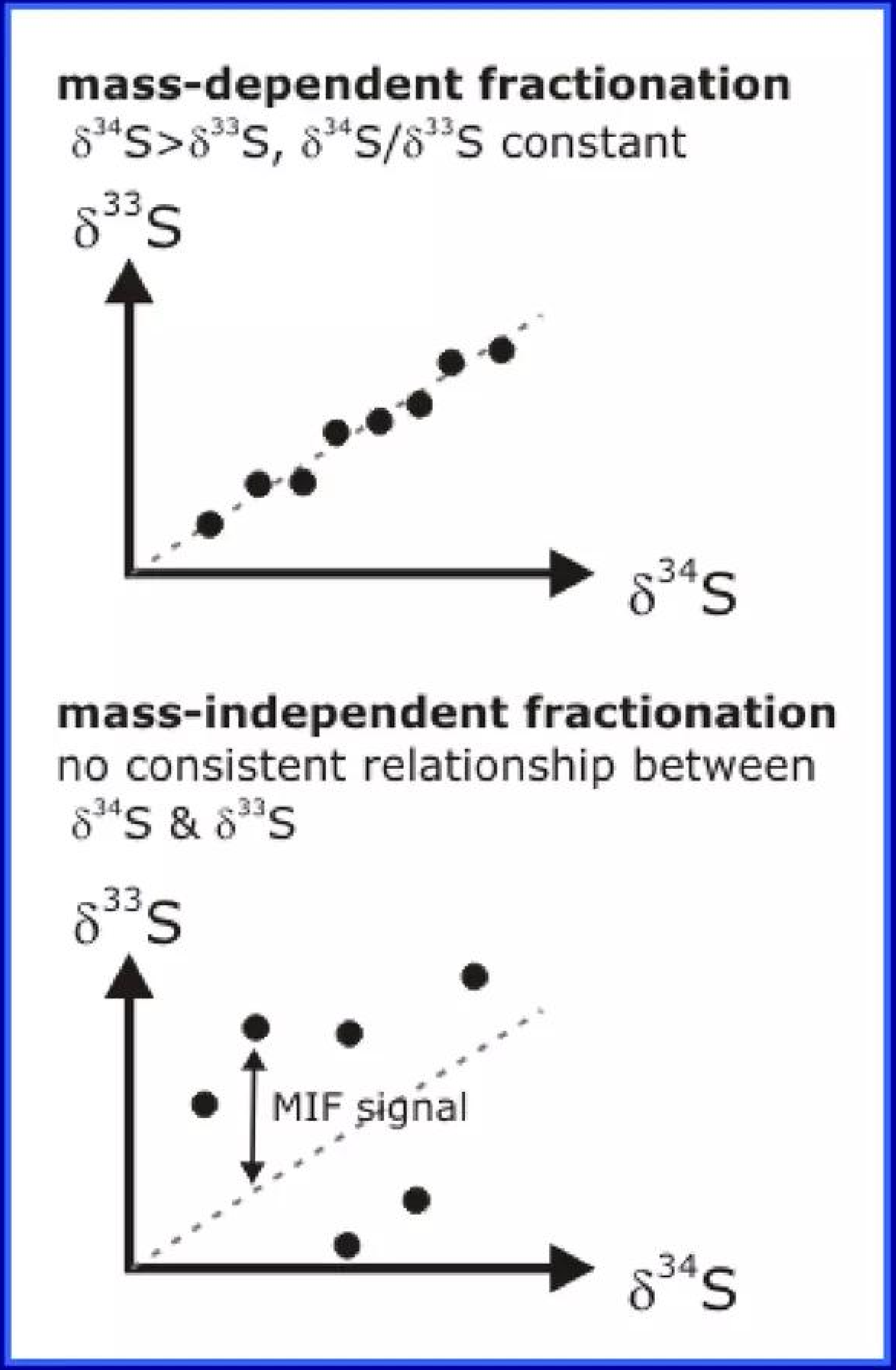
Collective many-body surface patches of protons can become LENR-active sites

1. Collectively oscillating, quantum mechanically entangled, many-body patches of Hydrogen (either +-charged protons or deuterons) will form spontaneously on metallic hydride surfaces or at certain types of interfaces, e.g. metal/oxide
2. Born-Oppenheimer approximation spontaneously breaks down, allows E-M coupling between local surface plasmon electrons and patch protons; application of input energy creates nuclear-strength local electric fields >2.5 x 10^{11} V/m - increases effective masses of surface plasmon electrons in patches
3. Heavy-mass surface plasmon electrons formed in many-body patches then react directly with electromagnetically interacting protons; process creates neutrons and neutrinos via many-body collective electroweak $e + p$ reaction
4. Neutrons collectively created in patch have ultralow kinetic energies and are all absorbed locally by nearby atoms - no dangerous energetic neutron fluxes escape apparatus; any locally produced or incident gammas are converted directly into safe infrared photons (heat) by unreacted heavy electrons (Lattice patent US# 7,893,414 B2) - no hard MeV-energy gamma emissions
5. Transmutation of elements and formation of craters at active sites begins

LENR processes can mimic effects of chemical fractionation

Theoretical chemists assume no nucleosynthesis occurs in their systems

- ✓ For ~ 60 years, a body of theory has been developed and articulated to explain progressively increasing numbers of stable isotope anomalies observed in a vast array of mass spectroscopic data obtained from many different types of natural and experimental, abiological and biological systems. Central ideas in this chemical fractionation theory embody equilibrium as well as irreversible, mass-dependent, mass-independent, nuclear field shifts, and more recently “self-shielding” chemical processes claimed to be very able to separate isotopes, thus explaining reported isotopic anomalies
- ✓ Although not explicitly acknowledged by fractionation theorists, an intrinsic bedrock *fundamental* assumption underlying all of this theory and interpretation of data is that nucleosynthetic processes capable of altering stable isotope ratios and/or producing new mixtures of different elements over time have not operated in such systems after the initial creation in stars; ergo, ordinary chemical processes are able to explain everything
- ✓ **If LENRs are occurring in some of these systems, the above-noted fundamental assumption will be violated**



Release of nuclear binding energy produces usable heat

Several different mechanisms produce clean heat in LENR-active sites

Widom-Larsen explains what generates calorimetrically measured excess heat

- ✓ Conceptually, LENR neutrons act like catalytic ‘matches’ that are used to ‘light the logs’ of target fuel nuclei. A neutron-catalyzed LENR transmutation network operates to release nuclear binding energy that has been stored and locked away in nuclei ‘fuel logs’ since they were originally produced at multi-million degrees in fiery nucleosynthetic processes of long-dead stars, many billions of years ago
- ✓ LENR transmutation networks can produce copious heat that comes mainly from:
    - Direct conversion of gamma photons (γ) into infrared photons (IR) by heavy electrons; e.g., γ from neutron captures or β and other types of decays. IR is then scattered and absorbed by local matter, increasing its temperature (heat)
    - Nuclear decays of unstable neutron-rich isotopes that emit energetic particles (e.g., betas, alphas, protons, etc.); these particles then transfer their kinetic energy by scattering on local matter, which increases its temperature (heat)
- ✓ Neutrino photons from weak interactions do not contribute to any production of excess heat; they will essentially bleed-off a small portion of released nuclear binding energy outward into space; unavoidable neutrino emissions are part of the energetic cost of obtaining energy releases in LENR networks from β^- decays

W-L theory explains creation of LENR-active sites

Needed to produce neutrons that induce transmutation of elements

Hydrogen (protons or deuterons) and heavy-mass electrons are key reactants

- ✓ Substantial quantities of Hydrogen isotopes must be brought into intimate contact with fully-H-loaded metallic hydride-forming metals (or non-metals like Se); e.g., Palladium, Platinum, Rhodium, Nickel, Titanium , Tungsten, etc. Please note that collectively oscillating, 2-D surface plasmon (SP) electrons are intrinsically present and cover the surfaces of such metals. At full lattice loading (saturation) of Hydrogenous isotopes, many-body, collectively oscillating island-like LENR active sites comprised of protons p^+, deuterons d^+, or tritons t^+ will form spontaneously at random locations on surfaces
- ✓ Or, delocalized collectively oscillating π electrons comprising outer covering surfaces of fullerenes, graphene, benzene, and polycyclic aromatic hydrocarbon (PAH) molecules behave identically to SPs; when such molecules are hydrogenated, they create many-body, collectively oscillating, entangled quantum systems that per W-L theory are functionally equivalent molecular analogues of metal hydrides. In this case, LENRs are triggered on aromatic rings; strong tendency to transmute ring Carbons
- ✓ Born-Oppenheimer approximation breaks down in LENR active sites composed of nearly homogenous collections of collectively oscillating p^+, d^+, and/or t^+ ions; enables E-M coupling between nearby SP or π electrons and hydrogen ions at active sites and creates nuclear-strength local electric fields > 2×10^{11} V/m. Effective masses of electrons in such E-fields are increased to multiple of an electron at rest ($e \rightarrow e^*$) determined by required ~simultaneous energy input(s); called “mass renormalization”

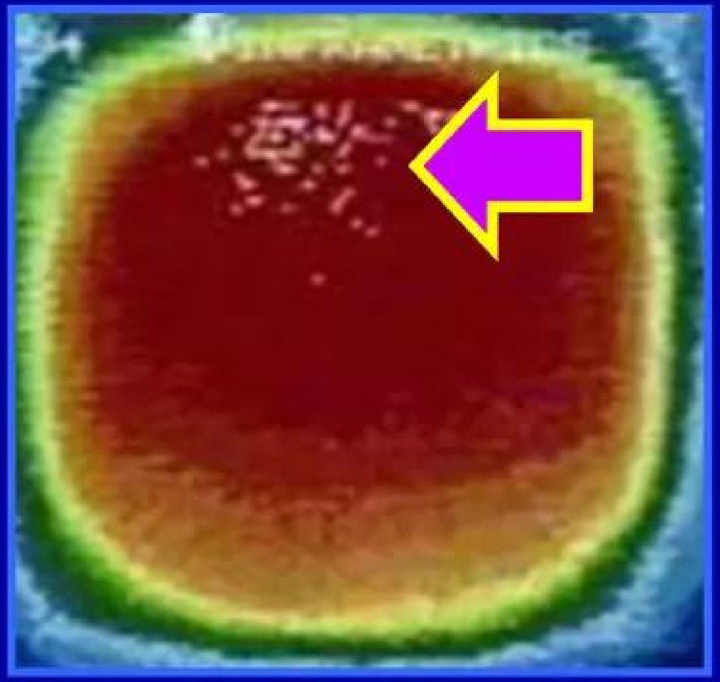
Widom-Larsen provides description for LENR-active sites

Size of these active sites ranges from 2 nanometers up to ~100^+ microns

Active sites have limited lifetimes before being destroyed by fast nuclear heating

- ✓ Per Widom-Larsen theory LENRs occur in localized micron-scale LENR-active sites on ~planar surfaces: at certain types of interfaces\; or curved surfaces of various shaped nanoparticles
- ✓ Tiny LENR-active sites live for less than ~300 - 400 nanoseconds before being destroyed by intense heat; local peak temps range from 4,000 - 6,000º C; LENR-active sites spontaneously reform under right conditions in well-engineered LENR thermal devices
- ✓ Microscopic 100-micron LENR hotspot can release as much as several Watts of heat in < 400 nanoseconds; create crater-like features on surfaces that are visible in SEM images and show evidence for flash-boiling of both precious & refractory metals
- ✓ Peak local LENR power density in microscopic LENR-active sites can hit > 1.0×10^{21} Joules/sec·m^3 during brief lifetimes
- ✓ Control macroscopic-scale temperatures in LENR systems by tightly regulating total input energy and/or total area/volumetric densities of LENR-active sites present in the reaction chambers

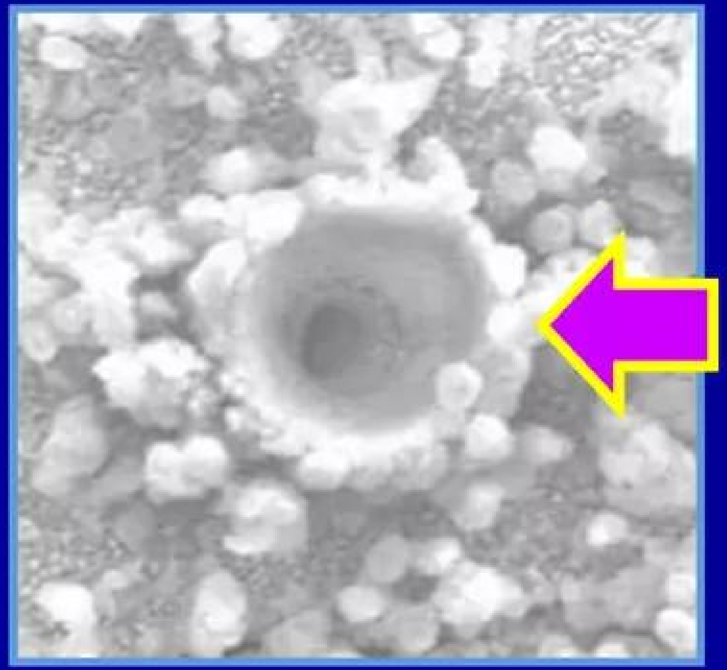
LENR hotspots on Pd cathode
Infrared video of LENR hotspots



Credit: P. Boss, U.S. Navy

http://www.youtube.com/watch?v=OUVmOQXBS68

100 μ LENR crater in Palladium
Electrochemical LENR cell



Credit: P. Boss, U.S. Navy

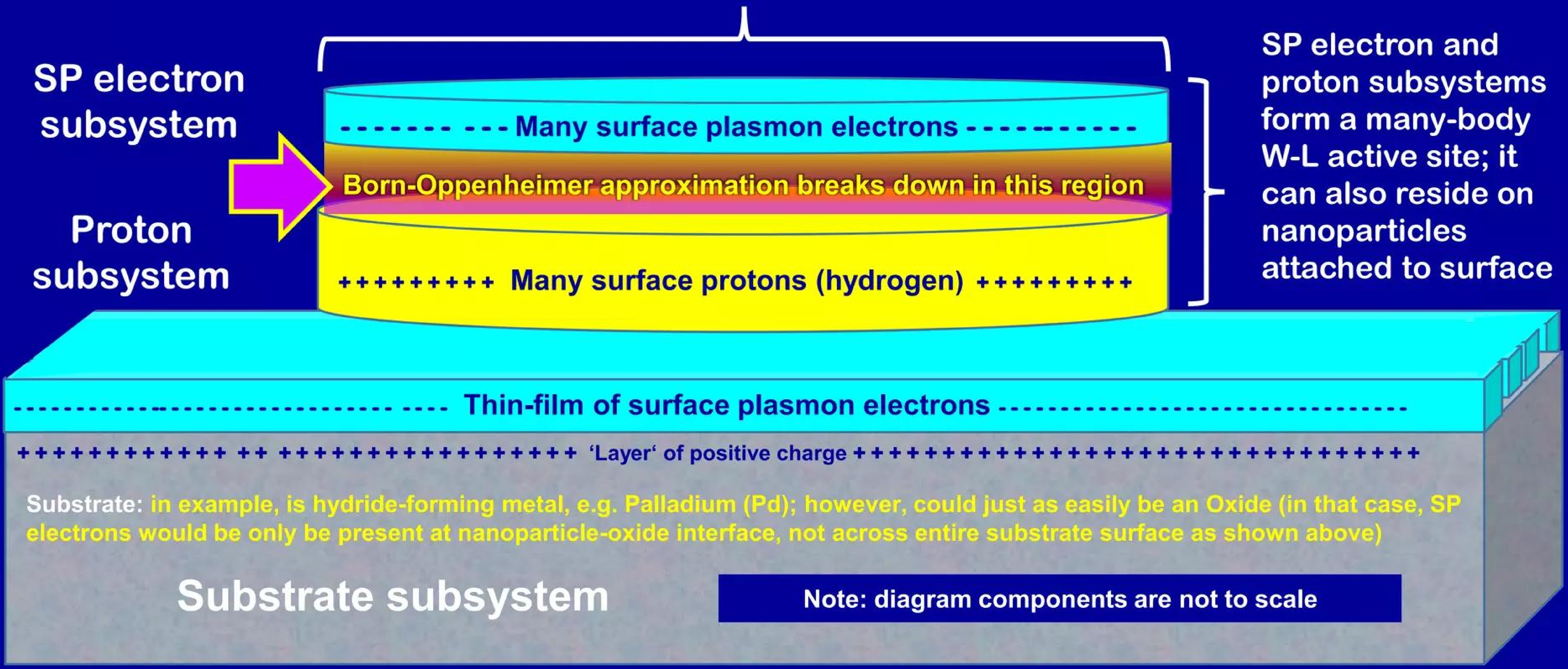
W-L concept of a microscopic LENR-active surface site

Comprised of many-body patches of protons and electrons on surface

SP electrons and protons oscillate collectively and are mutually Q-M entangled

Diameters of many-body active sites randomly range from several *nm* up to ~ 100^+ microns

Single nascent LENR-active site



SP electron subsystem

Proton subsystem

- - - - - - - - - - Many surface plasmon electrons - - - - - - - - - - -

Born-Oppenheimer approximation breaks down in this region

+++++++++ Many surface protons (hydrogen) +++++++++

SP electron and proton subsystems form a many-body W-L active site; it can also reside on nanoparticles attached to surface

- Thin-film of surface plasmon electrons -

+++++++++++++ ++ +++++++++++++++++ 'Layer' of positive charge +++++++++++++++++++++++++++++++++++

Substrate: in example, is hydride-forming metal, e.g. Palladium (Pd); however, could just as easily be an Oxide (in that case, SP electrons would be only be present at nanoparticle-oxide interface, not across entire substrate surface as shown above)

Substrate subsystem

Note: diagram components are not to scale

Input energy creates high electric fields in LENR active sites

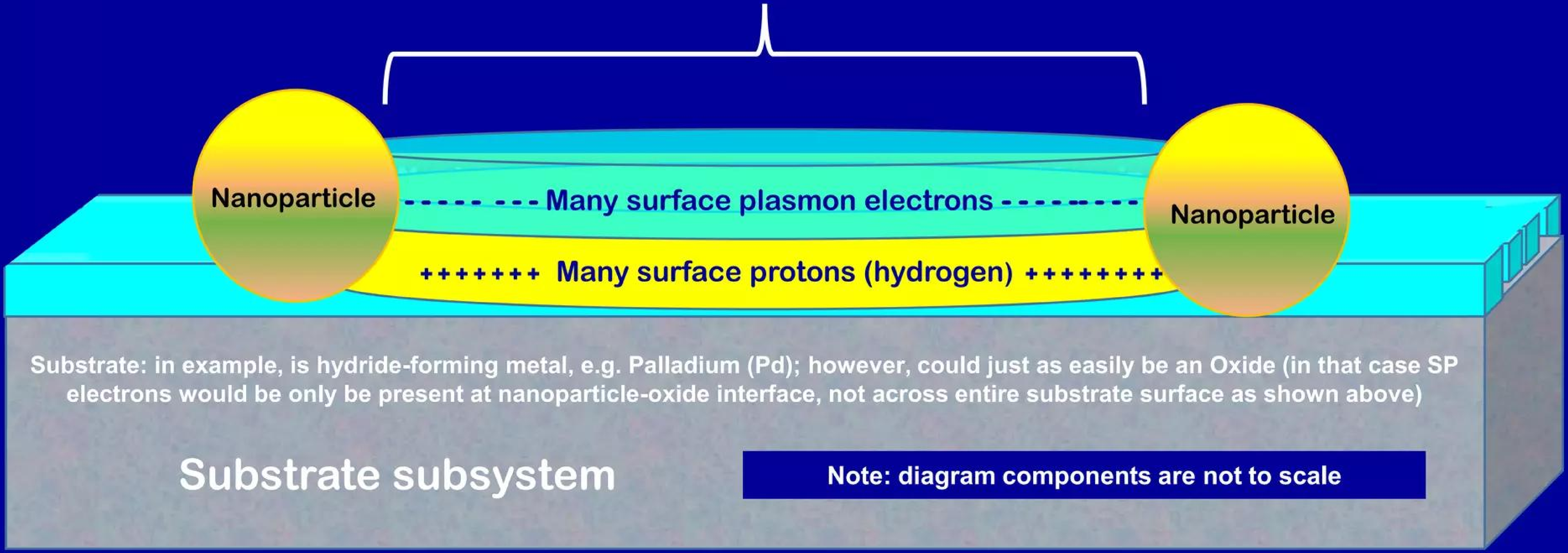
Born-Oppenheimer breakdown enables nuclear-strength local E-field

Huge electric field increase effective masses of some patch SP electrons

Correct input energies create huge local E-fields > 2.5 x 10^{11} V/m between adjacent nanoparticles

$$\text{Input energy}_{\text{E-field}} + e^{-}_{sp} \rightarrow e^{-*}_{sp} + p^{+} \rightarrow n + \nu_e \quad \text{[condensed matter surfaces]}$$

Single nascent LENR-active site



Nanoparticle

----- --- Many surface plasmon electrons --------

Nanoparticle

+++++++ Many surface protons (hydrogen) ++++++++

Substrate: in example, is hydride-forming metal, e.g. Palladium (Pd); however, could just as easily be an Oxide (in that case SP electrons would be only be present at nanoparticle-oxide interface, not across entire substrate surface as shown above)

Substrate subsystem

Note: diagram components are not to scale

LENRs occur in microscopic active sites found on surfaces

Many-body collections of protons and electrons form spontaneously

Ultralow energy neutrons produced & captured close to LENR-active sites

After being produced, neutrons capture on targets in/around active sites

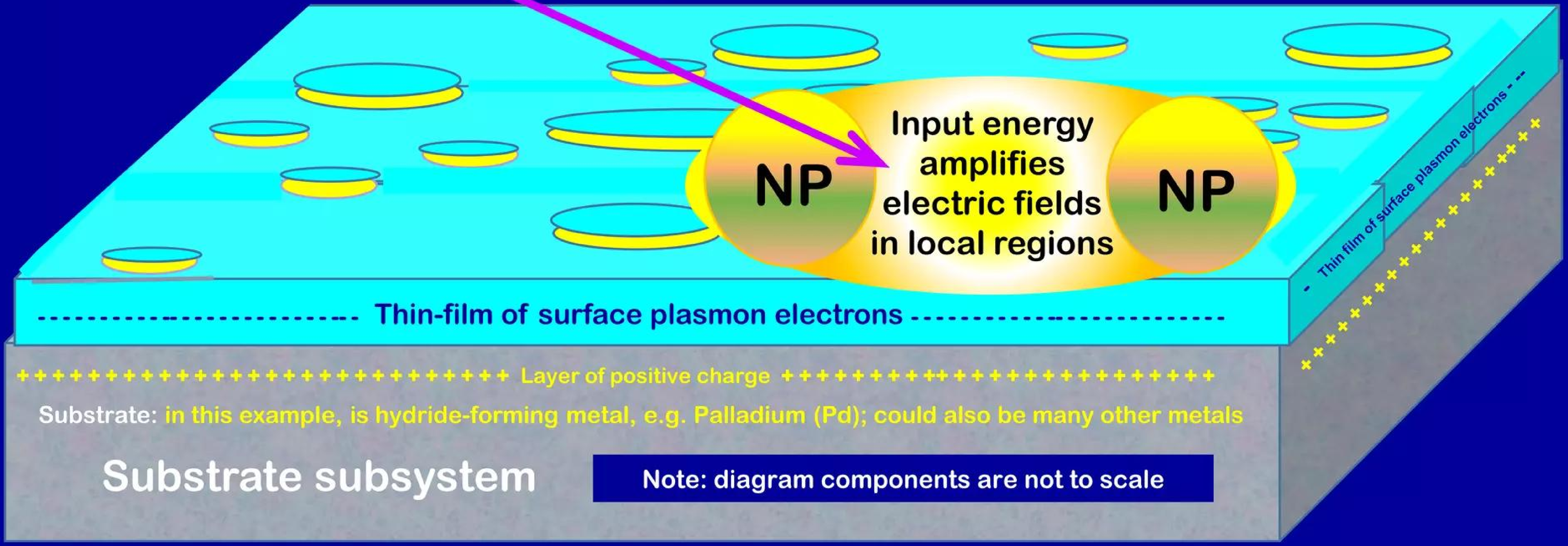
Intense heating in LENR-active sites will form μ-scale event craters on substrate surfaces

$n + (Z, A) \rightarrow (Z, A+1)$ [neutrons capture on nearby target atoms]

$(Z, A+1) \rightarrow (Z+1, A+1) + e_{\beta}^{-} + \nu_e$ [beta$^-$ decay]

Often followed by β^- decays of neutron-rich intermediate isotopic products

● = Metallic nanoparticle (NP)



LENR-active sites create flash-melted craters on surfaces

SIMS and NanoSIMS detect isotopic shifts and transmutation products

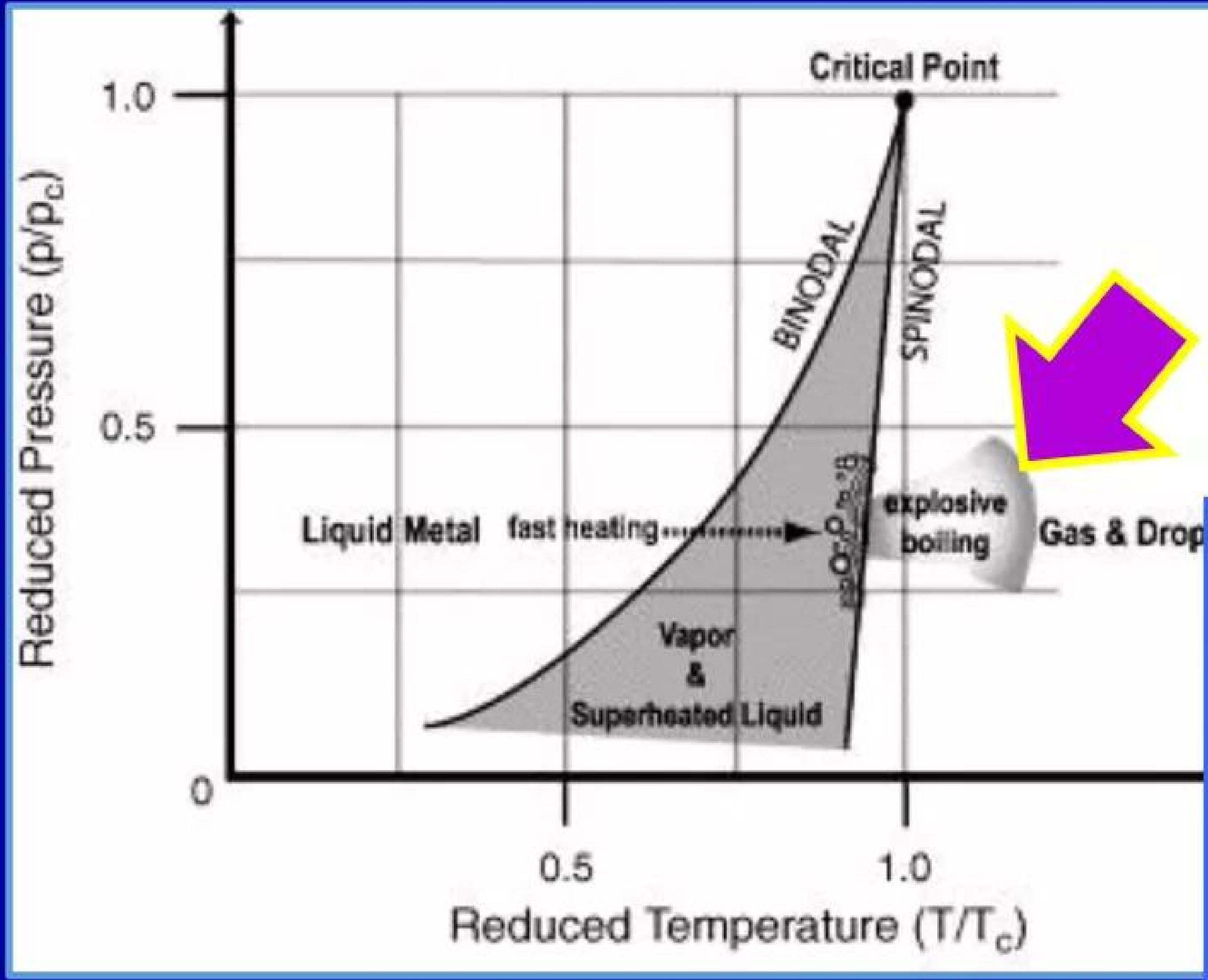
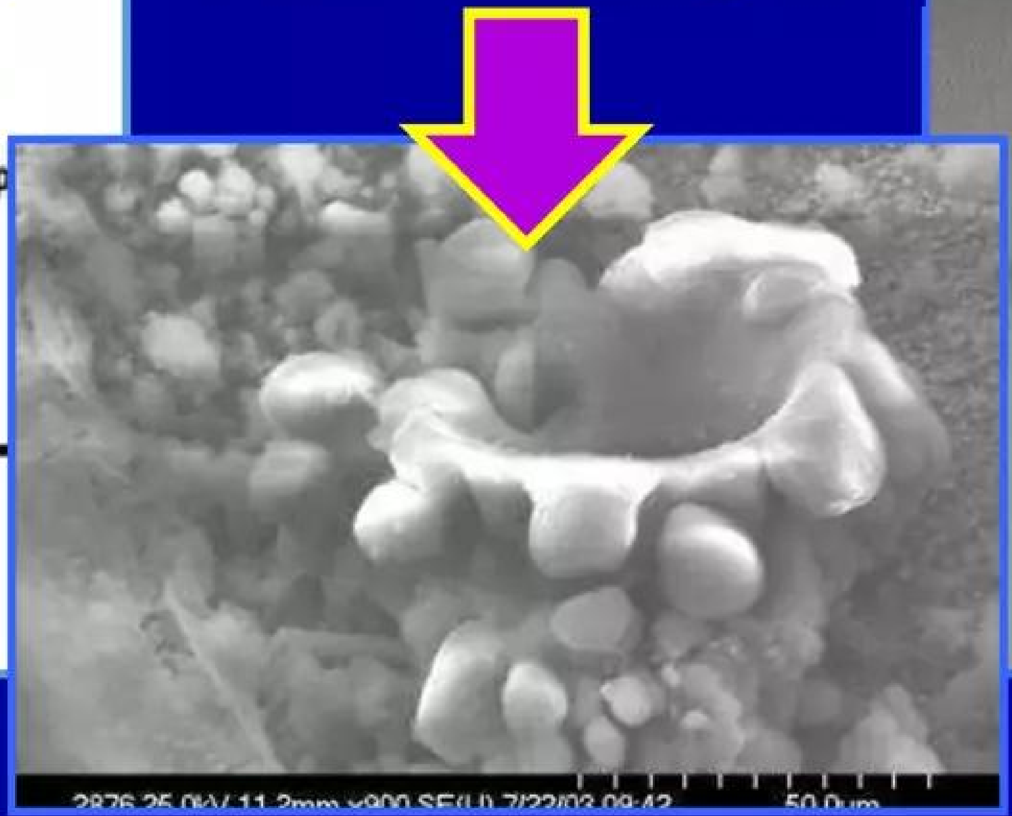


Fig. 1. Phase stability diagram of a liquid metal near the critical point. For fast heating, as obtained during *ns* laser ablation, the melt can be pushed close to critical conditions (superheating), which favors the realization of explosive boiling

LENR crater on Palladium cathode surface after electrolysis



Pd surface post-experiment SEM
P. Boss *et al.*
U.S. Navy - SPAWAR

Hydrodynamic analogue of boiling

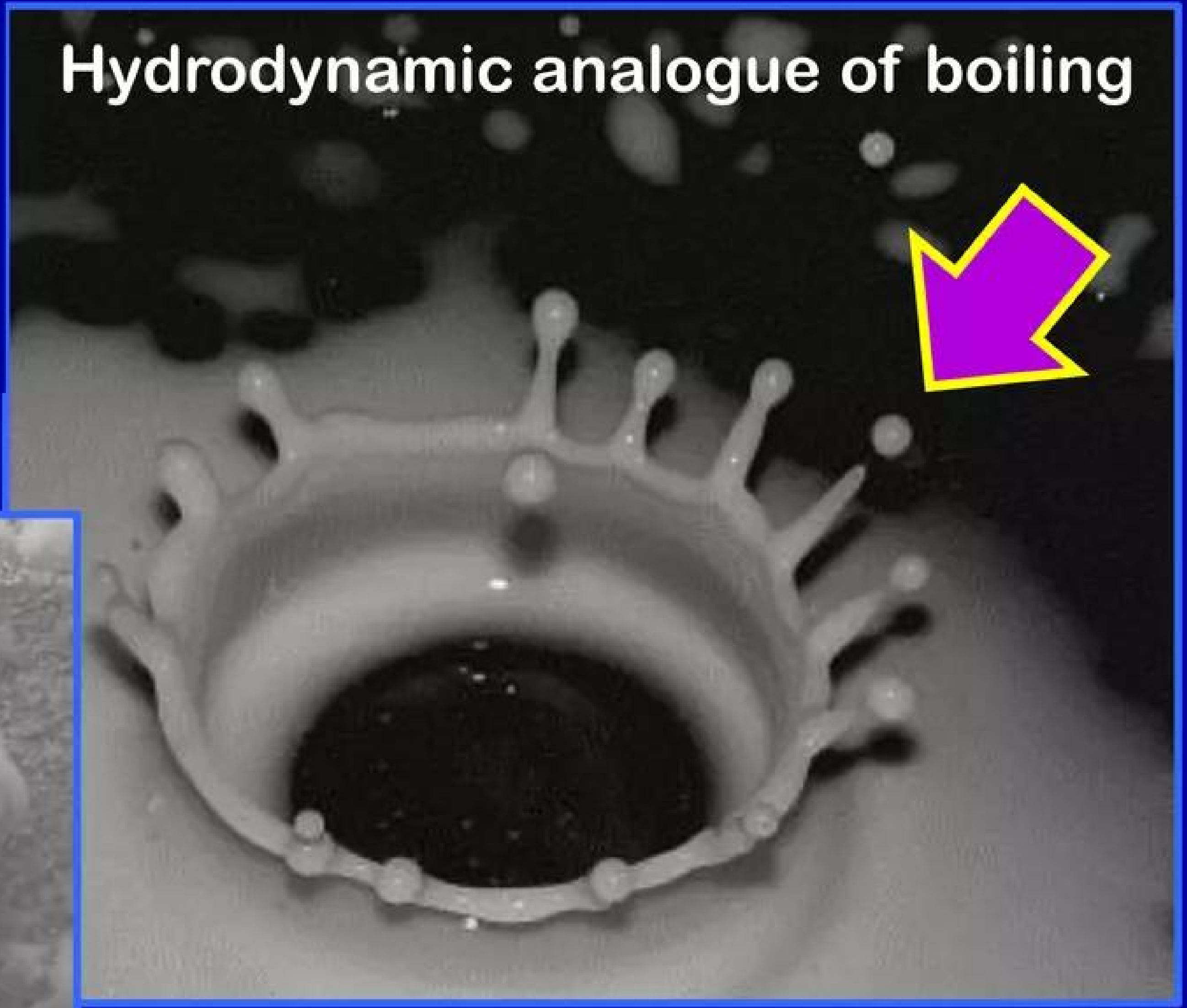


Fig. 2. Schematic visualization of the hydrodynamic evolution of a fluid system under and impulse stress (here milk). Note the non-deterministic formation of jets at the sides and their break-up into droplets. From Ref. [58].

Excerpted and quoted from: "Multiplicity and contiguity of ablation mechanisms in laser-assisted analytical micro-sampling" D. Bleiner and A. Bogaerts *Spectrochimica Acta Part B: Atomic Spectroscopy* 61 pp. 421 - 432 (2006)

http://www.sciencedirect.com/science/article/pii/S0584854706000437

Condensed matter LENR-active sites size from 2 nm to ~100μ

LENRs create heterogeneous elemental compositions on μ length-scales

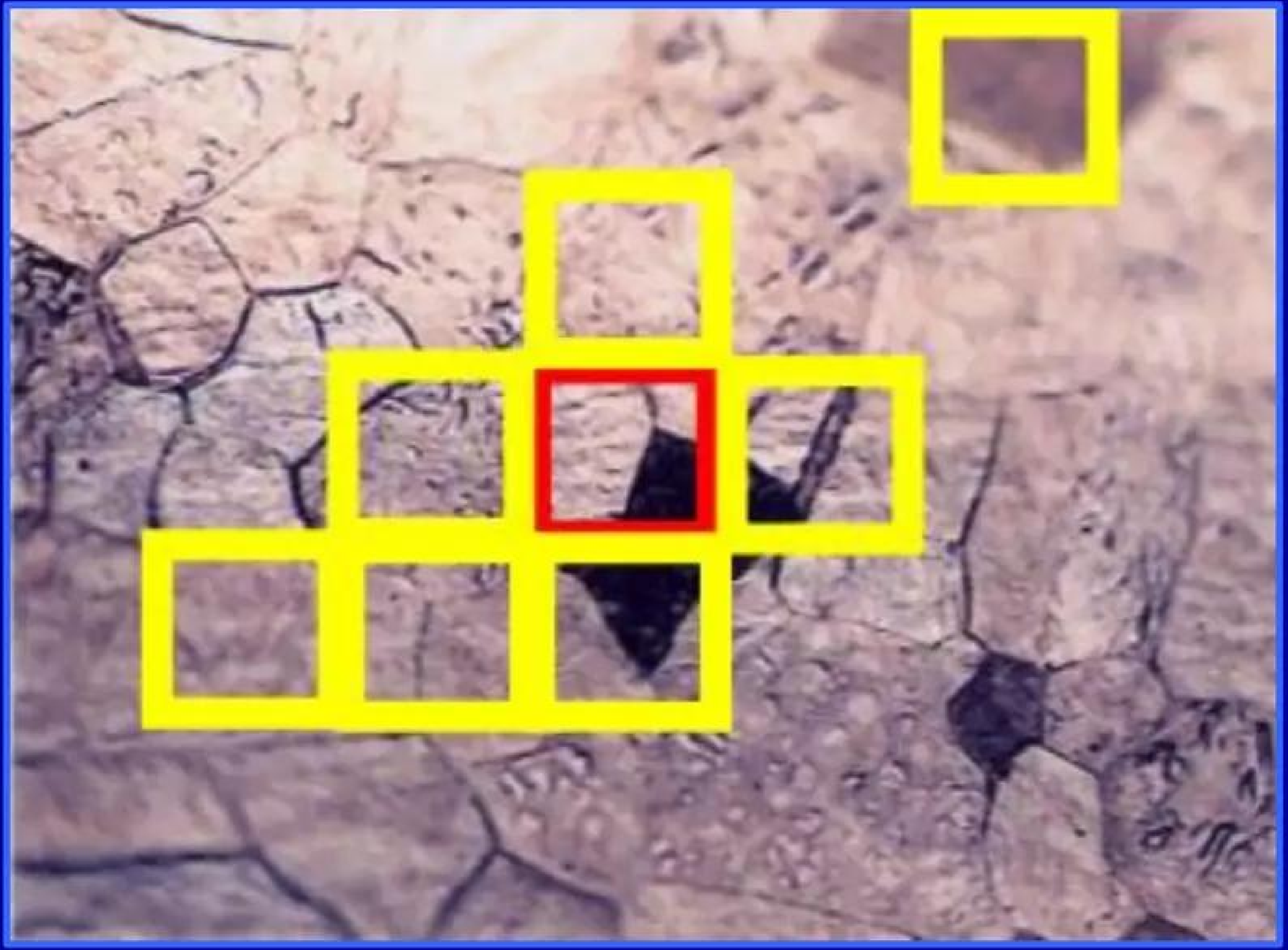
Mitsubishi Heavy Industries has observed this effect while transmuting Cs → Pr

$$^{133}_{55}Cs \rightarrow \, ^{141}_{59}\mathrm{Pr}$$

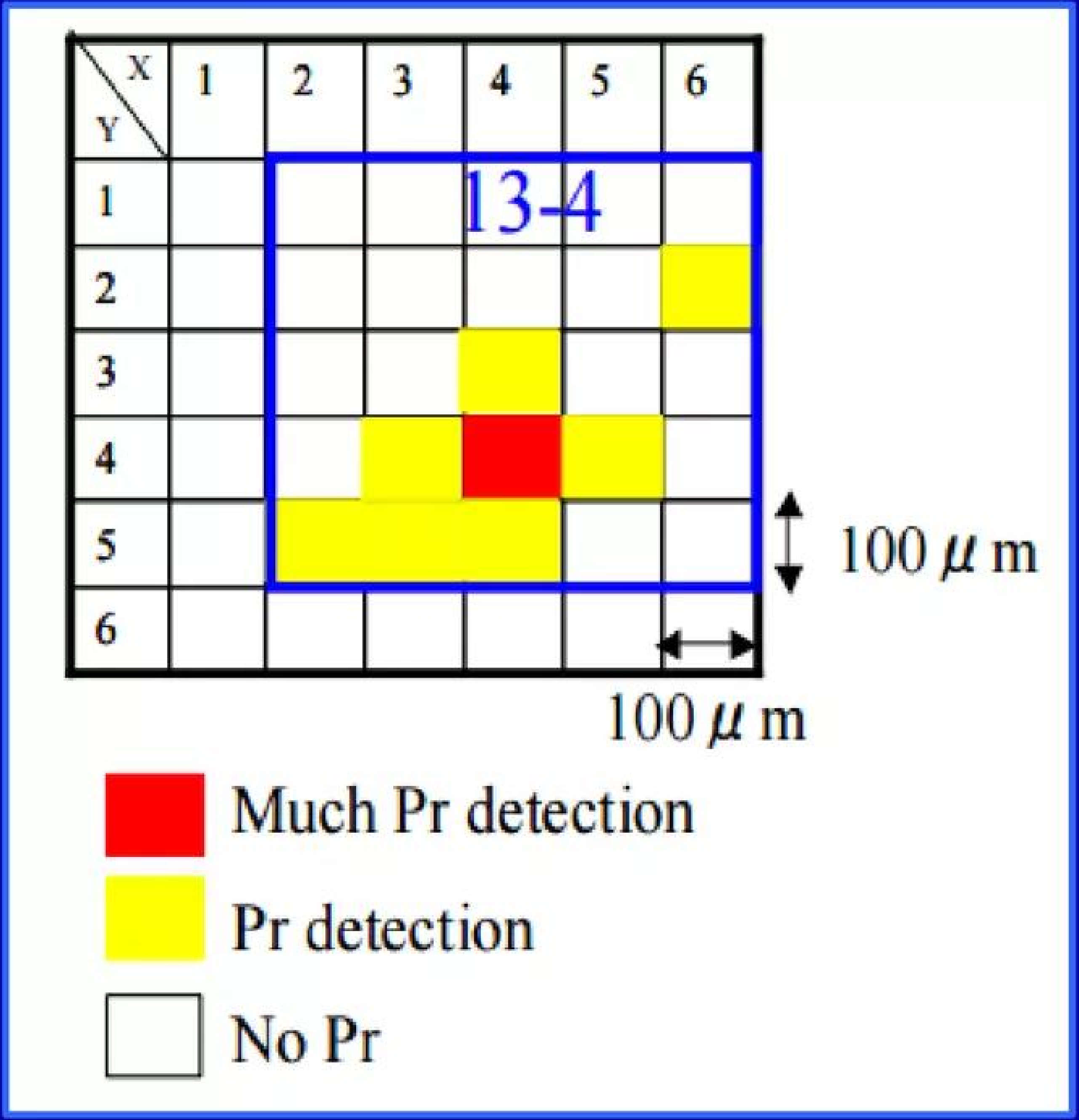
MITSUBISHI
HEAVY INDUSTRIES, LTD.
Our Technologies, Your Tomorrow

Implanted Cesium
↓
Praseodymium

Surface of thin-film Pd/oxide heterostructure after experiment



Credit: Mitsubishi Heavy Industries



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3				🟨		
4			🟨	🟥	🟨	
5		🟨	🟨	🟨		
6						

🟥 Much Pr detection
🟨 Pr detection
☐ No Pr

See Slide #44 in the following Mitsubishi PowerPoint conference presentation (2013):

http://tinyurl.com/zcr3azt

LENRs are green: no energetic radiation or radwastes

Lack of hard radiation obviates need for shielding and containment

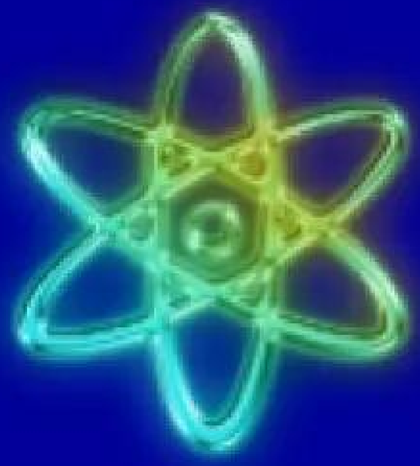
Major opportunity to develop safe, battery-like portable LENR power sources

Fission and fusion processes both emit deadly MeV-energy neutron and gamma radiation

Fission reactors need 1 foot of steel and 3 feet of concrete to protect humans from hard radiation and wastes emitted by reactor; makes systems intrinsically large and heavy

LENRs enable devices something like this: small, portable battery-like power sources that are safe and disposable

Revolution in green nuclear technology



Much larger LENR devices based on dusty plasma embodiments can potentially scale-up to megawatts; akin to today's power plants

Characteristics of LENR and chemical catalytic active sites

Chemical and nuclear processes can coexist and interoperate on surfaces

Parameter	Characteristics of catalytically active sites that greatly increase reaction rates		
Energy scale	Nuclear - keV up to multiple MeVs	Chemical - up to several eVs or thereabouts	
Type of system	Electroweak catalysis in condensed matter	Biological enzyme	Inorganic chemical
Are extremely high local electric fields important?	Yes, it is crucial to electroweak catalysis of LENRs in condensed matter at ~STP	Yes, see Fried *et al.* *Science* (2014)	Yes, Aragones *et al.* *Nature* (2016)
Are many-body collective effects important?	Yes, it is crucial to electroweak catalysis of LENRs in condensed matter at ~STP	Yes, see Herschlag *et al.*, *Biochem*. (2013)	Yes, probably
Is quantum mechanical entanglement of protons (Hydrogen) important?	Yes, adsorbed H in surface active sites and H on aromatic rings that rest on surfaces, including metals, fullerenes, graphene	Yes, see Wang *et al.* *PNAS* (2014)	Yes, H adsorbed on surfaces or at interfaces
Quantum mechanical entanglement of electrons?	Yes, amongst surface plasmons and π electrons found on aromatic rings	Yes, π electrons on Carbon aromatic rings	Yes, with surface plasmons
Any deadly MeV-energy gamma emissions?	None: heavy-mass electrons convert γ to safe infrared per US Patent #7,893,414 B2	None	None
Any deadly MeV-energy neutron emissions?	None: almost all are captured locally; see Widom & Larsen, *EPJC* (2006)	None	None
Extreme specificity for reactants and products?	Yes, $e + p$ or $e + d$ or $e + t$ → [1, 2, or 3] $n + \nu_e$ (neutron, neutrino)	Yes, extremely	Somewhat; can vary greatly
Is catalytically active site conserved and reusable?	No, exists for ~200 to 400 nanoseconds and then Q-M coherence thermally destroyed	Yes, essentially unchanged and viable	Mostly, for a while
Are species of chemical elements conserved in catalytic process?	No, relative isotopic ratios of stable elements can shift; species and quantities of chemical elements present can change	Yes, all species of chemical elements are fully conserved, i.e. do not change; when measurable, isotopic shifts should always mass-balance	

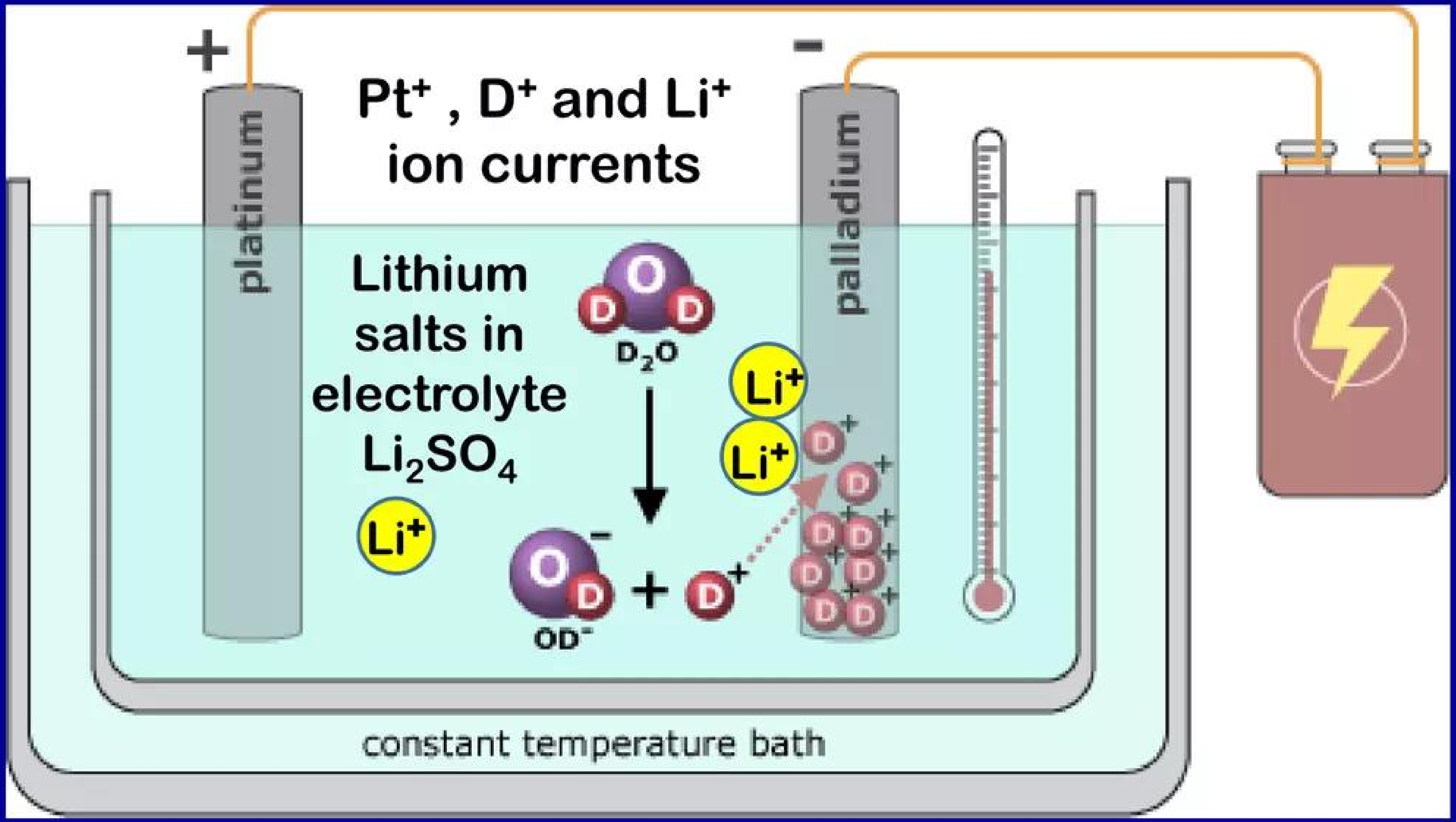
Comparison of Lithium batteries vs. electrochemical LENRs

Examples of:	Lithium-ion Batteries	Electrochemical LENRs
Reversibility	Coulombic efficiency for EVs > .99995%	Irreversible; transmutes elements
Basic reactions and transport	$AB + C \rightarrow A + B^+ + e^- + C \rightarrow A + BC$ $B^+ = Li^+$ (via electrolyte) and e^- (via wire)	$e^- + p^+ \rightarrow 1\ n^0 + \nu_e$ $e^- + d^+ \rightarrow 2\ n^0 + \nu_e$
Proton sources	$-CH_x$ side groups, Carbon aromatic rings	Aqueous: H_2O, D_2O
Electrons	Ordinary conduction electrons in materials and electrolytes; no quantum mechanical entanglement of charged particles needed	Surface plasmons (metal surfaces); or at some interfaces; π electrons on aromatic groups and graphene
Anode materials	A = Lithium (metal); Carbon (graphite)	Platinum Pt, Tungsten W, Carbon C
Cathode materials	C = $LiCoO_2$; $LiFePO_4$; $LiMn_2O_4$	Pd, Ni, Ti, W, other metal hydrides
Electrolytes	$(CH_2O)_2CO$ (ethylene carbonate) $OC(OCH_3)_2$ (dimethyl carbonate)	H_2O, D_2O (Hydrogen bubbles will form on cathode surfaces)
Electrolyte salts	$LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiCF_3SO_3$	$LiOD$, $LiOH$, Li_2SO_4, H_2SO_4, K_2CO_3
Operating voltages	Generally 3 - 4 V No materials work reliably at ~ 5 V today	Huge range of experimental values: 2 V all the way up to > 350 V
Local electric field strengths	Quasi-static ~ 10^9 to 10^{10} V/m in very close proximity to surfaces of electrodes	Briefly > 2.5×10^{11} V/m to produce LENR ultralow energy neutrons
Cell operating temperature range	Generally for safety < 60° C Stores electricity with minimal heating	Laboratory experiments ≤ 100° C Note: LENR active-site hotspots briefly hit 4,000 - 6,000° C Generates excess heat

Conceptual overview of an LENR electrolytic chemical cell

Platinum anode, Palladium cathode, Lithium salts, aqueous electrolyte

Pt anode **Pd cathode** **DC electrical power source**



Credit: website "Understanding Science" by the University of California Museum of Paleontology (UCMP)

Above is a conceptual schematic for an aqueous D_2O heavy-water electrolytic chemical cell used in many LENR experiments; typically use DC power supply as a source of electrical input energy. Using modern mass spectroscopy for post-experiment analyses of cathode materials, LENR researchers have carefully documented and reported the production (via LENR transmutation) of minute amounts of many different elements and isotopically shifted stable isotopes on cathode surfaces in such cells. In some cases, ultralow energy neutron fluxes were $>10^{12}$ cm^2/sec which then created a broad array of stable LENR transmutation products over the course of several weeks of electrolysis

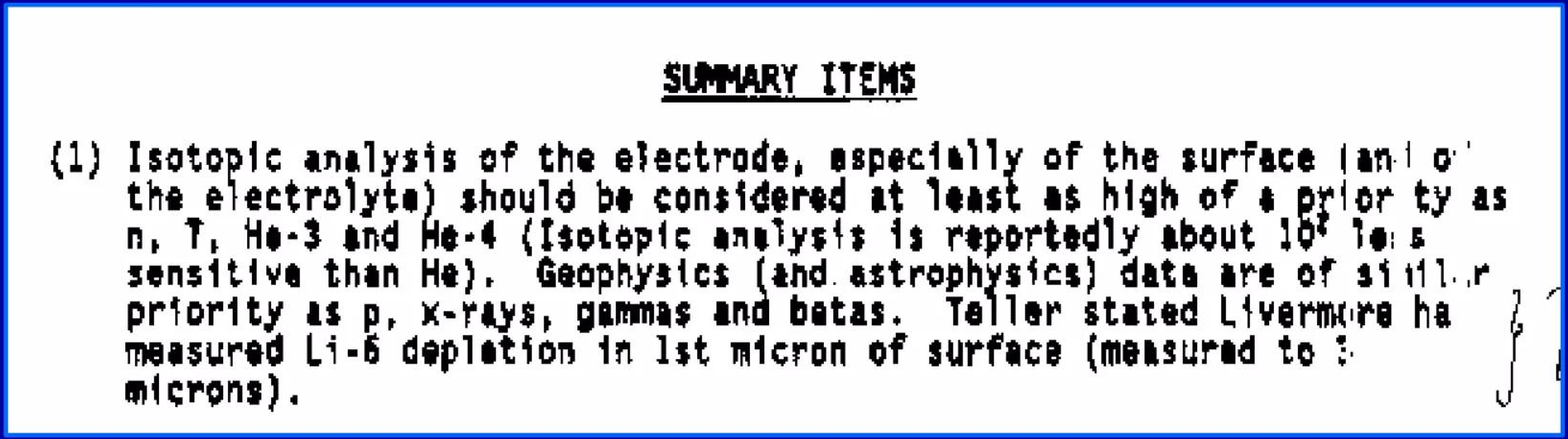
Lawrence Livermore National Lab: 1989 EPRI-NSF workshop

Edward Teller reported LLNL had seen clear isotopic shifts in Lithium

Reported Lithium-6 isotope had been depleted on Pd cathode surfaces

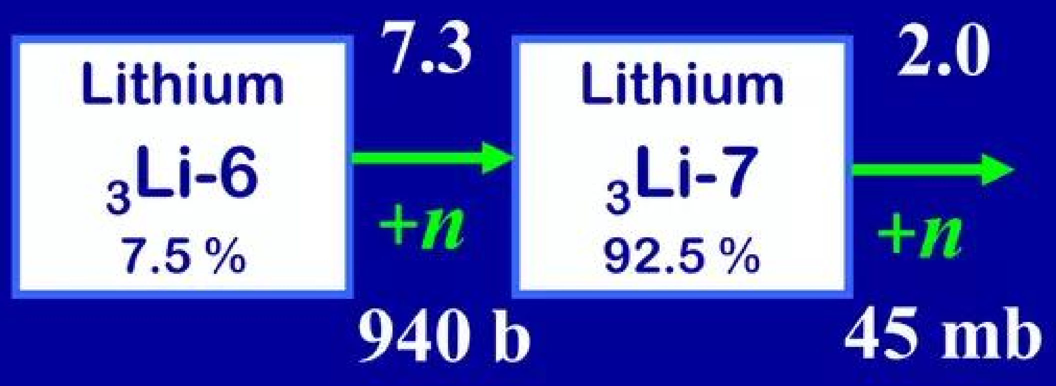
Experiments involved Pt anode, Pd cathode, LiOD, D_2O electrochemical cells

Unexpected anomaly: this should only happen in stars or fission reactors



SUMMARY ITEMS

(1) Isotopic analysis of the electrode, especially of the surface (and o the electrolyte) should be considered at least as high of a priority as n, T, He-3 and He-4 (Isotopic analysis is reportedly about 10^4 less sensitive than He). Geophysics (and astrophysics) data are of similar priority as p, x-rays, gammas and betas. Teller stated Livermore ha measured Li-6 depletion in 1st micron of surface (measured to 3 microns).



LENR neutron captures (green arrows) go from left-to-right; Q-value of capture (MeV) is number above it and thermal neutron capture cross-section (barns) is below the arrow

Li-7/Li-6 isotopic ratio will *increase* (Li-7 is enriched)

Note: two stable Lithium isotopes in Nature: Li-6 (natural abundance = 7.5%; thermal neutron capture cross-section = 940 barns) and Li-7 (natural abundance = 92.5%; thermal neutron capture cross-section = 45 millibarns). Neutron capture cross-section for Li-6 is vastly larger than for Li-7; if LENR neutron fluxes are present on a cathode's surface, Li-6 will preferentially *deplete* vs. Li-7, which will then *increase* in abundance (Li-7 will be enriched) due to much faster rate of neutron capture on Li-6

Lithium isotopic shifts observed in other LENR experiments

Results of various researchers reported by T. Passell at ICCF-9 in 2002

"Evidence for Lithium depletion in Pd exposed to gaseous Deuterium and Hydrogen"
T. Passell (EPRI) at ICCF-9 conference, Tsinghua University, Beijing, China 2002

http://newenergytimes.com/v2/library/2002/2002Passell-Li6-Depletion.pdf

Note: in LENR experiments, Lithium forms intimate alloys with Pd on cathode surfaces

Abstract: "Some 17 samples of Palladium, 14 of small diameter particulates and 3 wires were analyzed by Time of Flight Secondary Ion Mass Spectroscopy (TOF SIMS). All had been exposed to gaseous Deuterium or Hydrogen for long periods (months) … While the Zinc isotopes were found to be within reasonable uncertainty limits of terrestrial Zinc, impurity Lithium showed Li-7/Li-6 ratios much higher than the 12.48 value for terrestrial Lithium. This observation lead to the consideration of hypotheses involving Lithium as an active agent in production of excess heat and Helium observed in the experiments by the investigators providing the samples."

Discussion: "Two samples Pd-B and Li Tsinghua Sample E, were observed early in the investigation, and being so much above terrestrial Li-7/Li-6 ratios, gave a high expectation for the success of this hypothesis. However, it is not entirely original with this paper. Thompson of Johnson-Matthey Company showed a similar result at ICCF-1 in March, 1990, indicating Li-7/Li-6 ratios of 24, 19.9, and 20.3 for three separate measurements by TOF SIMS in the surface layer of 2 solid Palladium cathodes producing excess heat in [electrochemical] cells …"

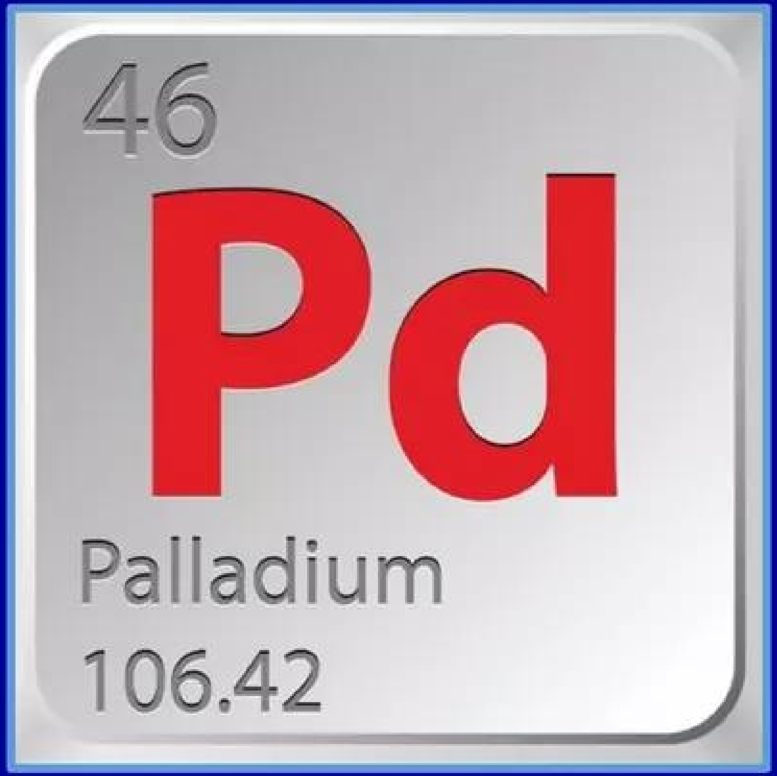
U.S. Naval Research Laboratory: 1989 EPRI-NSF workshop

Reported large isotopic shifts and production of unstable isotopes of Pd

Experiments conducted with Pt anode, Pd cathode and D_2O electrochemical cells


MASS/CHARGE ANOMALIES IN Pd AFTER ELECTROCHEMICAL LOADING WITH DEUTERIUM

- ✓ Rolison & O'Grady of U.S. Naval Research Laboratory reported dramatic relative enrichment of Pd-106 and substantial parallel depletion of lighter Pd-105 isotope in same experimental cathode
- ✓ Clearly observed the production of normally absent, unstable isotopes of Palladium (e.g., Pd-103, Pd-107, Pd-109, and Pd-111) during experiment PdD#4 (note post-experiment appearance of these additional Pd mass-peaks back in Fig. 1 shown earlier) but made no special note of this isotope anomaly on cathode
- ✓ All this data is obviously well-explained by neutron captures on Palladium isotopes but Rolison *et al.* were reluctant to speculate because there was no clearly measurable evidence for the presence of substantial neutron fluxes during their experiments



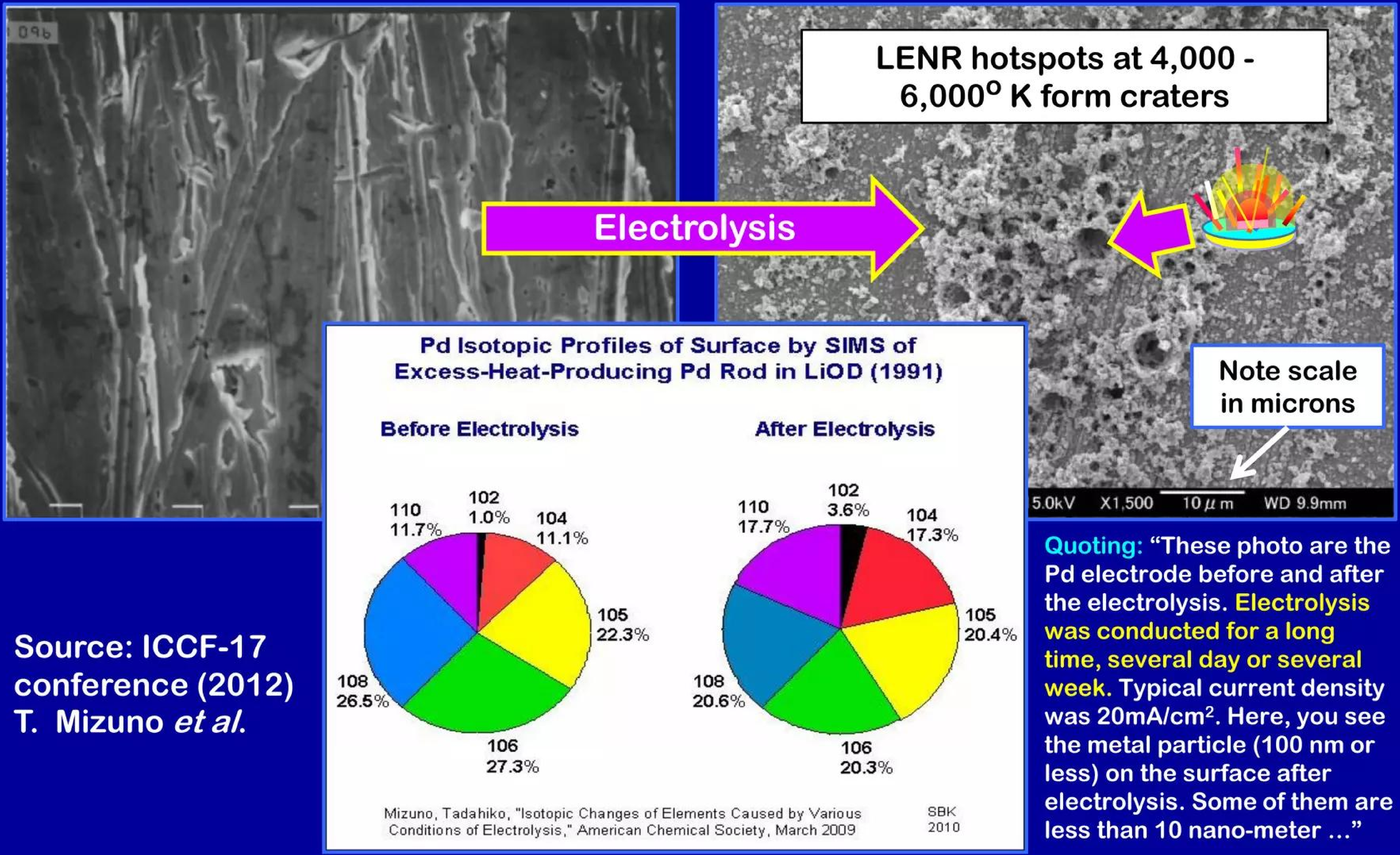
- ✓ For detailed technical discussion of all this please see: http://www.slideshare.net/lewisglarsen/lattice-energy-llc-us-government-labs-reported-clearcut-neutron-capture-data-from-pf-cells-in-oct-1989-may-13-2015

Palladium isotopic ratios are shifted in electrochemical cells

Mizuno et al. (2012) reported major changes in Palladium (Pd) isotopes

Before: smooth Palladium cathode surface

After: rugged surface with μm-scale craters



LENR hotspots at 4,000 - 6,000° K form craters

Electrolysis

Note scale in microns

Pd Isotopic Profiles of Surface by SIMS of Excess-Heat-Producing Pd Rod in LiOD (1991)

Before Electrolysis **After Electrolysis**

Mizuno, Tadahiko, "Isotopic Changes of Elements Caused by Various Conditions of Electrolysis," American Chemical Society, March 2009

Source: ICCF-17 conference (2012) T. Mizuno *et al.*

Quoting: "These photo are the Pd electrode before and after the electrolysis. Electrolysis was conducted for a long time, several day or several week. Typical current density was 20mA/cm^2. Here, you see the metal particle (100 nm or less) on the surface after electrolysis. Some of them are less than 10 nano-meter …"

Graphic: New Energy Times

LENRs create changes in mixture of elements on Pd surfaces

Zhang & Dash (2007) electrochemically transmuted Palladium into Silver

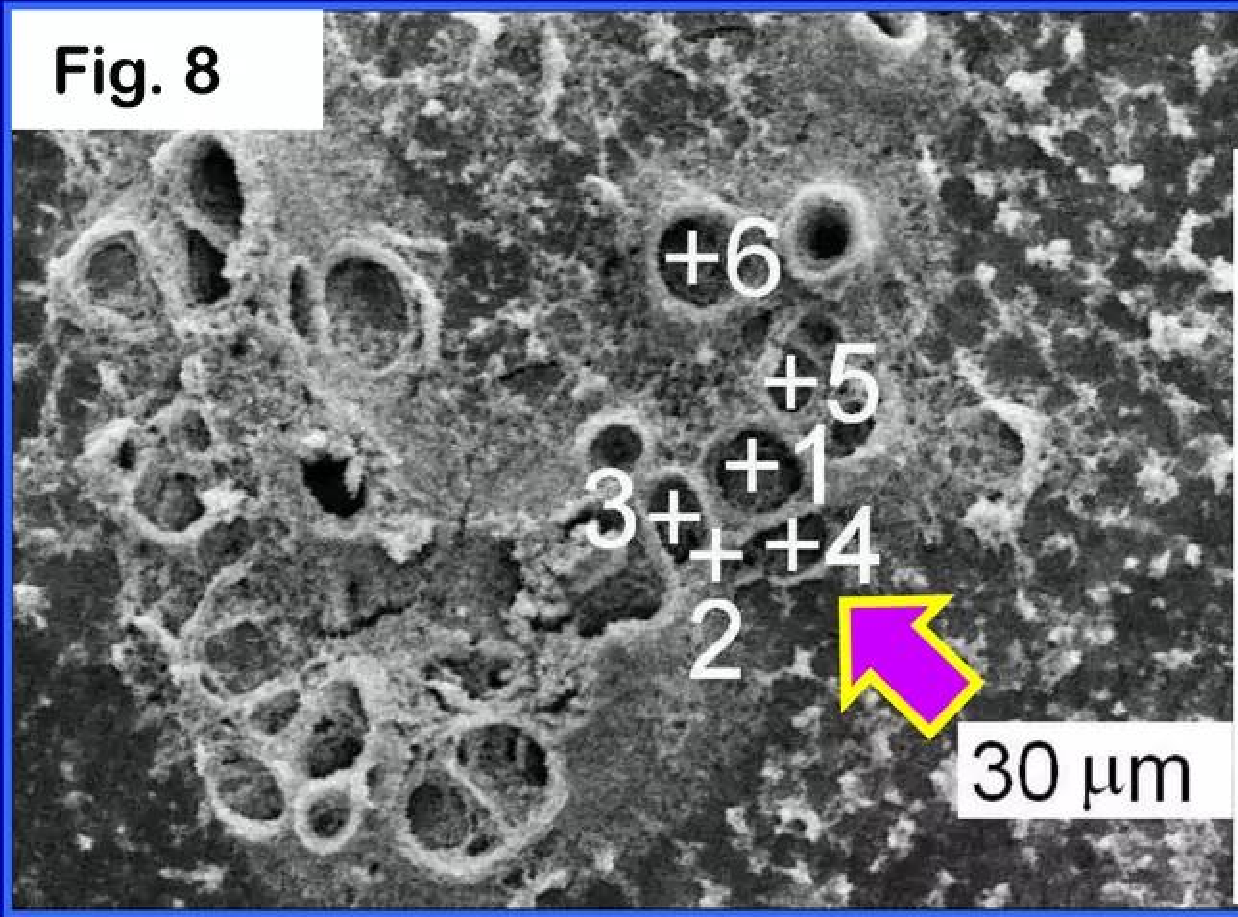
Widom-Larsen theory explains neutron-capture driven production of Ag from Pd

Pd + *n* → [unstable neutron-rich Pd isotopes] → Ag [two stable Silver isotopes]

http://www.lenr-canr.org/acrobat/ZhangWSexcessheat.pdf

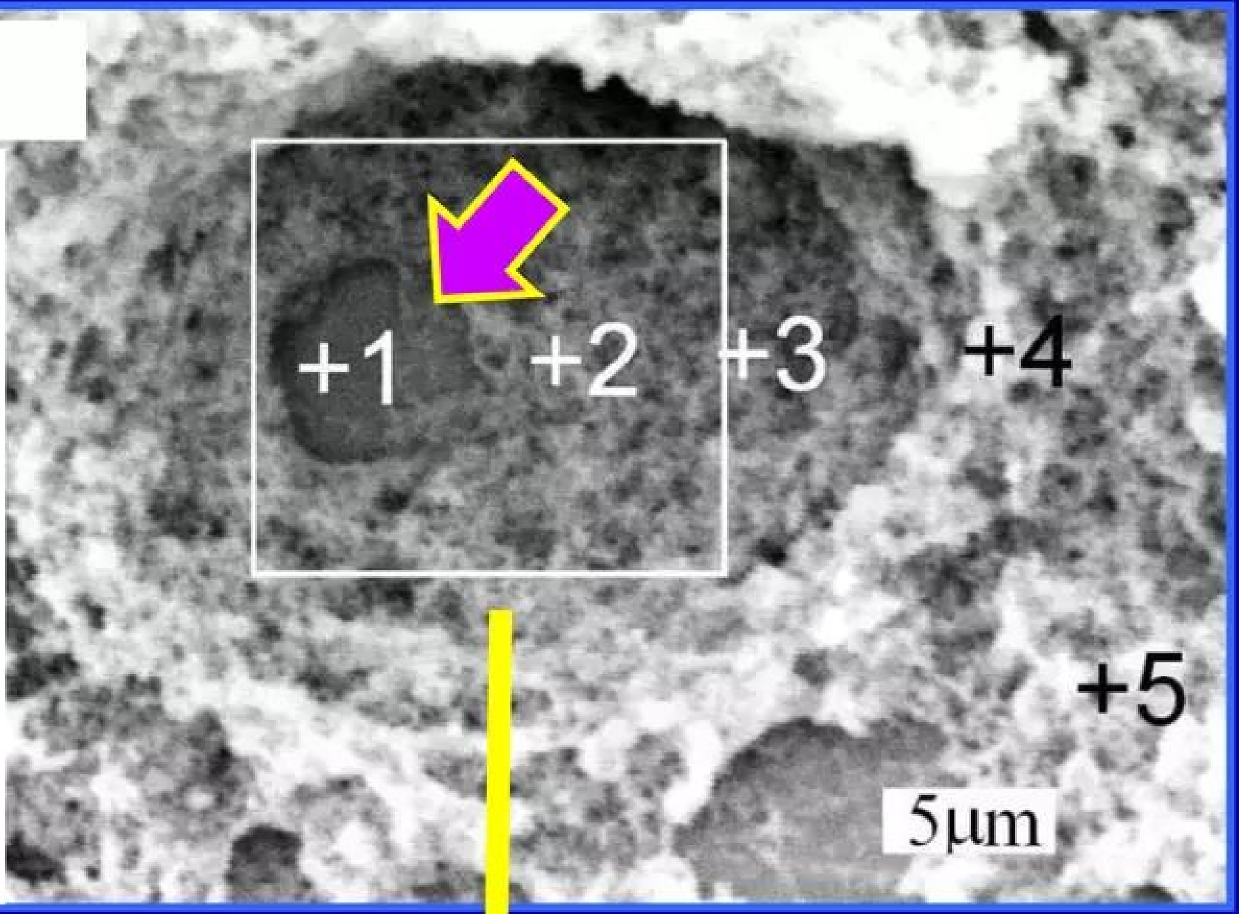
Pd cathode surface after lengthy electrolysis - Zhang & Dash (2007) - Figs. 8 and 9

Fig. 8



"The most common finding is that Silver occurs in craters, such as those shown in Fig. 8. These craters with rims almost certainly formed during electrolysis. Pt deposition was concentrated on these protruding rims."

Fig. 9



Zhang & Dash: Table IX. Relative atomic percent concentrations of Silver (Ag) in area and spots shown in Fig. 9

Spot #	wa*	area**	+1	+2	+3	+4	+5
Ag/(Pd+Ag)	1.2 +/- 0.5	5.6 +/- 0.4	6.8 +/- 0.4	5.6 +/- 0.3	6.3 +/- 0.4	3.6 +/- 0.6	1.2 +/- 0.5

*wa = whole entire area comprising image in Fig. 9

** area = delimited by the white square outlined in Fig. 9

Pd boiling point = 2,970° C

Li-7/Li-6 isotopic shifts observed in Lithium-ion batteries

Reported by K. Okano *et al*. (2015) during the charging of a LiMnO cell

Mass spectroscopy was used to measure the changes in Li-7/Li-6 isotope ratios

"Lithium isotope effects upon electrochemical release
from Lithium manganese oxide" K. Okano *et al.*
Energy Procedia 71 pp. 140 - 148 (2015)

http://www.sciencedirect.com/science/article/pii/S1876610214026939

Abstract: "Lithium was electrochemically released from Lithium manganese oxide ($LiMn_2O_4$) to an electrolyte solution, a 1:2 v/v mixed solution of ethylene carbonate (EC) and ethylmethyl carbonate (EMC) containing 1 M Lithium perchlorate or Sodium perchlorate (EC/EMC/$LiClO_4$ or EC/EMC/$NaClO_4$) to observe the Lithium isotope effects that accompanied the Lithium release. The lighter isotope of Lithium, ^{6}Li, was preferentially fractionated to the electrolyte solution phase, with the value of the Lithium isotope separation factor ranging from 0.989 to 0.971 at 25 °C. The degree of the Lithium isotope fractionation was slightly smaller in the $LiMn_2O_4$-EC/EMC/$NaClO_4$ system than in the $LiMn_2O_4$-EC/EMC/$LiClO_4$ system. The present systems are in great contrast with the Lithium cobalt oxide ($LiCoO_2$)-the electrolyte solution systems concerning the direction and magnitude of the Lithium isotope effects, which seems mostly ascribable to the structural difference between $LiMn_2O_4$ and $LiCoO_2$."

3. Results and discussion: " … the cathode is enriched in the heavier isotope, ^{7}Li, after the Lithium release in every experiment."

Li-7/Li-6 isotopic shifts observed in Lithium-ion batteries

Reported by K. Okano *et al*. (2015) during the charging of a LiMnO cell

Energy
Procedia

K. Okano *et al.*
Energy Procedia 71 pp. 140 - 148 (2015)

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Eq.(6)

$$^{7}\mathrm{Li}_{\text{A-cathode}} + {}^{6}\mathrm{Li}_{\text{A-electrolyte}} = {}^{6}\mathrm{Li}_{\text{A-cathode}} + {}^{7}\mathrm{Li}_{\text{A-electrolyte}}$$

Note: Eq. (6) in their paper is effectively an assumption of mass-balance between the two stable Lithium isotopes. It is *violated* if these isotopes capture any neutrons

3.1 Lithium isotope effects: “For the Mn-Na system, the value of *S* ranges from 0.977 to 0.989, slightly larger (closer to unity) that that for the Mn-Li system. That is, the direction of the isotope fractionation in the Mn-Na system is the same as that of the Mn-Li system, but the degree of the isotope fractionation is smaller in the former than in the latter. These findings are explainable as a partial manifestation of the equilibrium isotope effects based on Eq. (6) as in the case of the Lithium isotope effects with $LiCoO_2$ electrodes, although the direction of the effects is just opposite in the two systems [10] … In the Mn-Na system, the magnitude of the deviation of the value of *S* from unity is an increasing function of the proportion of the released Lithium (Table 1), which seems to support this speculation … The above explanation for the Lithium isotope effects observed in the present work is based on the equilibrium isotope effects [19].”

Li-7/Li-6 isotopic shifts observed in Lithium-ion batteries

Reported by K. Okano *et al*. (2015) during the charging of a LiMnO cell

Energy Procedia

K. Okano *et al.*
Energy Procedia 71 pp. 140 - 148 (2015)

ELSEVIER CrossMark

Eq.(4) $LiMn_2O_4 \rightarrow Li_{1\text{-}x}\,Mn_2O_4 + xLi^+ + xe^-$ Cathode

3.1 Lithium isotope effects (continued): “The explanation based on the kinetic isotope effects [23] may also be possible and more straightforward. The reaction rate of the lighter isotope is in general larger than that of the heavier counterpart. In the present case, the lighter isotope of Lithium transferred faster from the cathode to the electrolyte solution, which leads to the preferential fractionation of ^{6}Li in the electrolyte solution phase, giving the value of separation factor smaller than unity. This explanation, however, cannot be applied to the results of the experiments with the $LiCoO_2$ cathode. The explanation based on the equilibrium isotope effects seems more generally applied. At the present stage of the progress of our study on the Lithium isotope effects at the cathode/electrolyte solution interface by the charge reaction, however, it is difficult to draw a decisive conclusion on what is the origin of the observed Lithium isotope fractionation; equilibrium or kinetic isotope effects or their combination. We need to accumulate more experimental data, and, towards that direction, we have already started the work to observe Lithium isotope effects by the charge reaction using such potential electrode materials as Lithium iron phosphate and Lithium nickel oxide.”

Li-7/Li-6 isotopic shifts observed in Lithium-ion batteries

Reported by Y. Takami *et al*. (2013) during the charging of a LiCoO cell

Mass spectroscopy was used to measure the changes in Li-7/Li-6 isotope ratios

"Observation of Lithium isotope effects accompanying release from Lithium cobalt oxide" Y. Takami *et al.*
Zeitschrift für Naturforschung A 68 pp.73 - 78 (2013)

https://www.researchgate.net/publication/253342151_Observation_of_Lithium_Isotope_Effects_Accompanying_Electrochemical_Release_from_Lithium_Cobalt_Oxide

Eq.(3) $$\mathrm{LiCoO_2} \rightarrow \mathrm{Li}_{1-x}\mathrm{CoO_2} + x\mathrm{Li} + xe^-$$ Cathode

Abstract: "Change in the Lithium isotope composition in a Lithium cobalt oxide ($LiCoO_2$) cathode for Lithium ion secondary batteries accompanying the electrochemical Lithium release from the cathode into an organic electrolyte solution was observed. The ^{7}Li/^{6}Li isotopic ratios of the electrodes after the release of 37.2 to 55.4% Lithium were 1.018 to 1.033 times smaller than that before the release. This means that the heavier isotope, ^{7}Li, is preferentially transferred to the electrolyte solution."

Conclusion: "The Lithium isotopic variation factor, defined as the ^{7}Li/^{6}Li isotopic ratio of the cathode before the charge reaction (electrolysis) divided by that after the electrolysis ranged from 1.018 to 1.033 at 25 C."

Li-7/Li-6 isotopic shifts observed in Lithium-ion batteries

Li isotopic shifts reported in 2013 and 2015 were in opposite directions

Chemical fractionation may be plausible but it shouldn't go in different directions

- ✓ Compared to recent $^7Li/^6Li$ mass spectroscopy measurements by Japanese battery researchers, previous LENR electrochemical experiments (in which Lithium, Palladium, and Silver isotopes on Pd cathodes were measured) generally involved much longer electrolysis times on the order of days to several weeks (vs. 1.3 to ~7.0 hours for Japanese $LiMn_2O_4$ and $LiCoO_2$ battery cathodes) and significantly higher cell operating voltages, namely at least 5 V and up for LENR electrolytic cells (vs. 4.2 or 4.4 V for all of the Japanese Lithium-ion battery cells)

- ✓ In K. Okano *et al.*'s (2015) experiments with a $LiMn_2O_4$ cathode, they remarked that " … the cathode is enriched in the heavier isotope, ^7Li, after the Lithium release in every experiment." Interestingly, this is the same result as what was reported for many LENR cathodes on which Lithium isotope ratios were measured. While this similarity in experimental results is quite intriguing and consistent with neutron captures on Lithium-6, it is not yet proven that LENRs are occurring in Lithium-ion batteries because --- as we noted earlier --- chemical fractionation effects and LENRs can sometimes mimic each other. In case of LENR Palladium cathodes, shifts in ratios of Pd isotopes occurred simultaneously with the enrichment of ^7Li

- ✓ K. Okano *et al.* attempted to explain their observed $^7Li/^6Li$ isotope shifts as the result of "equilibrium or kinetic isotope effects or their combination." Even so, they expressed concern about the weird difference between $LiMn_2O_4$ and $LiCoO_2$

Need more analysis of elements/isotopic shifts in batteries

SIMS and nanoSIMS-50L: excellent measurement tools for such work

SEM imaging/SIMS analyses of nanostructures on anode/cathode surfaces

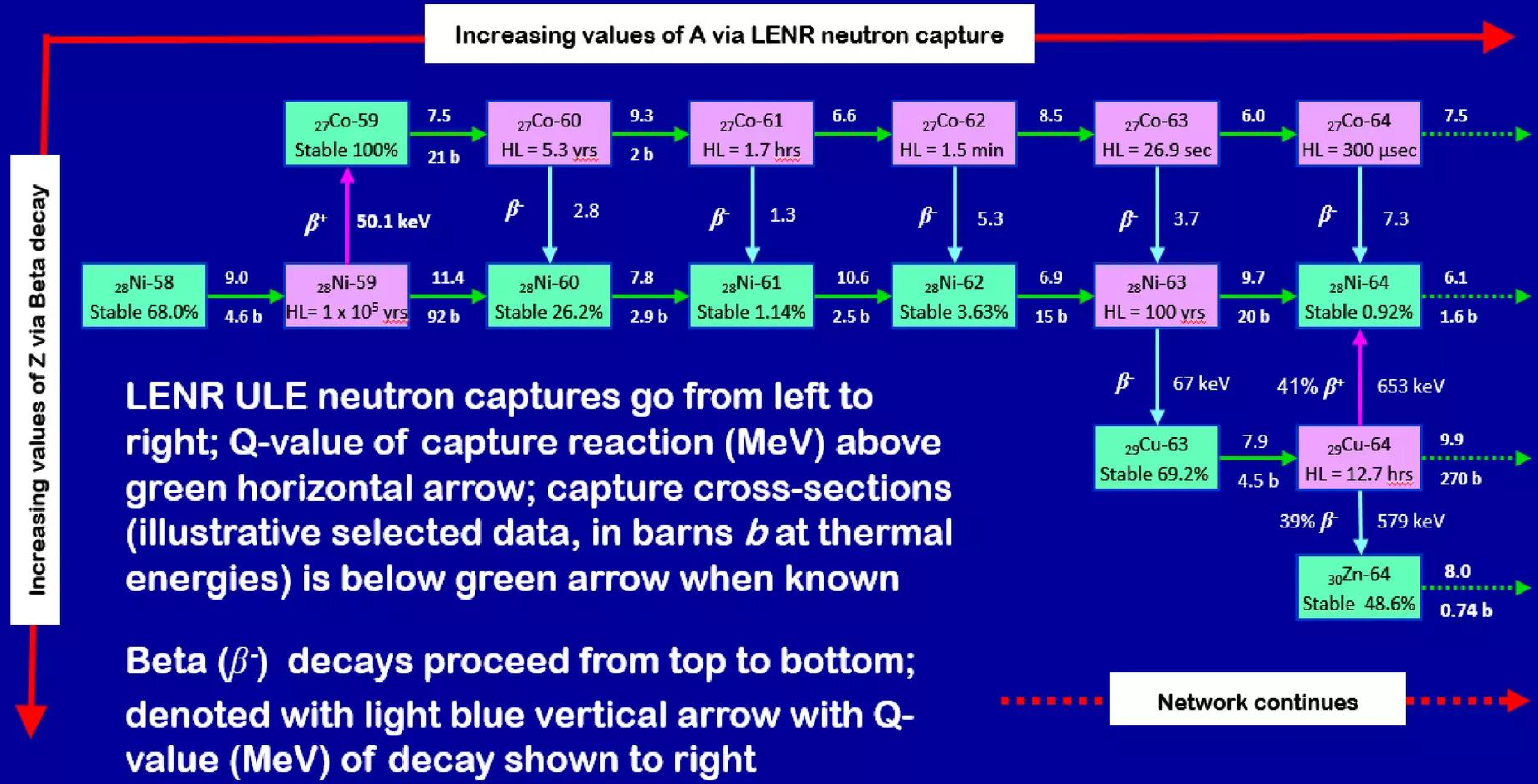
- ✓ LENRs don't emit energetic MeV gamma or neutron radiation and don't produce appreciable quantities of long-lived radioactive isotopes (stable isotopes are strongly favored as detectible end-products). Consequently, mass spectroscopy is best type of analytical tool for measuring the final products of LENR neutron-catalyzed transmutation processes. SIMS systems and Cameca nanoSIMS-50L machines are excellent instruments for detecting and measuring elements in battery materials because LENRs create inhomogeneities in discrete 'patches' with dimensions that are generally on order of 100 microns or less. EDX analysis can be used to survey elements across larger areas to see where to focus SIMS
- ✓ Since LENRs and chemical fractionation can mimic each other, it is important to be able to discriminate between the two very different processes. For example, extremely large isotopic shifts relative to natural abundances would be indicative of LENRs, especially if such shifts were to occur with more than one element in very same battery and if it involves transition metals. If chemical composition of pristine pre-1st-charging, sealed batteries is extremely well-characterized and new elements *not previously known to be present* in given battery are detected when battery materials are later analyzed, it would be indicative of LENRs. This is because --- if external contamination can be excluded as a source --- chemical processes cannot create elements. However, LENRs certainly do transmute them

Mass spectroscopy of battery materials extremely important

Cobalt used in Lithium-ion batteries only has one stable isotope: Co-59

Capture of > than one neutron transmutes Cobalt into stable Nickel isotopes

Anomalous Nickel detected in Lithium-cobalt batteries may not be a contaminant that occurred during the manufacturing process: could be an LENR transmutation product



LENR ULE neutron captures go from left to right; Q-value of capture reaction (MeV) above green horizontal arrow; capture cross-sections (illustrative selected data, in barns *b* at thermal energies) is below green arrow when known

Beta (β^-) decays proceed from top to bottom; denoted with light blue vertical arrow with Q-value (MeV) of decay shown to right

Need greater analysis of anode/cathode surfaces in batteries

Theory predicts that LENRs may occur in vicinity of SEI and double-layer

Possibility that LENRs create metal “contaminant” particles causing runaways

- ✓ Accurate, absolute isotopic mass-balance measurements of abundance ^{6}Li and ^{7}Li would provide conclusive proof that LENRs are really occurring in batteries; unfortunately, this type of measurement may be practically impossible in reality
- ✓ Although they don’t do it 100% of the time, LENRs often create crater-like surface structures with very distinctive morphologies. Surfaces of battery materials can be rapidly surveyed with SEM imaging. If such “craters” are visible, they can be locally analyzed for elemental and isotopic shift anomalies with SIMS. Scientists at Mitsubishi Heavy Industries and academic institutions in Japan have observed many instances of LENR transmutation products in close proximity to craters
- ✓ If, as Lattice suspects, LENRs occur in batteries, then the Widom-Larsen theory predicts that LENR active sites would most likely be able to form in regions of very high electric fields that are present in close proximity to the double-layer and SEI on anode and cathode surfaces. It is less probable that LENR active sites could also form at interfaces between battery electrode materials and Aluminum or Copper metallic current conductors. At LENR active sites, theory also requires that there must be a local breakdown of the Born-Oppenheimer approximation, and that there must be ~2-D many-body collections of mutually Q-M entangled protons (Hydrogen atoms) interacting with surface plasmon or π electrons

Microscopic details of LENRs in electrochemical batteries

Active LENR sites would be rare but create very high local temperatures

LENRs can damage separators & electrodes: trigger shorts and thermal runaways

- ✓ Conditions conducive to triggering LENRs can occur in microscopic, micron-scale regions in random scattered locations on dendrites or other conductive nanostructures located on or near electrode surfaces in advanced batteries
- ✓ Although hard-radiation-free, LENRs involving neutron captures on Lithium are an extremely energetic nuclear processes – can release more than a million times more heat than even the most exothermic types of violent chemical reactions
- ✓ Microscopic 100^{+} micron LENR hotspot can release several Watts of heat in < 400 nanoseconds; local nuclear reactions can raise hotspot temps to 4,000 - 6,000º C
- ✓ Micron-scale LENR-active sites that happen to be located very close to a plastic battery anode/cathode separator (with or without a ceramic layer) will vaporize and flash-ionize a local region on a separator. Furthermore, an LENR hotspot that occurs on the surface of a Lithium cobalt oxide cathode or Carbon anode could potentially directly trigger irreversible combustion of a superheated electrode
- ✓ In rare events, LENRs can induce internal electric shorts and trigger catastrophic thermal runaways in advanced batteries with different types of chemistries, including $LiFePO_4$ which some industry participants have at times claimed to be “immune” to thermal runaways. It isn’t immune, but a lesser chance of runaways

Microscopic details of LENRs in electrochemical batteries

LENR active sites can trigger Joule heating and combustion of materials

Small number of LENR sites won't necessarily kill battery cell and trigger runaway

- ✓ If it happens to occur in vulnerable physical location deep inside a battery cell and adjacent to the surface of a plastic separator only 25 microns thick, a single blazing hot LENR-active site measuring only 30 microns in diameter can effectively vaporize a tiny local region of the separator, almost instantly turning it into a dense, micron-sized ball of highly conductive plasma. This would in turn create an electrical short between anode and cathode at that location, triggering a large inrush of electrical current through the breach in an insulating separator. Intense local Joule heating would ensue from the sudden current, further enlarging a breach and spatially expanding reactive superheated regions inside a given battery cell. Depending on many complex, event-specific details, such a conflagration may or may not grow to engulf an entire cell; rare LENR events will not inevitably cause thermal runaways
- ✓ Under exactly the right conditions, *microscopic* LENR sites can trigger chains of energetic electrical (Joule heating) and chemical (exothermic reactions) processes that altogether create spatially autocatalytic, very *macroscopic* thermal runaway events that can destroy battery cells billions of times larger than the volumes of LENR-active sites. In course of these runaways, $99.9^{+}\%$ of the total amount of energy released during the event is *non-nuclear* --- LENRs and internal shorts are effective "hot spark" triggering mechanisms

Microscopic details of LENRs in electrochemical batteries

Heating drives competing mixture of chemical reactions near LENR sites

Armageddon events in batteries may involve thermite reactions and pyrotechnics

- ✓ Within as little as milliseconds after the creation of a nano-spark or a mini electric arc or an LENR-active site: nm- to cm-scale local regions of a battery cell at or near such locations can become a super-hot, fiendishly complicated chemical witches' brew consisting of many different types of old and newly created compounds, expected thermal decomposition products, various ionized species, and many mutually competing chemical reaction pathways
- ✓ Positive thermal (heat) feedback loop: the hotter a heated region gets, the faster local chemical reactions accelerate therein and the more widely the conflagration spreads into previously unaffected regions of a given battery cell --- this is the causative root of the thermal runaway process and thermal fratricide that can quickly propagate between many spatially contiguous cells
- ✓ Evolution of such complex chemical systems is very rapid and incompletely understood - quite unpredictable with respect to final results: outcomes can range from minor thermal damage to single cell; to combustion of flammable electrolytes and charring of materials inside case and to outside via venting; and at worst, to complete combustion of all materials located inside of and including cell casings - even all contents of surrounding multi-cell enclosures. Worst-case Armageddon events involve thermite-like, violent super-fast-reacting pyrotechnic processes that can lead to gas explosions

Thermite reactions can occur in battery Armageddon events

Temperatures can get so high that metals will burn and doom a battery

Nano-energetic materials created inside batteries during thermal runaways

Examples of two very exothermic thermite reactions:

$Fe_2O_3 + 2\ Al \rightarrow 2\ Fe + Al_2O_3$

Al_2O_3 $\Delta f\ H^o$ (solid) = - 780 kJ/mol.

$3\ CuO + 2\ Al \rightarrow 3\ Cu + Al_2O_3$

Note: Al, Fe, Cu, and O are all available somewhere inside many types of batteries; current collectors typically composed of Aluminum (Al) and Copper (Cu)

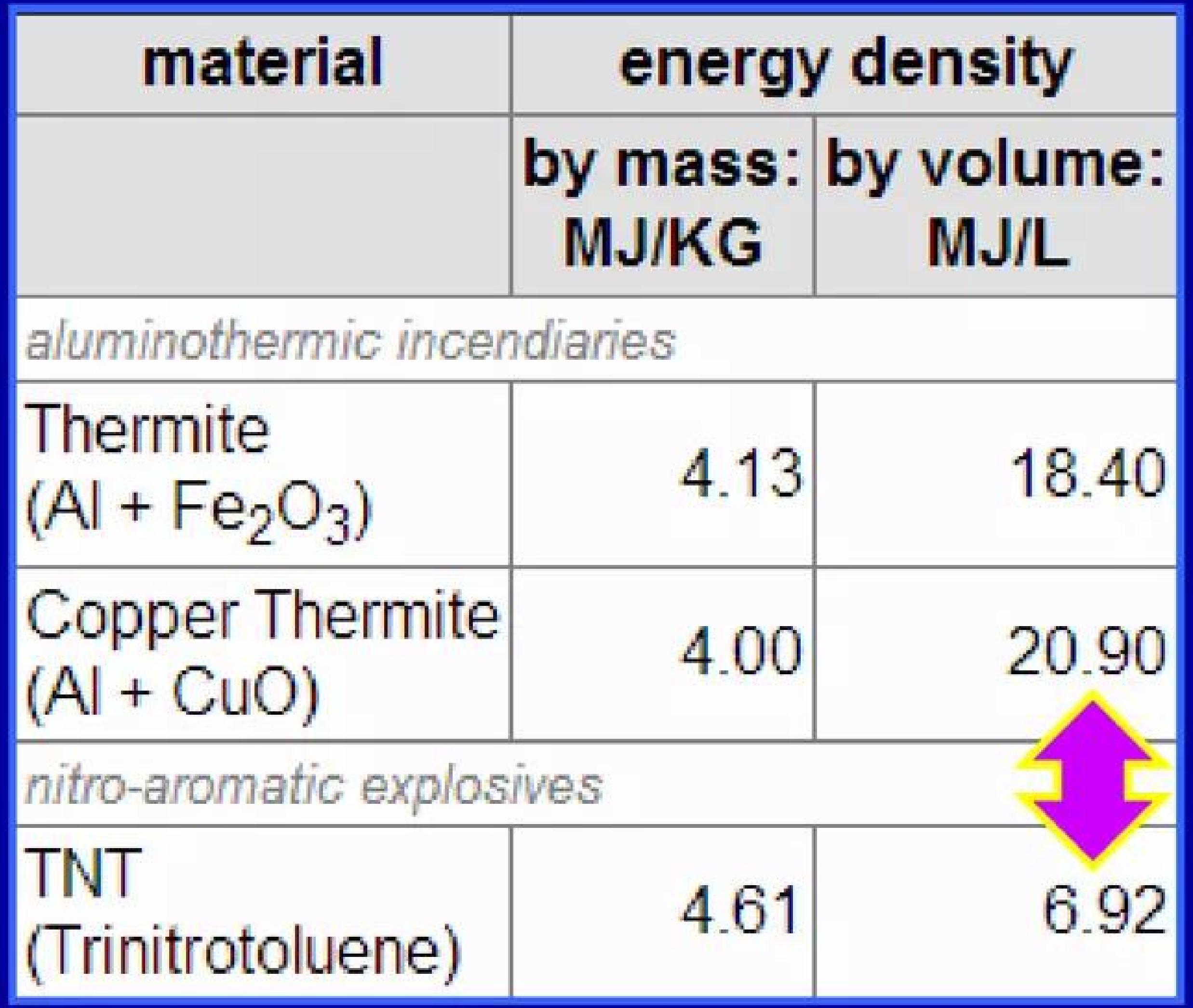
✓ Please recall that LiF can be formed in some battery cells; when it is heated enough beyond its boiling point (1,681º C) in witches' cauldrons it decomposes to form HF, which can then enable the following:

$$2\ Al(s) + 6\ HF(g) \xrightarrow{400 - 600^o\ C} 2\ AlF_3(s) + 3\ H_2(g)$$

AlF_3 $\Delta f\ H^o$ (solid) = - 1510.4 kJ/mol.

✓ Highest-temperature regions in and around localized witches' cauldrons (almost star-like in many ways) can be hot enough to liberate metal ions which can then react with Oxygen to effectively create burning metals; typically a very high-temperature process:

Cobalt metal burns in air at ~2,760º C; Aluminum at ~3,827º C; Iron at ~870º C; etc. -- bottom line is that burning metal spells big trouble in Lithium batteries



material	energy density	
	by mass: MJ/KG	by volume: MJ/L
aluminothermic incendiaries		
Thermite ($Al + Fe_2O_3$)	4.13	18.40
Copper Thermite (Al + CuO)	4.00	20.90
nitro-aromatic explosives		
TNT (Trinitrotoluene)	4.61	6.92

(Al + HF) energy release is 2x (CuO + Al) and ~6x TNT

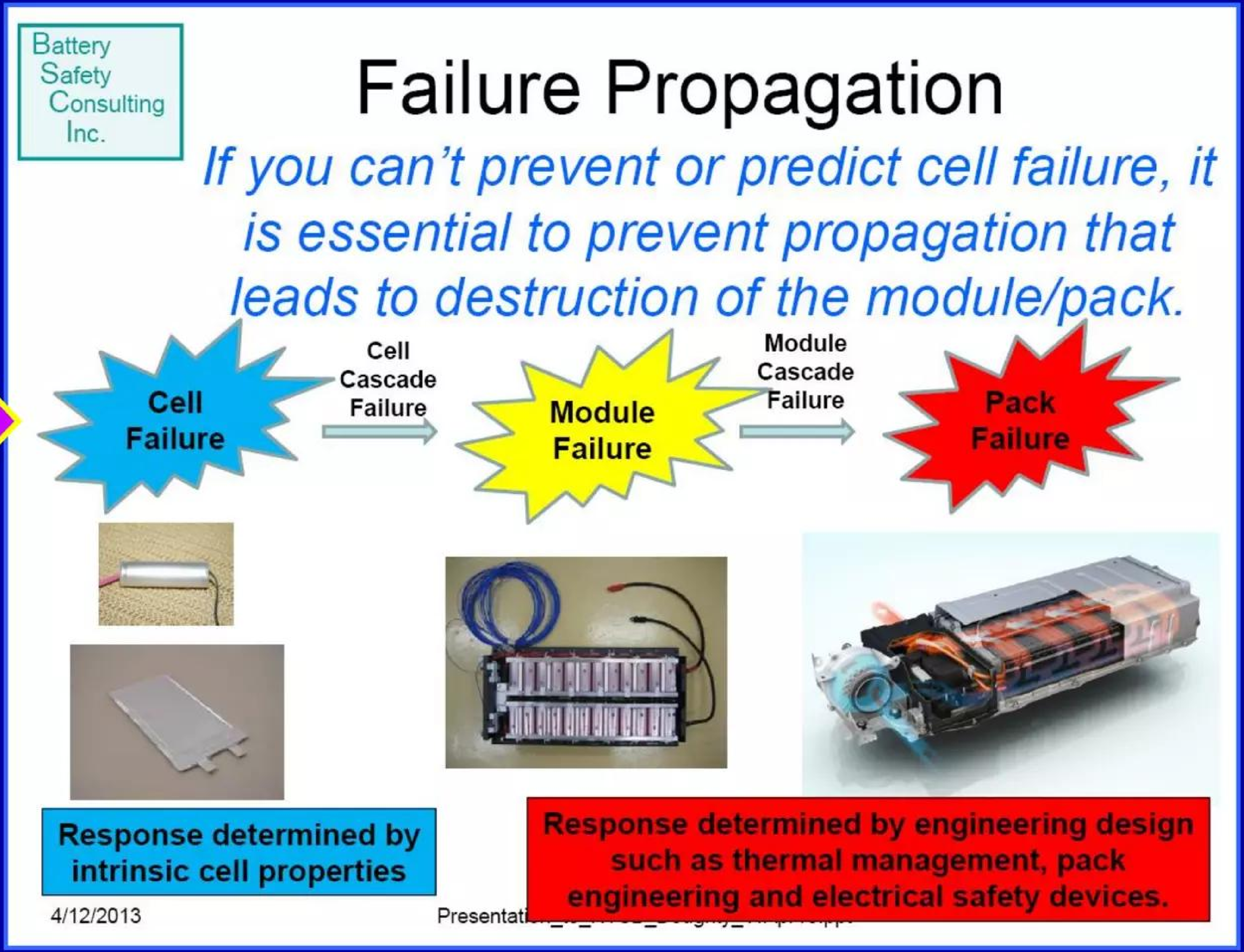
Can potentially synthesize explosive nano-energetic compounds in local regions

Mitigation of battery safety risks with system engineering

Engineer for worst-case runaway event within realistic cost constraints

“Failure mechanisms of Li-ion batteries”
Dr. Daniel Doughty, Battery Safety Consulting, Inc.
NTSB Battery Forum 12 MS-PowerPoint slides April 11, 2013

http://www.ntsb.gov/news/events/Documents/2013_Lithium_Batteries_FRM-Panel1d-Doughty.pdf



Battery
Safety
Consulting
Inc.

Failure Propagation

If you can’t prevent or predict cell failure, it is essential to prevent propagation that leads to destruction of the module/pack.

Cell Failure → Cell Cascade Failure → **Module Failure** → Module Cascade Failure → **Pack Failure**

Response determined by intrinsic cell properties

Response determined by engineering design such as thermal management, pack engineering and electrical safety devices.

4/12/2013

Presentati

Mitigation of battery safety risks with system engineering

Large battery packs operated with people nearby need to be very safe

No such thing as battery “immune” to thermal runaways; also can’t predict well

- ✓ Utilization of Lithium-ion batteries in all-electric plug-in passenger vehicles has lead to development of very large battery packs capable of providing adequate operating ranges for such cars; most notable example is Tesla’s successful Model S sedan - newest Model S battery pack stores ~ 90 kWh of electricity; enables 253 mile range

- ✓ While too numerous to mention here, Tesla engineers have made Herculean effort to engineer as many multi-level safety features into the car’s battery system as they possibly could within realistic cost constraints. In our opinion, the Tesla battery pack is probably the best-engineered, safest EV battery system in the world today. Battery engineers elsewhere would be wise to emulate Tesla’s excellent work on vehicle safety

- ✓ That said, Tesla Model S has nonetheless experienced three catastrophic battery pack thermal runaway fires, two in 2013 and one in January 2016. Tesla claimed that both immolations in 2013 were caused by piercing of the battery pack by metallic highway debris; Lattice begs to differ - see URL below. While Tesla is understandably reluctant to admit that internal field failures may have triggered the 2013 and 2016 runaways, they should be overjoyed that their huge investment in battery safety engineering paid off. In spite of major pack failures, drivers had just enough time to get away from their dying vehicles without injuries - failure was graceful. If field failures cannot be easily predicted or prevented, the best alternative is to engineer systems that fail gracefully

http://www.slideshare.net/lewisglarsen/lattice-energy-llc-technical-discussionoct-1-tesla-motors-model-s-battery-thermal-runawayoctober-16-2013

Mitigation of battery safety risks with system engineering

Tesla's new 90 kWh battery pack superb example of engineering for safety

Tesla Model S battery pack uses 18650As with NCA chemistry; that is, a Lithium nickel cobalt aluminum (NCA or chemically = $LiNiCoAlO_2$) cathode chemistry developed by Panasonic. The ~7,000 such batteries contained in a Model S pack contain specialized formulation of NCA and other unique characteristics that have been specifically optimized for EV applications (creating a so-called "automotive grade" 18650A cell). Please note this is not exactly the same as commodity 18650 battery cells that Panasonic manufactures and sells for the consumer retail market

Panasonic NCR18650A 3100mAh $LiNiCoAlO_2$ 18650 battery cells

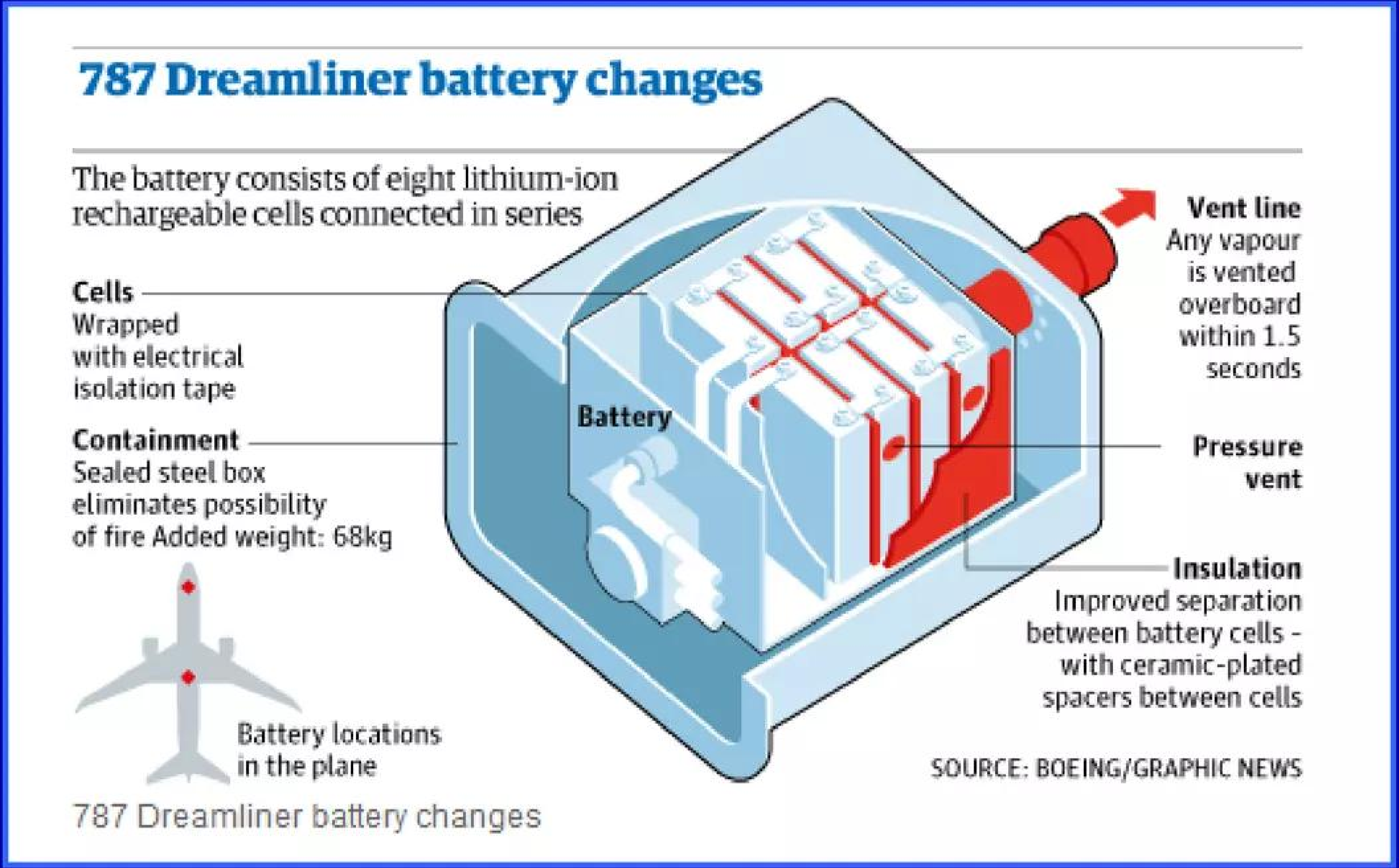
Credit: Panasonic

Batteries oriented vertically in Tesla pack's modules

http://hackaday.com/2014/11/11/draft-an-intverview-with-tesla-battery-hacker-wk057/

Mitigation of battery safety risks with system engineering

Containment vessels can reduce dangers of thermal runaways on aircraft



787 Dreamliner battery changes

The battery consists of eight lithium-ion rechargeable cells connected in series

Cells
Wrapped with electrical isolation tape

Containment
Sealed steel box eliminates possibility of fire Added weight: 68kg

Vent line
Any vapour is vented overboard within 1.5 seconds

Pressure vent

Insulation
Improved separation between battery cells - with ceramic-plated spacers between cells

Battery locations in the plane

SOURCE: BOEING/GRAPHIC NEWS

787 Dreamliner battery changes

Stainless steel battery containment vessel (m.p. ~1,480º C) and Titanium metal exhaust tube (m.p. ~1,650º C)

New battery case installed inside stainless steel containment box

Redesigned aluminum case for the GS-Yuasa battery system

Schematic above shows battery containment box with Titanium exhaust tube (vent line) as installed in retrofitted Dreamliners

Mitigation of battery safety risks with system engineering

Back to the future: glass cases for batteries used in liquid-cooled packs

Active liquid H_2O coolant used as heat sink; runaways radiate energy in IR and UV

"High elastic moduli of a $54Al_2O_3$ - $46Ta_2O_5$ glass fabricated via containerless processing" G. Rosales-Sosa *et al.*, *Scientific Reports* **5** Article # 15233 (2015)

http://www.nature.com/articles/srep15233

- ✓ Many years ago, certain types of batteries had clear glass cases as shown in images to right
- ✓ Recently, researchers have developed new types of ultra-strong clear glass (see *SR* article above) as well as earlier types of Corning "Gorilla glass"
- ✓ While glass would not be cost-effective in cheaper batteries, should be investigated for use in large battery packs that will have active liquid cooling
- ✓ Thermal runaways radiate strongly in infrared and ultraviolet bands; Aluminum (Al) metal cases very opaque to this emitted radiation and will heat-up
- ✓ Glass case would allow IR and UV to escape and be absorbed by actively circulated coolant; added bonus: m.p. of glass ~1,500º C; Al m.p. is 660º C

Antique glass battery cases

Conclusions

- ✓ Excellent functional fit between Lithium-ion batteries' higher energy densities and increased power requirements of component-dense portable electronic devices of all kinds has driven truly enormous unit growth in global Lithium-ion battery markets that has continued unabated from way back in the early 1990's right up until today in 2016
- ✓ Lithium-sulfur and Lithium-air now appear to be the most likely chemistries that will be used in the next-generation of advanced commercial batteries
- ✓ Fantastic market success of Lithium-ion batteries and very substantial improvements in energy density have encouraged battery technologists totally familiar with relatively smaller-scale applications to scale-up into huge battery packs that may contain thousands of battery cells. These are designed to satisfy much larger electrical energy storage capacity requirements of stationary backup systems and mobile platforms that include hybrid and all-electric plug-in vehicles as well as advanced new aircraft like drones and Boeing Dreamliners. Unfortunately, this has lead to unforeseen product safety issues that were not obvious to anyone (unknown unknowns) or simply irrelevant in the context of smaller-scale commercial applications
- ✓ It is probable that micron-scale LENRs are intimately involved with heretofore mysterious, spontaneous internal electrical shorts; they are therefore implicated in possibly triggering an unknown % of field-failures and related types of catastrophic, high temperature battery thermal runaway events

Conclusions

- ✓ Hardly a week goes by without another glowing PR announcement from some researcher or organization to the effect that they have achieved a new technical breakthrough that will either substantially increase battery energy density or drastically reduce if not eliminate the risk of thermal runaway fires or explosions. However, near the end of the press release there is usually a caveat that it will require more funding and years of additional effort before the advance can be commercialized. Some have dubbed this the "battery hype cycle;" extensive media promotion of Lithium-air is a recent example of this recurring phenomenon

- ✓ While modest gradual improvements in battery energy density, lifetime, and safety are very likely, quantum upward leaps in these crucial commercial performance parameters are becoming increasingly more difficult to achieve. This is occurring because chemical battery technology is maturing and, as we predict, will finally begin to approach its fundamental limits during course of the next 10 - 15 years

- ✓ Going forward from today's advanced commercial batteries, future gains in system energy density, product safety, and $ cost/kwh will not be restrained by needed improvements in cell chemistry, materials science, or nanotechnology. What will constrain and limit dramatic increases in future battery performance are intrinsic issues related to quasi-static high electric fields (10^9 - 10^{10} V/m) that will inevitably form in the immediate vicinity of the still little-understood SEI and double-layer on battery anode and cathode surfaces. Micron-scale inhomogeneities and short-time-transient *upward* fluctuations in local current densities and electric field strengths create problems today and could be the Achilles' heel of future batteries

Conclusions

- ✓ There should be a concerted effort by manufacturers to determine whether LENRs are really occurring in batteries. If they are, then LENRs are certainly causing some as-of-today indeterminate % of mysterious internal shorts and subsequent thermal runaways, fires, and in very worst cases even explosions
- ✓ If LENRs are established as a valid product safety issue for batteries, then future safety engineering strategies - especially for large, high capacity battery packs – should be adjusted. It may turn-out that 100% prevention of LENRs is essentially impossible; in that case, system-level safety engineering will have to shoulder much of the risk mitigation burden, e.g., worst-case event containment systems
- ✓ Interestingly, adjusting battery chemistry might help mitigate LENRs. From data reported in LENR experiments, it appears likely that the presence of Fluorine interferes with formation of LENR active sites by destroying quantum coherence of protons (H + F reaction is very fast and violent; it rips-apart active sites). While admittedly speculative at this point, this possibility might be useful in the future
- ✓ While some companies are claiming that conditions conducive to internal battery shorts can be detected in advance with proper monitoring, to the degree that LENRs may be involved we are doubtful that their claims will be substantiated
- ✓ Energy densities ultimately attained by chemical batteries could be limited by the presence of LENRs. However, LENR technology was first incubated in battery-like electrochemical systems. That being the case, LENRs are an opportunity for battery makers to diversify into much higher performance future power sources

Nuclear energy density surpasses any chemical technology

LENR-based power generation could have vast competitive advantage

Future possibility of converting Carbon aromatics to CO_2-free LENR fuels

LENRs Versus Chemical Energy Sources: Batteries, Fuel Cells, and Microgenerators

Source of Energy	Approximate Energy Density (Watt*hours/kg)	
Alkaline Battery	**164**	Chemical
Lithium Battery	**329**	
Zinc-Air Battery	**460**	
Direct Methanol Fuel Cell (35% efficient)	**1,680**	
Gas Burning Microgenerator (20% efficient)	**2,300**	
100% Efficient Combustion of Pure Methanol	**5,930**	
100% Efficient Combustion of Pure Gasoline	**11,500**	
LENRs (based on an assumption of an average of 0.5 MeV per nuclear reaction in an LENR system)	**57,500,000** (maximum theoretical energy density – only a fraction would be achievable in practice)	LENRs

~2,000 Wh/kg might be practical with Lithium-air

~11,680 Wh/kg is theoretical maximum with Lithium-air

Working with Lattice

Partnering on commercialization and consulting on certain subjects

1-312-861-0115 lewisglarsen@gmail.com

L. Larsen c.v.: http://www.slideshare.net/lewisglarsen/lewis-g-larsen-cv-june-2013

- ✓ Lattice welcomes inquiries from large, established organizations that have an interest in discussing the possibility of becoming Lattice’s strategic capital and/or technology development partner
- ✓ Lewis Larsen also independently engages in fee-based consulting. This separate work covers subjects such as: micron-scale, many-body collective quantum effects in condensed matter; Lithium-ion battery safety engineering issues including minimizing risks for occurrence of thermal runaways; and development of ultra-high-temperature superconductors. Additional areas of expertise include: long-term strategic implications of LENRs for high cap-ex long term investments in power generation technology; energy storage technologies; and LENR impact on petroleum-related assets. Will consult on these subjects as long as it does not involve disclosing Lattice proprietary engineering details relating to developing LENR power generation systems

Lattice's technical reports on Lithium battery safety issues

"Technical discussion - October 1 Tesla Motors Model S battery thermal runaway"
October 16, 2013 [82 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llc-technical-discussionoct-1-tesla-motors-model-s-battery-thermal-runawayoctober-16-2013

"On Oct 1 Tesla Model S caught fire on highway - has company's luck run out"
October 3, 2013 [23 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llcon-oct-1-tesla-model-s-caught-fire-on-highwayhas-companys-luck-run-outoct-3-2013

"Electronic cigarette explodes, burns child sitting in car seat - LENRs in batteries"
September 25, 2013 [58 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llc-electronic-cigarette-explodes-burns-child-sitting-in-car-seatlenrs-in-batteriessep-25-2013

"Large increases in battery energy densities drive convergence between energetic materials, LENRs and batteries"
September 6, 2013 [108 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llc-increased-energy-densities-drive-convergence-of-batteries-and-lenrssept-6-2013

Lattice’s technical reports on Lithium battery safety issues

“LiFePO$_4$ immune to runaways: another fool’s paradise?”
August 21, 2013 [35 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llclithium-iron-phosphate-batteries-are-not-immune-to-thermal-runawaysaug-21-2013

“Containing battery thermal runaways: a fool’s paradise?”
August 6, 2013 [93 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llc-containment-of-lithiumbased-battery-firesa-fools-paradiseaug-6-2013

“Technical discussion: NTSB reports indicate very high temperatures”
May 7, 2013 [51 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llc-technical-discussionntsb-logan-dreamliner-runaway-data-suggest-high-local-tempsmay-7-2013

“Steel microspheres in NTSB Dreamliner battery SEM images suggest high local temps”
April 30, 2013 [33 slides]
http://www.slideshare.net/lewisglarsen/lattice-energy-llc-steel-microsopheres-in-ntsb-dreamliner-battery-sem-images-suggest-high-local-tempsapril-30-2013

Lattice's technical reports on Lithium battery safety issues

Lattice makes comments on, "Microscopic Dendrites Focus in Boeing Dreamliner Probe" - *Wall Street Journal* article published on Feb. 11, 2013
February 11, 2013 [4-pages in MS-Word format]

http://www.slideshare.net/lewisglarsen/microscopic-dendrites-focus-in-boeing-dreamliner-probe-wall-street-journalfeb-11-2013

"LENRs potentially another mechanism for producing so-called field failures that can trigger catastrophic thermal runaway fires in Lithium-based batteries"
January 23, 2013 [28-pages in MS-Word format]

http://www.slideshare.net/lewisglarsen/lattice-energy-llc-field-failures-and-lenrs-in-lithiumbased-batteriesjan-23-2013

"Could LENRs be involved in some Li-ion battery fires? LENRs in advanced batteries"
July 16, 2010 [68 slides]

http://www.slideshare.net/lewisglarsen/cfakepathlattice-energy-llc-len-rs-in-liion-battery-firesjuly-16-2010

"Index to key concepts and documents"
v. #21 updated and revised through Sept. 7, 2015
L. Larsen, Lattice Energy LLC, May 28, 2013

http://www.slideshare.net/lewisglarsen/lattice-energy-llc-hyperlinked-index-to-documents-re-widomlarsen-theory-and-lenrs-september-7-2015