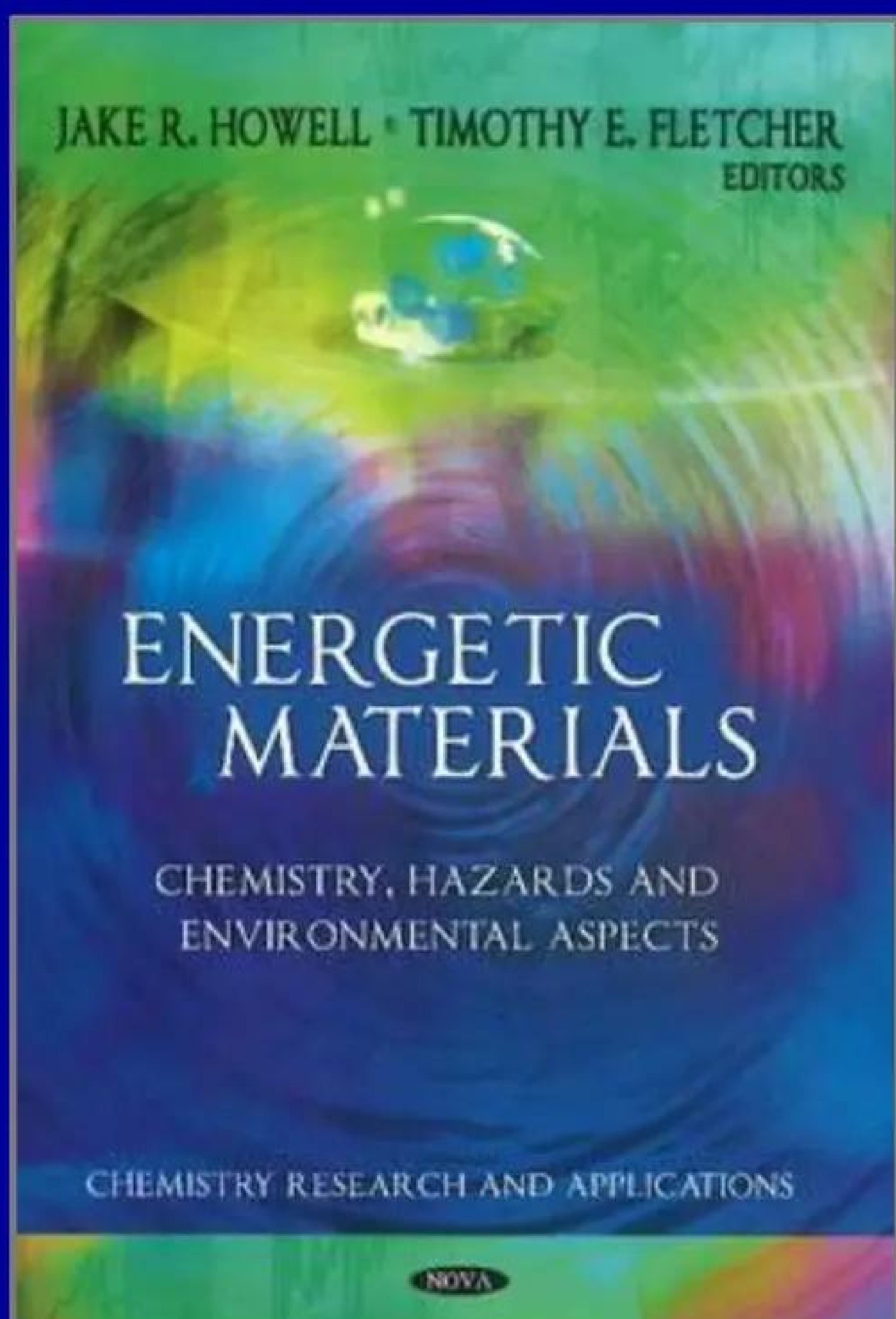
# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## Runaways occur in all lithium battery chemistries

### Myth propagated that lithium iron phosphate chemistry is ‘immune’

**Au contraire, well-documented thermal runaways reported in $LiFePO_4$**

**May 2013 incident at California Polytechnic State Univ. resulted in fire and explosion**




LENRs ⇨ nano energetic materials

## Examples and discussion

**Lewis Larsen**

President and CEO
Lattice Energy LLC
August 21, 2013

**“I have learned to use the word ‘impossible’ with the greatest caution.”**

**Wernher von Braun**

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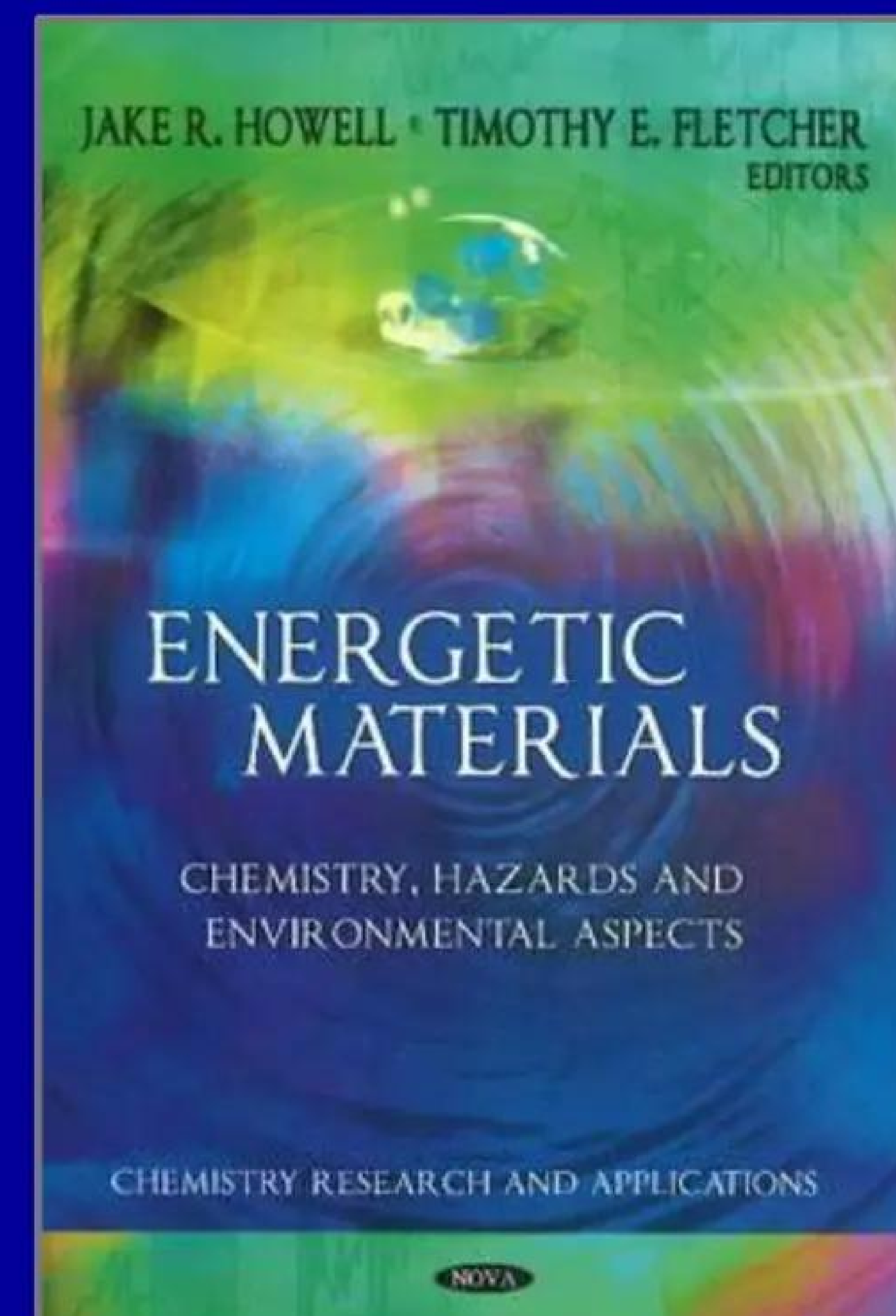
lewisglarsen@gmail.com
http://www.slideshare.net/lewisglarsen




LENRs ⇨ nano energetic materials

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

# Key

# take-aways

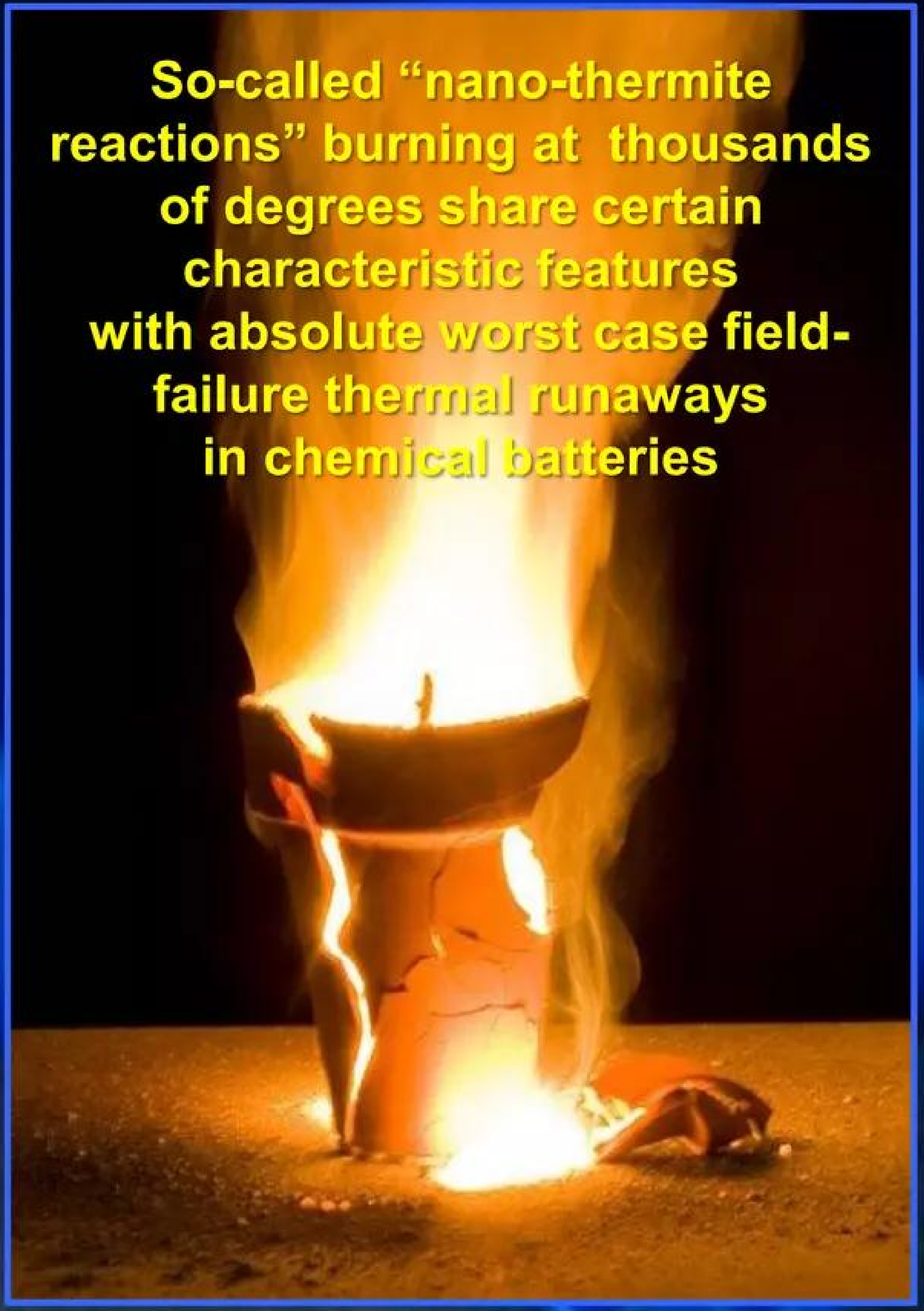
# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

# Key take-aways

- ✓ **Market success of lithium-based batteries and large increases in cell energy densities have encouraged battery technologists familiar with relatively small-scale applications to scale-up into physically larger lithium-based cells and huge arrays of cells that can address vastly larger electrical energy storage requirements of stationary back-up power systems and mobile platforms, e.g., hybrid and all-electric plug-in vehicles, as well as new aircraft such as the Boeing Dreamliner. Unfortunately, this scale-up has lead to unforeseen safety issues that were either simply not readily apparent to anyone or irrelevant risk factors in smaller-scale system applications**

- ✓ **There is really <u>no such thing</u> as a real-world Lithium battery chemistry that is 100% ‘immune’ to danger of thermal runaways and/or catastrophic field-failures. From risk management perspective, various lithium chemistries only differ in their relative probabilities; some are more or less problem-prone than others**

**Certain chemical reactions release enough heat to actually melt metals**




**Source: http://www.popsci.com/node/30347**

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

# Key take-aways

- ✓ MYTH: Lithium iron phosphate ($LiFePO_4$) battery chemistry is effectively immune' to any risk of thermal runaways and/or catastrophic field-failures; this statement is patently false
- ✓ Herein, we have provided several reasonably well-documented examples of serious thermal runaways or field-failures that have clearly occurred in lithium iron phosphate batteries
- ✓ Conclusion: although probabilities are lower, $LiFePO_4$ lithium-based batteries can experience catastrophic thermal runaway fires, field-failure events, and even powerful explosions. From a product safety perspective they should be viewed with same prudent circumspection and caution as other types of lithium-based batteries such as lithium-cobalt, lithium-manganese, and lithium-ion chemistries

Lithium-ion battery chemistry

Apple iPod Nano exploding in Japan (2010)

## $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

# Increases in energy density

# expand battery applications

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

$LiCoO_2$

$LiFeS_2$

$Li/AlMnO_2$

$LiFeS$

$LiFePO_4$

$LiPbCuS$

$LiFeS_2$

$LiCu_4O(PO_4)_2$

$LiCuO$

$LiSO_2Cl_2$

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

**Lithium-based batteries come in many different chemistries**

$LiAg_2CrO_4$

$Li(CF)_x$

$LiI_2$

$LiCuCl_2$

$Li_{22}Si_4$

$LiSOCl_2$

$Li_4Ti_5O_{12}$

Li-air

$LiBi_2O_3$

$LiAg_2V_4O_{11}$

$LiMnO_2$

$LiBi_2Pb_2O_5$

$LiAg_2CrO_4$

$LiPbCuS$

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

**A battery is an electrochemical device that actively stores input electrical energy in chemical bonds (charging); on-command, that stored energy can later be converted back into output electrical energy in the form of a current of electrons (discharging) that can pass through external conductive circuit wiring at some operating voltage and used to do energy-dependent work, e.g. operate power-hungry microprocessors, illuminate lights, run electric motors, etc.**

**Lead-acid**

**1859:** French inventor, Gaston Plante developed first practical storage lead-acid battery that could be recharged (secondary battery); commonly used as starter batteries on cars today in 2013 – well-known example is the DieHard brand

**Nickel metal hydride (NiMH)**

**1989:** first consumer-grade nickel metal hydride batteries became commercially available; resulted from almost 20 years of R&D at the Battelle-Geneva Research Center – work was sponsored by Daimler-Benz and Volkswagen AG (Germany)

**Nickel Cadmium (NiCad) and alkalines**

**1899:** Waldmar Jungner invented first nickel-cadmium rechargeable battery and alkaline (non-acidic electrolyte) primary battery; Thomas Edison claimed to have independently invented alkaline in 1901

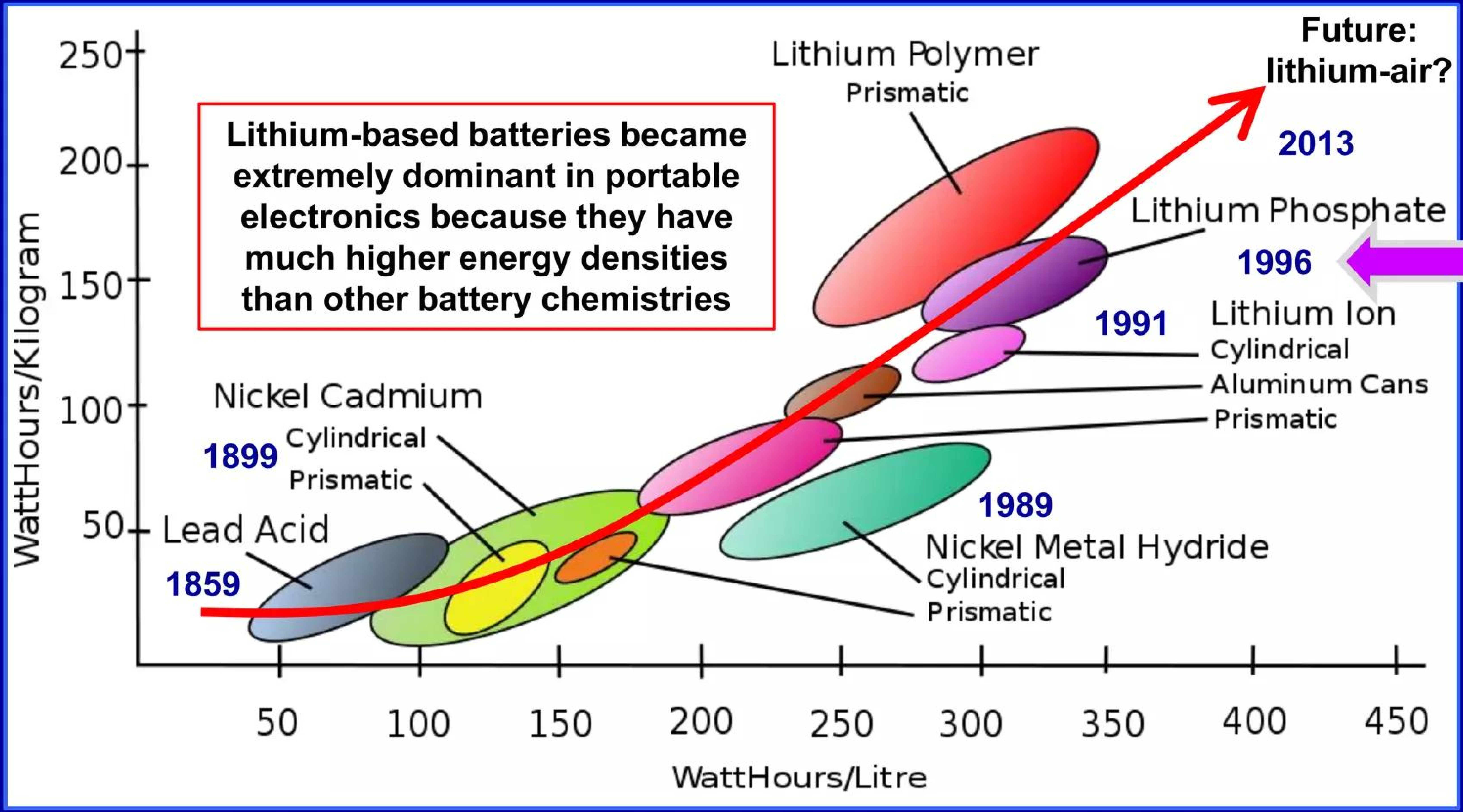
**Lithium ion (Li-ion) and Lithium iron phosphate**

**1991:** Sony and Asahi Kasei (Japan) released first commercial lithium-ion batteries; lithium batteries first proposed in 1970s by Whittingham while at Exxon; Goodenough proposed $LiFePO_4$ in 1996

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## Battery energy densities increased greatly from 1859-2013

### Large uptick in past 25 years; limited experience with such densities




Adapted from source: http://liteplusbattery.com/lifepo4-energy-density/

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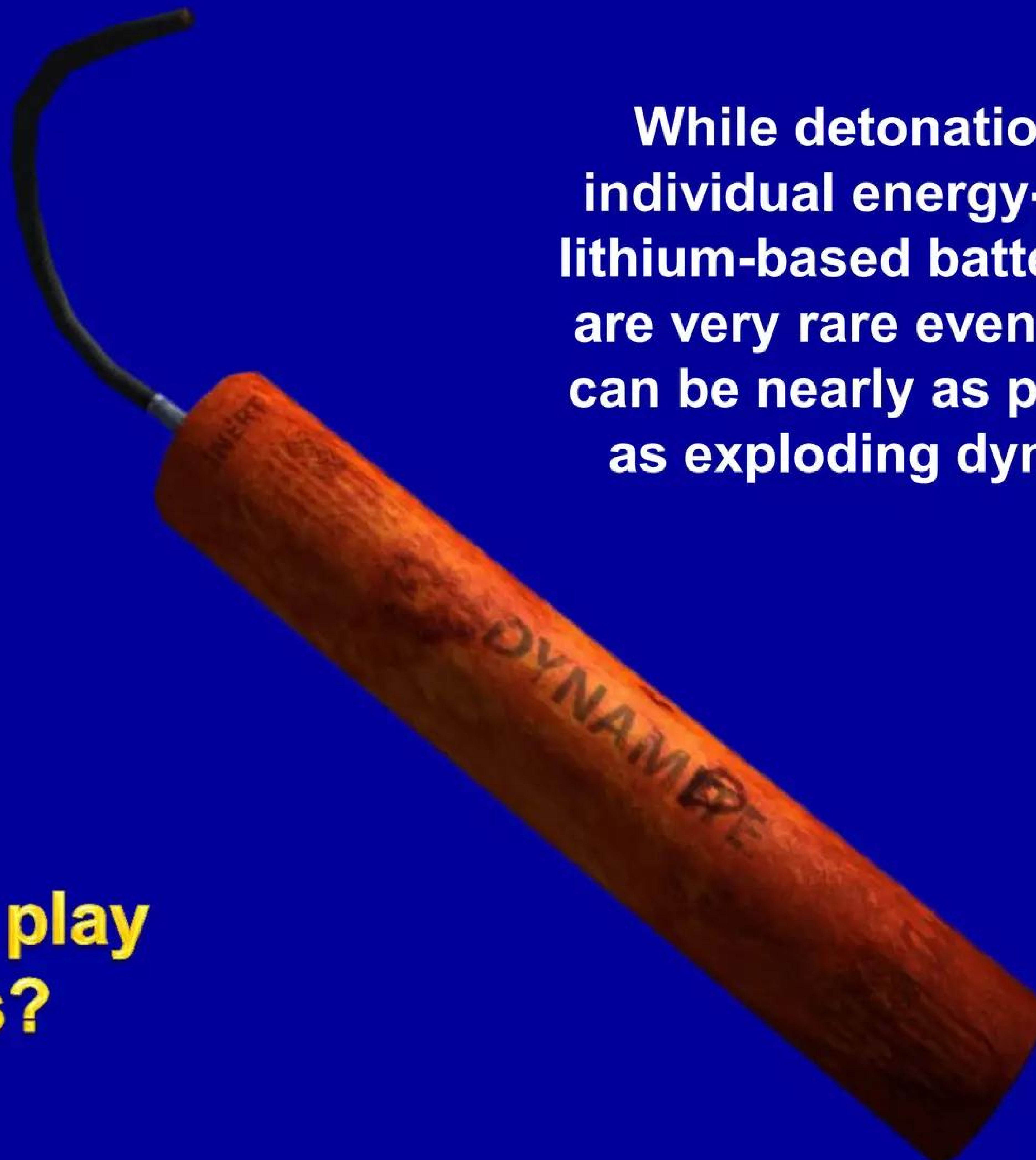


While detonations of individual energy-dense, lithium-based battery cells are very rare events, they can be nearly as powerful as exploding dynamite

**Would you play with this?**

# LiFePO$_4$ ‘immune’ to runaways: another fool’s paradise?

**And would you play with this?**


**US M67 fragmentation grenade developed post-Vietnam war**

**While detonations of very large arrays of energy-dense lithium-based batteries, such as multi-cell battery packs used in all-electric vehicles, are very rare events, they can be AS powerful as hand grenades and some IEDs**

**Or this device?**


**Improvised explosive device (IED) Ramadi, Iraq (2006)**

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## Examples: thermal runaways involving lithium-ion batteries

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

**Battery capacity scale-up**

**can increase safety risks**

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## Thermal runaways are now occurring on mobile platforms

### New applications for lithium-based batteries in autos and aircraft

**Fires and other dramatic incidents have received much attention in media**

## Bigger is better, right?

## Not necessarily.

**“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)**

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## Thermal runaways are now occurring on mobile platforms

### New applications for larger lithium-based batteries in autos and aircraft

**Fires and other dramatic incidents have received much attention in media**

**Within the past several years, there have been battery-caused:**

- ✓ Incinerations of hybrid and all-electric consumer vehicles
- ✓ Houses burned to the ground (EVs, laptop computers)
- ✓ Cargo aircraft destroyed in flight with multiple crew fatalities
- ✓ Thermal runaways on new passenger aircraft (Boeing 787)
- ✓ Bizarre explosion of a lithium-ion battery recycling plant
- ✓ Unexplained destruction of US Navy all-electric minisub
- ✓ And a myriad of other battery-related mishaps involving virtually every type of Lithium chemistry have been reported

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## Thermal runaways on mobile platforms

### New applications for lithium-based batteries in autos and aircraft

Fires and other dramatic incidents have received much attention in media

> Scale-up of any technology involves a certain level of inescapable intrinsic risks, some of which are known, and some which are not, e.g. Rumsfeld’s “unknown unknowns”

Battery industry has had less than 25 years of experience with high-energy density lithium-based batteries; most of that was in consumer portable electronics applications where power demand/storage was measured in Watt-hours, not kilowatt-hours

By contrast, lead-acid batteries have been used in the U.S. for 150 years, nickel-cadmium for 67 years, consumer alkaline for 54 years; those chemistries are tried-and-true and known to be relatively safe

Unfortunately, lead-acid batteries are impractical for all-electric vehicles and aircraft --- their energy densities are simply too low

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## Battery capacity scale-up can increase safety risks

Risks can increase with scale-up

**Thermal runaway event inside 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 wouldn't 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

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

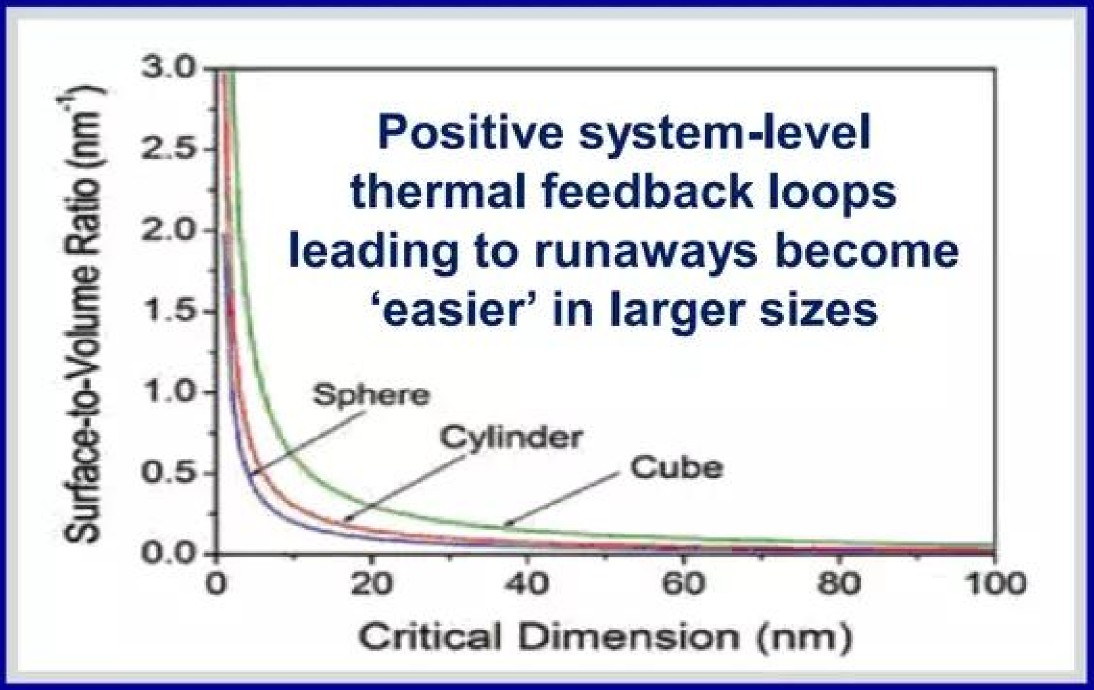
## Battery capacity scale-up can increase safety risks

### Thermal runaways become more likely if heat dissipation is impaired

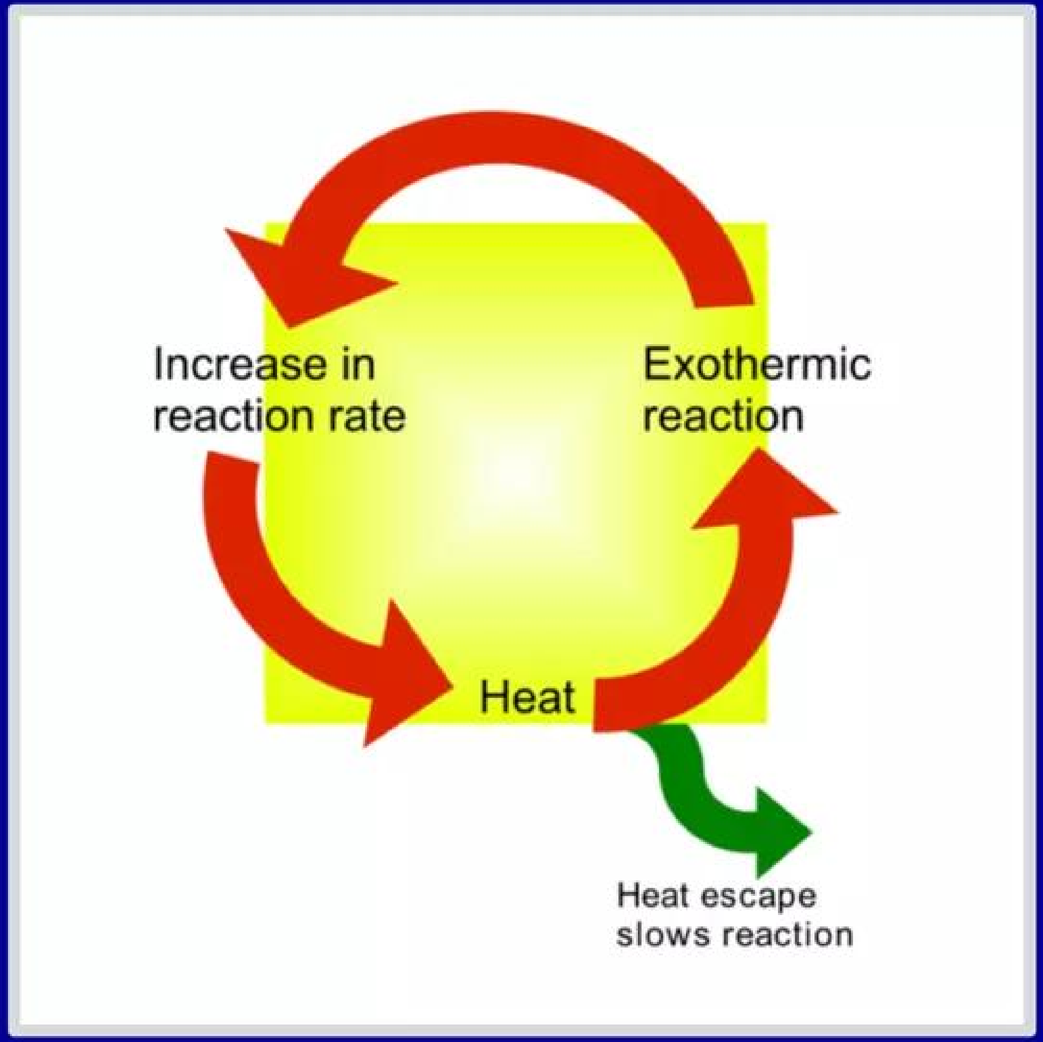
For exothermic electrochemical reactions that normally occur inside operating battery cells, total cell heat production scales with the cube of the size of the battery cell ($V \propto r^3$), but a cell's heat transfer capability scales with square of the size ($A \propto r^2$), so that rate of heat production-to-area ratio scales with the size ($V/A \propto r$)

End-result of this immutable scaling relationship between volumetric generation of heat within a given mass of reactants in a cell versus its area-related ability to dissipate produced heat is that chemistries that may well operate very safely in small cells are potentially dangerous and quite thermally unstable in considerably larger ones

<u>Consequence</u>: scale-up of the internal energy densities, electrical capacity, and sheer physical size of battery systems can lead to much larger, vastly more dangerous thermal runaway events




Surface area vs. volume <u>decreases</u> with increased size



# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## Battery capacity scale-up can increase safety risks

Since 1991: improved battery energy densities enabled by Lithium-ion chemistry mutually reinforced and supported meteoric increases in global unit sales of portable electronic devices including laptop computers and cellphones and more recently, tablets and smartphones (see following charts illustrating market expansion for EVs)

Using various different chemistries, next logical step for battery technologists was to scale-up arrays of batteries so that their total electrical storage capacity was enough for effective use in hybrid/all-electric vehicles (EVs) and even larger-scale applications

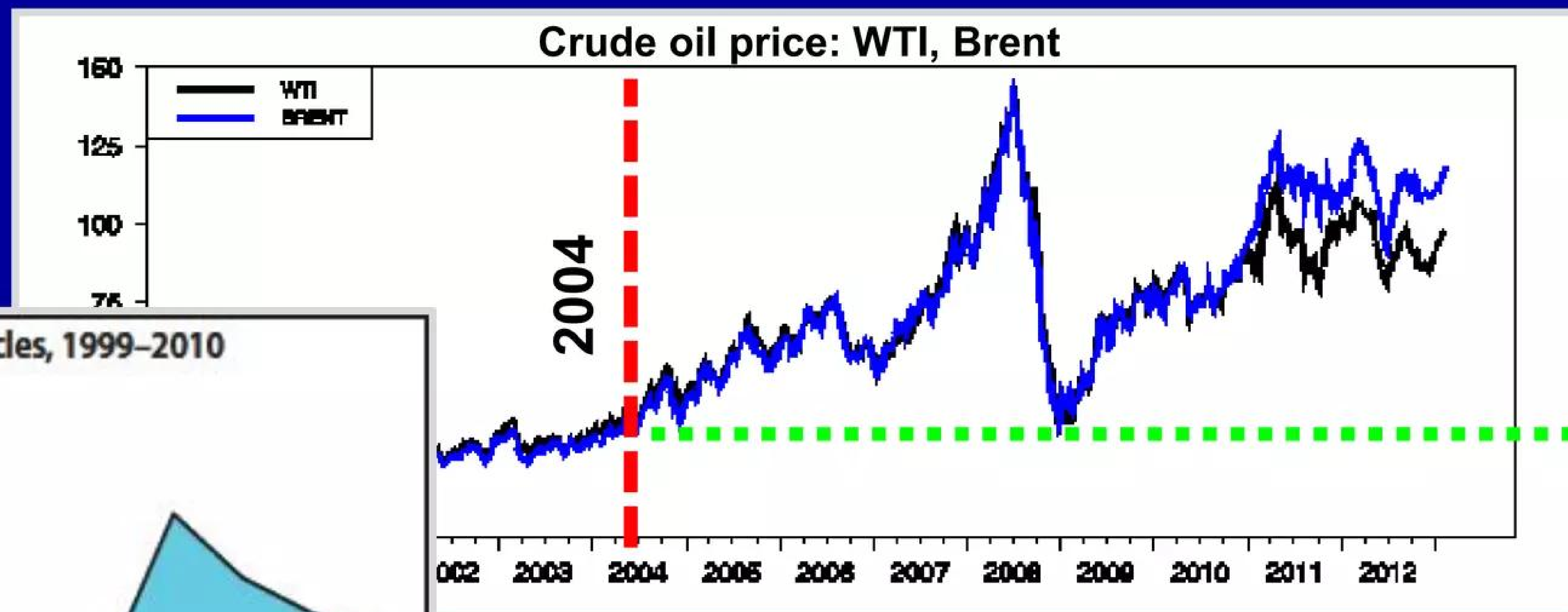
Persistently high gasoline prices encouraged CY 2000 global launch of first mass-produced, highly successful gasoline-electric hybrid car, the Toyota Prius. Market success of Prius along with continuing high gas prices and improvements in Li-ion technology encouraged development and sale of all-electric, plug-in vehicles by several new start-ups, notably Tesla (Roadster, 2008) and Fisker (Karma, 2012). Large established auto manufacturers now rising to meet upstarts' competitive challenge

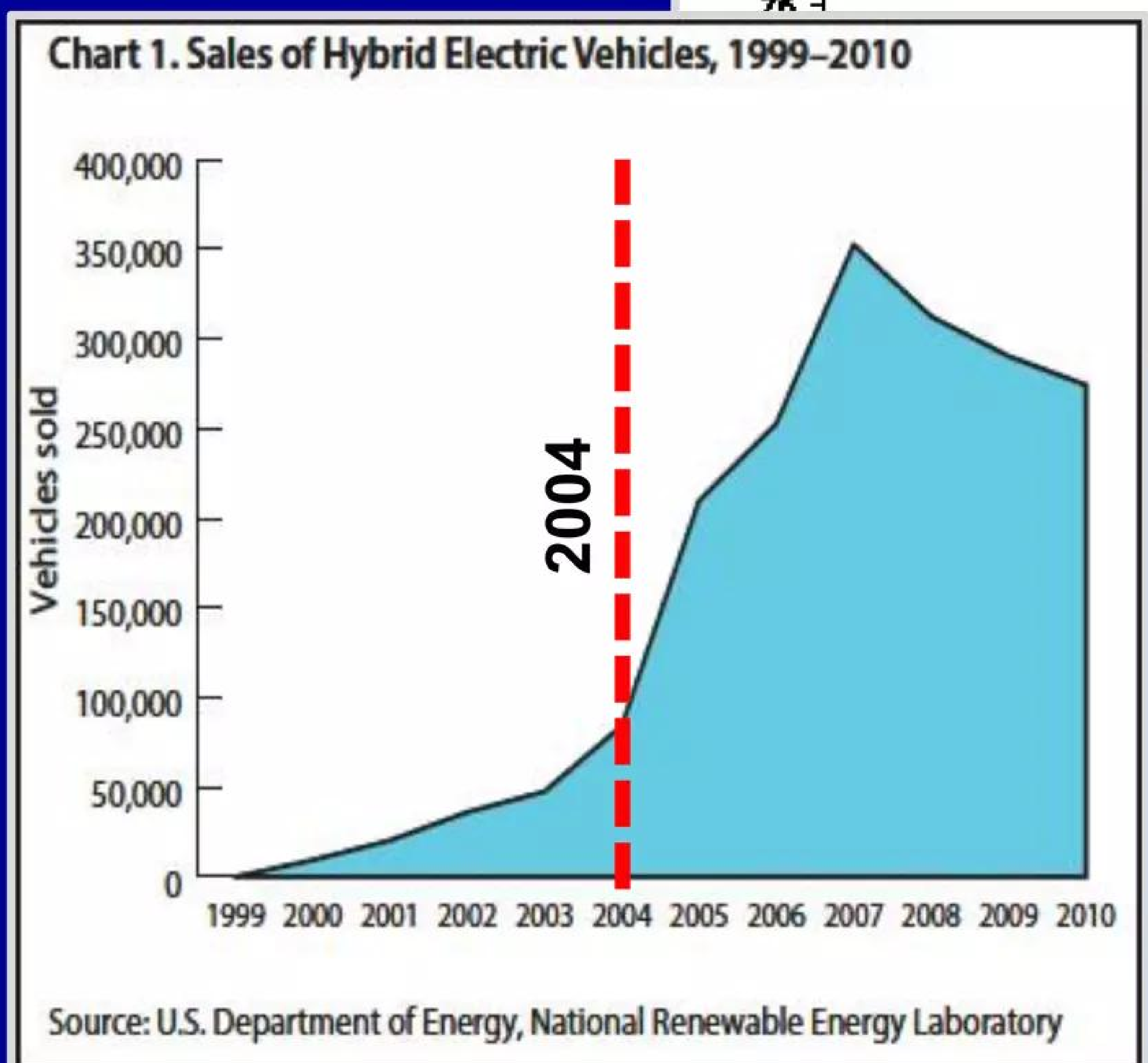
Also driven by high jet fuel prices, parallel developments also occurred in aircraft technology which encouraged adoption of much lighter-weight airframes (carbon-fiber composite vs. older tried-and-true aluminum) and more weight-efficient all-electric (vs. older hydraulic) critical aircraft systems; this led to a need for high-energy-density battery arrays for onboard backup power. These new technological thrusts were embodied in Boeing's 787 Dreamliner (2012) and Cessna Citation (2013)

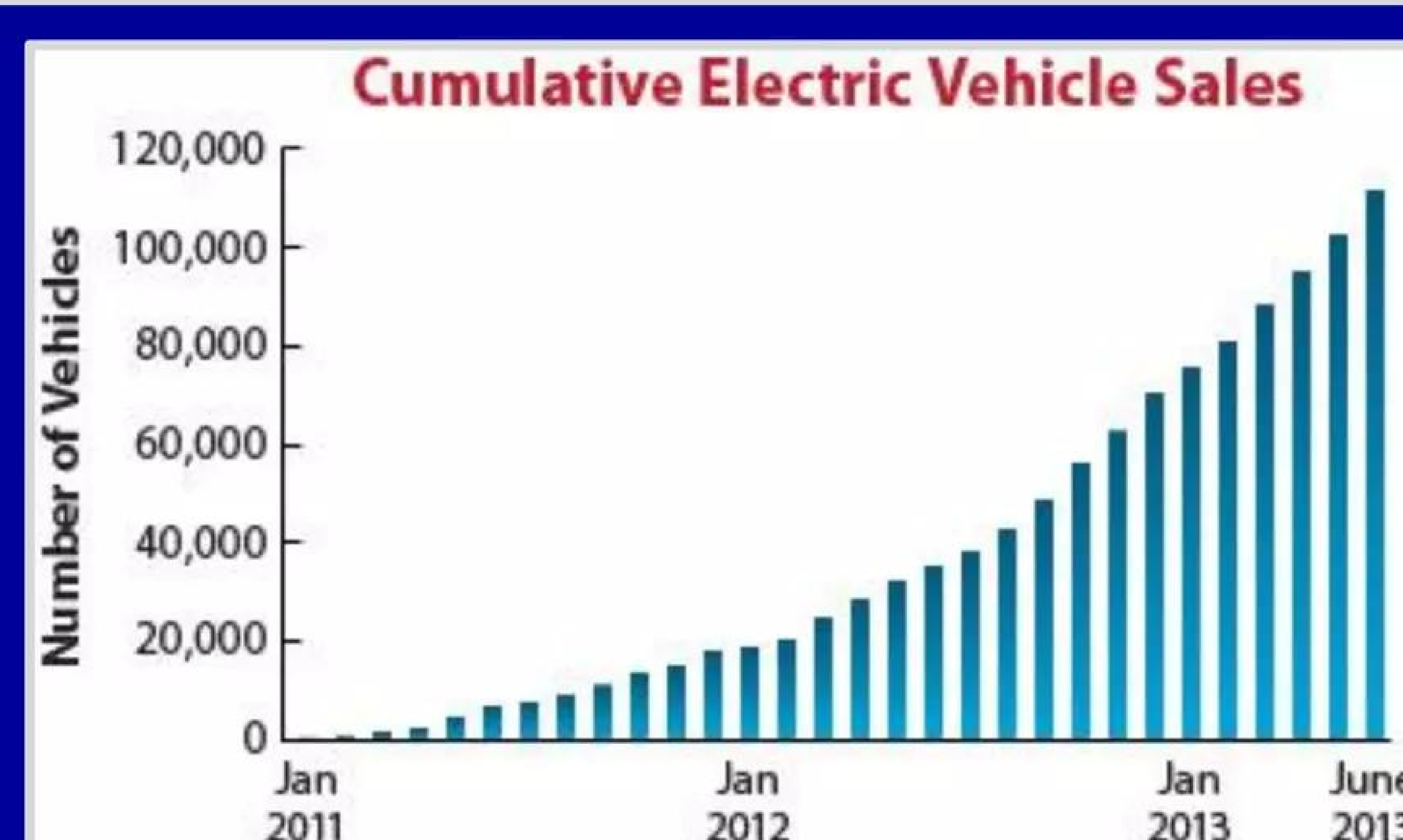
# LiFePO$_4$ 'immune' to runaways: another fool's paradise?

## Scale-up of batteries creates additional safety risks

### Persistently high gasoline prices since 2004 boosted demand for EVs



## $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

# Thermal runaways:

# batteries behaving badly

# LiFePO$_4$ 'immune' to runaways: another fool's paradise?

## Thermal runaways can occur in chemical storage batteries

- ✓ Typically well-controlled electrochemical reactions in batteries ordinarily generate a certain amount of unavoidable process heat which is then dissipated harmlessly simply by emitting invisible infra-red radiation from the battery case out into the local environment; during normal operation, contents of battery cells still remain well-within proscribed boundaries of designed range of optimal thermochemical operating temperatures
- ✓ On rare occasions, for a variety of different reasons, a battery cell's electrochemical reactions can suddenly start running at greatly elevated rates that create more process heat than a battery's normal thermal dissipative mechanisms can easily handle, which then starts raising the temperature of battery cell contents out beyond their ideal safe operating range; threshold for out-of-control danger has not yet been crossed

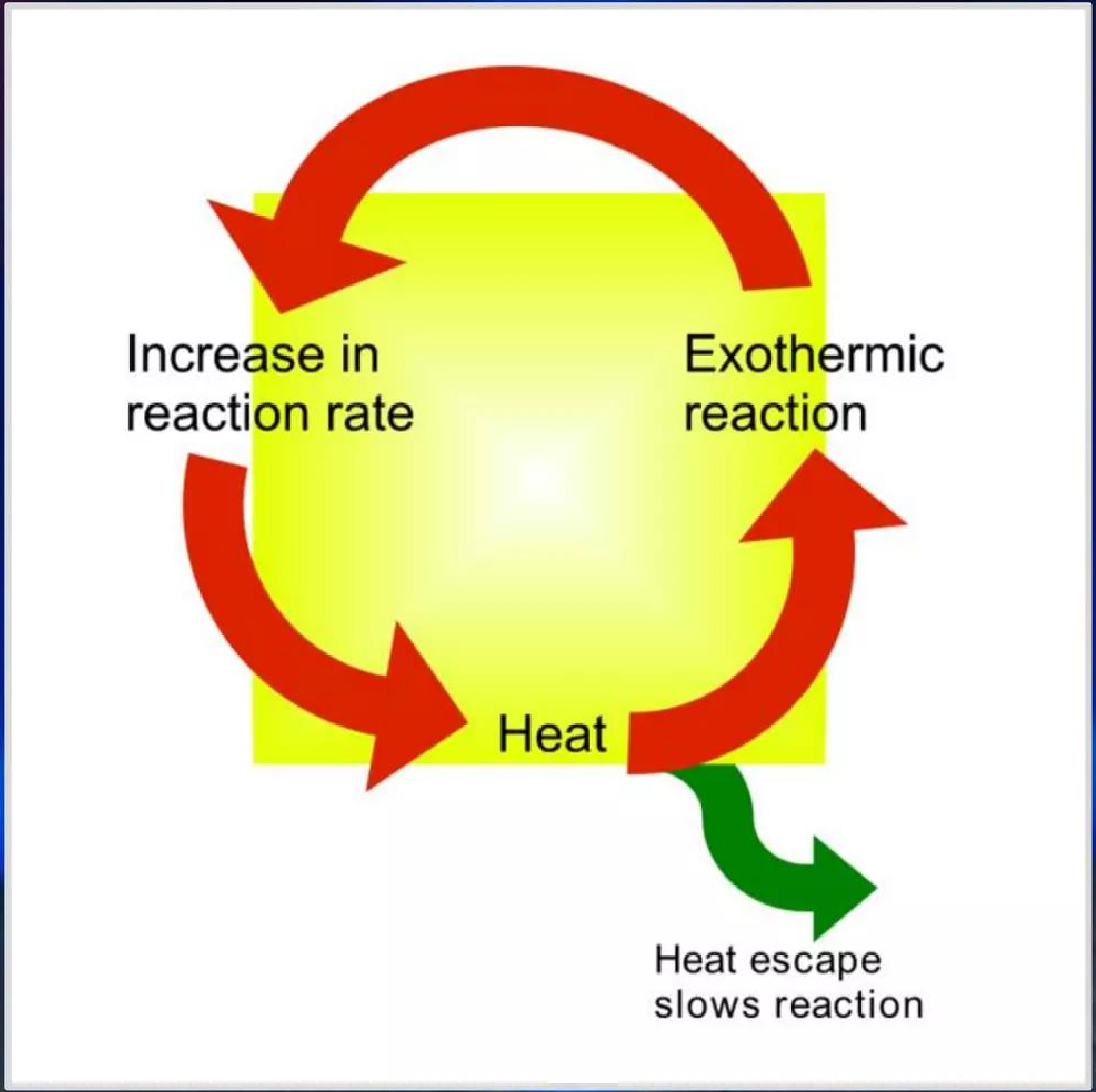
At key point --- call it the Rubicon River for a failing battery cell --- a very dangerous positive (+) feedback loop is created: whereby, increasing cell temperatures further accelerate electrochemical reactions in cells which produces even more heat, boosting local cell temperatures even higher, etc.

Thermal runaways are thus born: only question is how bad they get before destroying enough of a battery to stop + feedback-accelerated reactions

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## Thermal runaways: positive temperature feedback loop




Source: Wikipedia

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## Good news: thermal runaway events are statistically rare

### Bad news: when they do happen can have catastrophic effects

By any reasonable standard, lithium-based batteries are a pretty safe technology: ‘garden variety’ thermal runaways only occur at frequencies of one such event per several millions of battery cells

The very worst, least understood type of thermal runaway, which goes under innocuous-sounding sobriquet of “field-failure,” occurs at a rate of one such event per ~ 4 - 5 million lithium-based battery cells right off the production line and regardless of their chemistry or primary vs. secondary, according to statistics collected by a major Japanese manufacturer of lithium-ion consumer batteries

There’s one more issue: although it’s hard to quantitatively specify, probability of thermal runaways seems to increase significantly as batteries ‘age’ and go thru a great many charge-discharge cycles

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## Causes of 'garden variety' vs. field failures aren't identical

**'Garden variety' thermal runaways:**

- Reasonably well understood
- Triggered by substantial over-charging or excessively deep discharges
- 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
- Many believe triggered by electrical arc discharges (internal shorts); but what causes initial micro-arcs?
- Much higher peak temps vs. 'garden variety' events
- Lattice suggests: low energy nuclear reactions (LENRs) could well be triggers for some % of them

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

**Battery thermal runaways come in different ‘sizes’ and degrees of the severity of damage and nature of collateral processes caused by a given runaway event**

**‘Garden variety’ single-cell thermal runaways** can be as little as a battery that just heats-up a bit and simply stops functioning … or a battery’s case can bulge significantly from internally generated heat without designed venting and releasing of contents from the inside before it stops functioning and then starts cooling down on its own

A slightly worse variant of a ‘garden variety’ thermal runaway results in just a single cell venting or rupturing, but (in cases of flammable electrolytes) there are no hot, flaming battery contents spewed-out that could potentially ignite local combustibles and adjacent cells

**In worst-case ‘garden variety’ runaway, hot flaming electrolyte erupts from a ruptured battery cell,** which may ignite nearby materials and cells; in this event variant (that is still not the worst-of-the-worst), internal peak temperatures usually not yet hot-enough to melt metals

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## Field-failures are catastrophic events in chemical batteries

**Battery industry definition of a field-failure thermal runaway event:**

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 [14, 15]. When these rare safety incidents occur, lithium-ion batteries operating under otherwise normal conditions undergo what appear to be spontaneous 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 in the field are not preceded by any obvious external abuse*. We refer to these spontaneous safety incidents as "field-failures".

**Source:** "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)

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## Electric arc discharges and LENRs can trigger runaways

### Detailed description of catastrophic thermal processes in batteries

Within as little as milliseconds after the creation of an electric arc or 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 that are not normally present in operating battery cells

Positive thermal (heat) feedback loop: the hotter a given 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 causative root of thermal runaway effect and "thermal fratricide" that occurs between adjacent 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 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' scenarios involve thermite-like, violent super-fast-reacting pyrotechnic processes

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## Field-failures are catastrophic events in chemical batteries

## Absolute worst-case 'Armageddon' scenarios involve burning metals

Field-failure category of thermal runaways can reach extremely high peak temperatures of thousands of degrees Centigrade along with big electric arcs

Such temperatures are hot-enough to melt metallic structures inside batteries and combust almost anything and everything located within a battery case

If initiating 'spark' is hot-enough, battery materials containing chemically bound oxygen will release it as $O_2$; by creating its own oxygen supply, combustion process becomes self-sustaining, self-propagating flame front that consumes all burnable battery materials. Progressive thermal fratricide between cells can reduce batteries to unrecognizable debris; such fires could burn in a vacuum

In absolutely worst-case events, even METALS can start burning in very fast, thermite-like reactions that can boost temps up to ~ 4,000° C; this is nightmare scenario wherein even deadly explosions with shrapnel can potentially occur

# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

# $LiFePO_4$ = immune → false

# Proof by counterexamples

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

**Rechargeable $LiFePO_4$ batteries come in many varied electrical capacities, shapes, and sizes**


**“Drop-in” $LiFePO_4$ replacements for lead-acid starter batteries are manufactured by a number of large and small companies for many different vehicle brands and models; either vehicle owners or dealerships can easily install them**


# $LiFePO_4$ 'immune' to runaways: another fool's paradise?

## May 2013: $LiPO_4$ battery runaway and explosion at California Polytechnic

### Lithium battery catches fire in Building 17

**Posted: Sunday, May 19, 2013 9:00 pm**
**Micheala Ard, Lifestyle Editor**

**Source: http://www.thepolypost.com/news/lithium-battery-catches-fire-in-building/article_6a254736-bf27-11e2-b3a2-0019bb30f31a.html**

- **A lithium iron phosphate battery caught on fire while on a table in Building 17 at 10 a.m. on Friday.**

**The battery, in lab 1460, was meant for a solar racecar that is being constructed by mechanical engineering students, including fourth-year mechanical engineering student John Tran, who was not present during the fire.**

**According to Tran, the battery was worth approximately $1,000. The form of battery is usually one of the safer types of lithium batteries.**

- **Michael DeSalvio, a biosafety specialist from Environmental Health and Safety, was at the scene and noted that everything from the battery's casing to its foam bottom had melted.**

**"We may never know [what caused the fire]," said DeSalvio. "We weren't there to see it. So, from what they're telling us, it could have maybe been a faulty battery. It could have been a bunch of things."**

**According to Sergeant Matthew Lynn from the University Police Department, the battery caught on fire but did not explode.**

- **However, according to eyewitness Nickolas Roy, a second-year chemical engineering student, the battery was more than just aflame.**

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## May 2013: $LiPO_4$ battery runaway and explosion at California Polytechnic

“I was coming from physics class with my friend . . .and we got to the door and we see the window, and we see the entire lab covered with smoke,” said Roy. “We look in the window and we see a table is on fire.”

After Roy and his friend saw the flames and smoke, they began snapping pictures, but their photo shoot was quickly interrupted by something “exploding”.

“We stepped back . . . and we see the battery is exploding, or it could have also been an aerosol can, we didn’t know for sure,” said Roy. “After that, I think it was the IME technician who ran out and told us to get out of there.”

After the fire and possible explosion occurred, eighth-year Civil Engineering student Frank Lopez, took a fire extinguisher and attempted to douse the flames.

“I noticed as I was hitting it [with the fire extinguisher], it sounded like it was actually sizzling a little more, and then all of a sudden, it just lit up,” said Lopez.

According to CPP Public Affairs, bystanders quickly put out the fire and classes were able to resume 20 minutes later, after inspection by firefighters.

No one was injured during the fire and the table the battery was sitting on was fireproof. A fire truck and approximately five police officers were on the premises as well.

CalPoly $LiFePO_4$ battery prior to mishap

Image credit: Nathan Guerard/The Poly Post

Source: http://www.thepolypost.com/news/lithium-battery-catches-fire-in-building/article_6a254736-bf27-11e2-b3a2-0019bb30f31a.html

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

**During 2011: several suspicious, rather frightening fires occurred in Renault F1 race cars equipped with advanced batteries used in the cars’ KERS (kinetic energy recovery system); Saft batteries used in 2011 season’s Renault Formula 1 (F1) KERS were stated to have lithium iron phosphate chemistry**

**James Allen on F1**
***“A new take on Heidfeld’s Renault explosion”***
**Posted August 1, 2011**
**http://www.jamesallenonf1.com/2011/08/a-new-take-on-heidfelds-renault-explosion/**


**Location of KERS inside rocker panel**

**See on-the-scene videos of this spectacular incident:**

**http://www.liveleak.com/view?i=9e5_1312126530**

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

**http://www.youtube.com/watch?v=9Nk2IR9HYbE**

# $LiFePO_4$ ‘immune’ to runaways: another fool’s paradise?

## January 2013: Audi R8 supercar self-incinerated at rally in Mumbai, India

There is strong likelihood that Audi R8 fire’s causative factor could have been an owner- or dealership-installed aftermarket $LiFePO_4$ or Lithium-ion battery that replaced a lead-acid battery which was originally installed during assembly at the Audi factory in Germany. This particular R8 model included an optional factory-installed 465 Watt Bang & Olufsen multi-speaker auto stereo system, which may have prompted car’s owner to install an aftermarket lithium-based replacement battery with much greater electrical storage capacity than the standard factory installed lead-acid of comparable physical size (so powerful B&O stereo could be used like a mega-boom-box when engine was not running). Audi spokesman publicly chastised vehicle’s owner for making unspecified “unauthorized modifications” to car

“Audi R8 up in Flames in Mumbai at Parx Supercar Rally 2013”

https://www.youtube.com/watch?v=pu2Gxxh4a-E

https://www.youtube.com/watch?v=9YuCJrSLuuA

http://www.youtube.com/watch?v=ZcurEOijIX0

# LiFePO$_4$ 'immune' to runaways: another fool's paradise?


All energy-dense batteries should be treated with the respect due any device that contains a great deal of stored energy.

Source (aftermarket Lithium-ion): http://www.lithionicsbattery.com/racing.html