Batteries for Vehicular Applications

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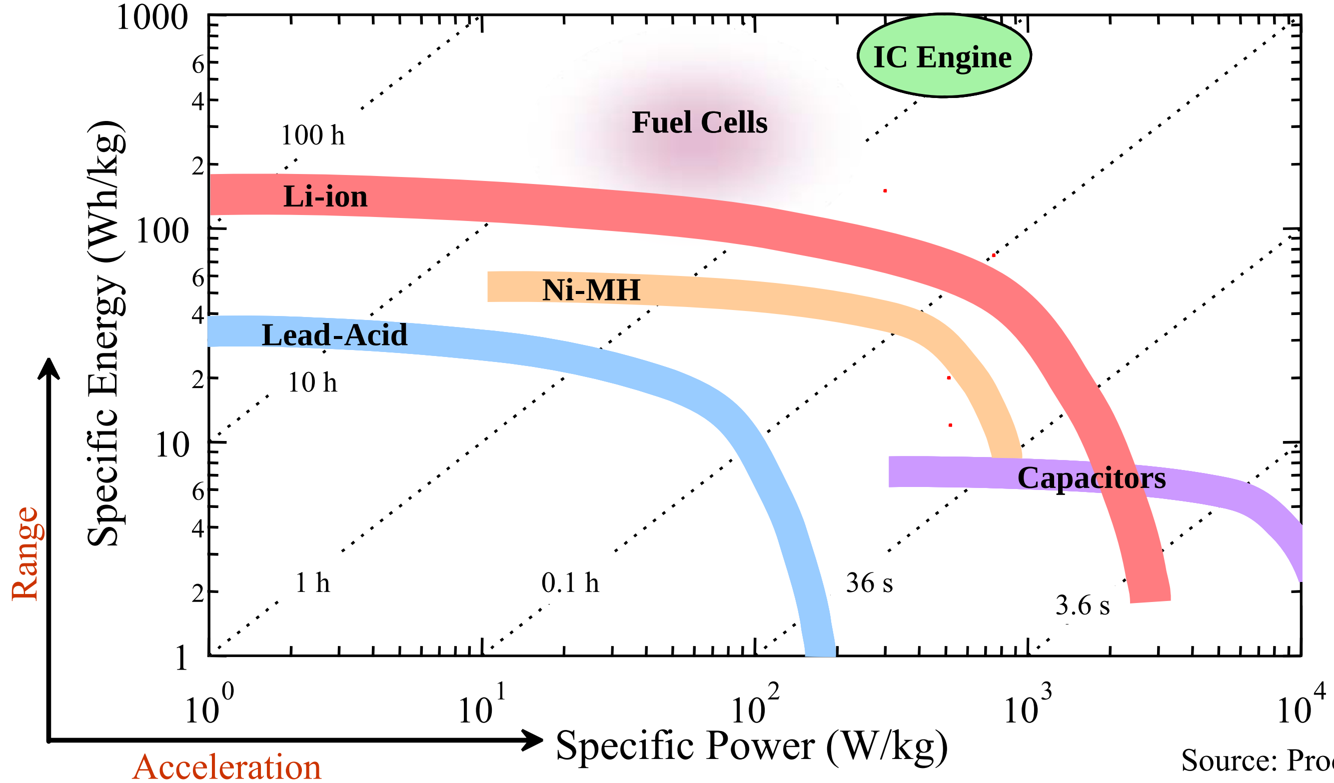
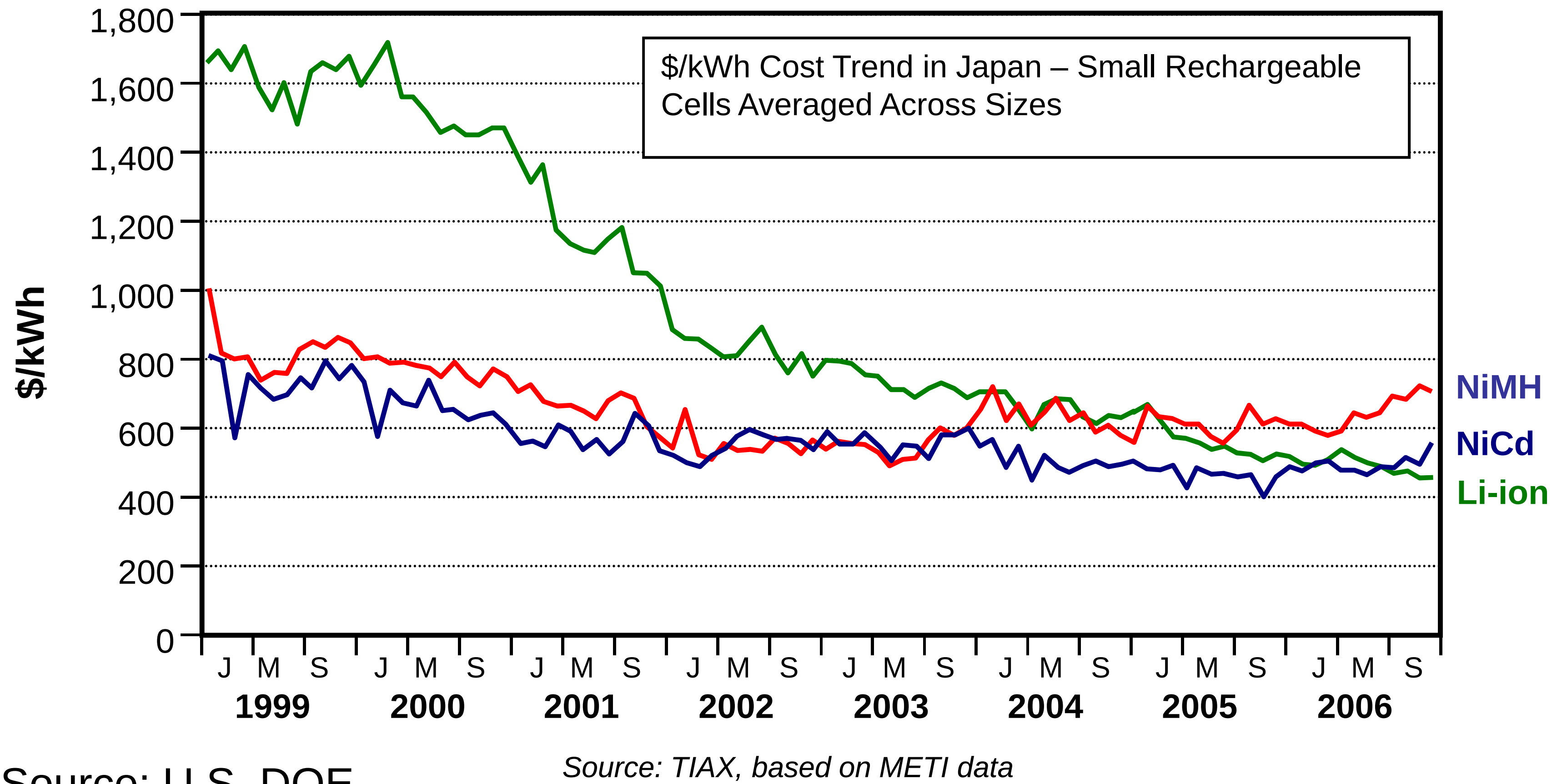
Relative Performance of Various Electrochemical Energy-Storage Devices



Source: Product data sheets

- Li-ion batteries have higher performance compared to Nickel-metal hydrides batteries
  - However, research is needed to simultaneously address the life, cost, and abuse tolerance issues

Cost of Consumer Electronics Batteries

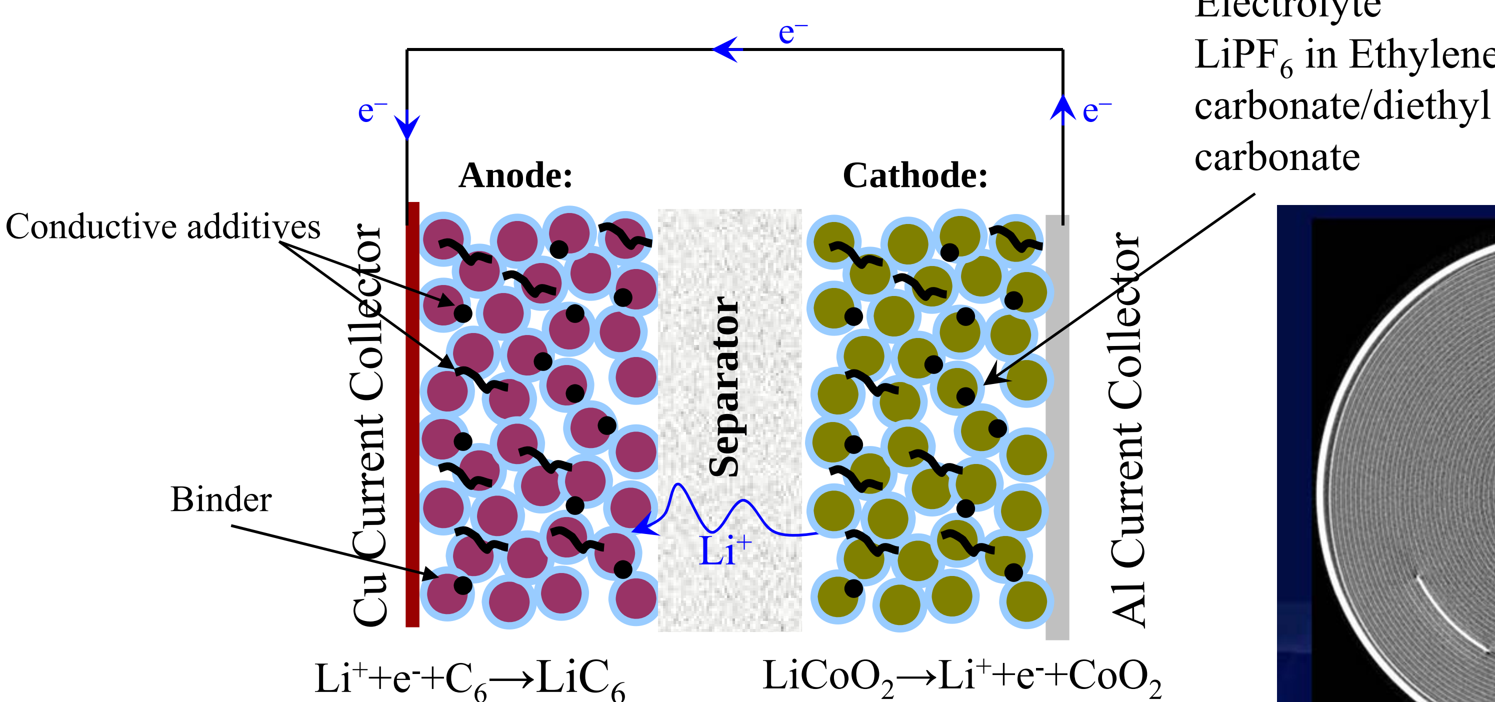


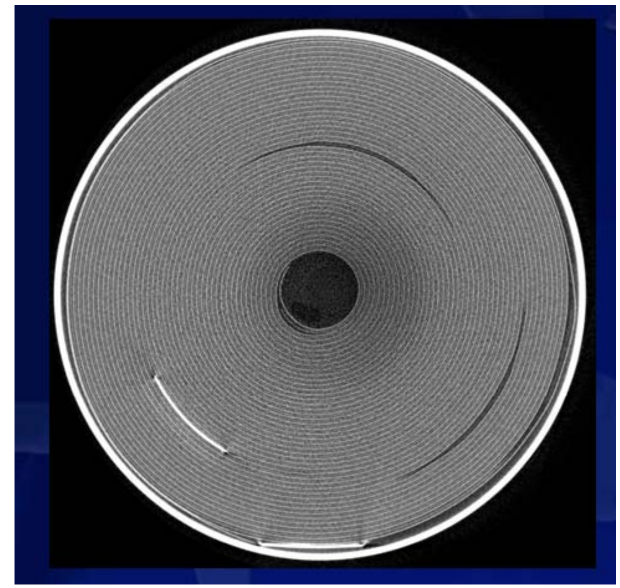
Source: U.S. DOE

Performance and cost drivers for Li-ion cells
However, numerous problems remain before use in vehicles

Modern Li-ion Battery

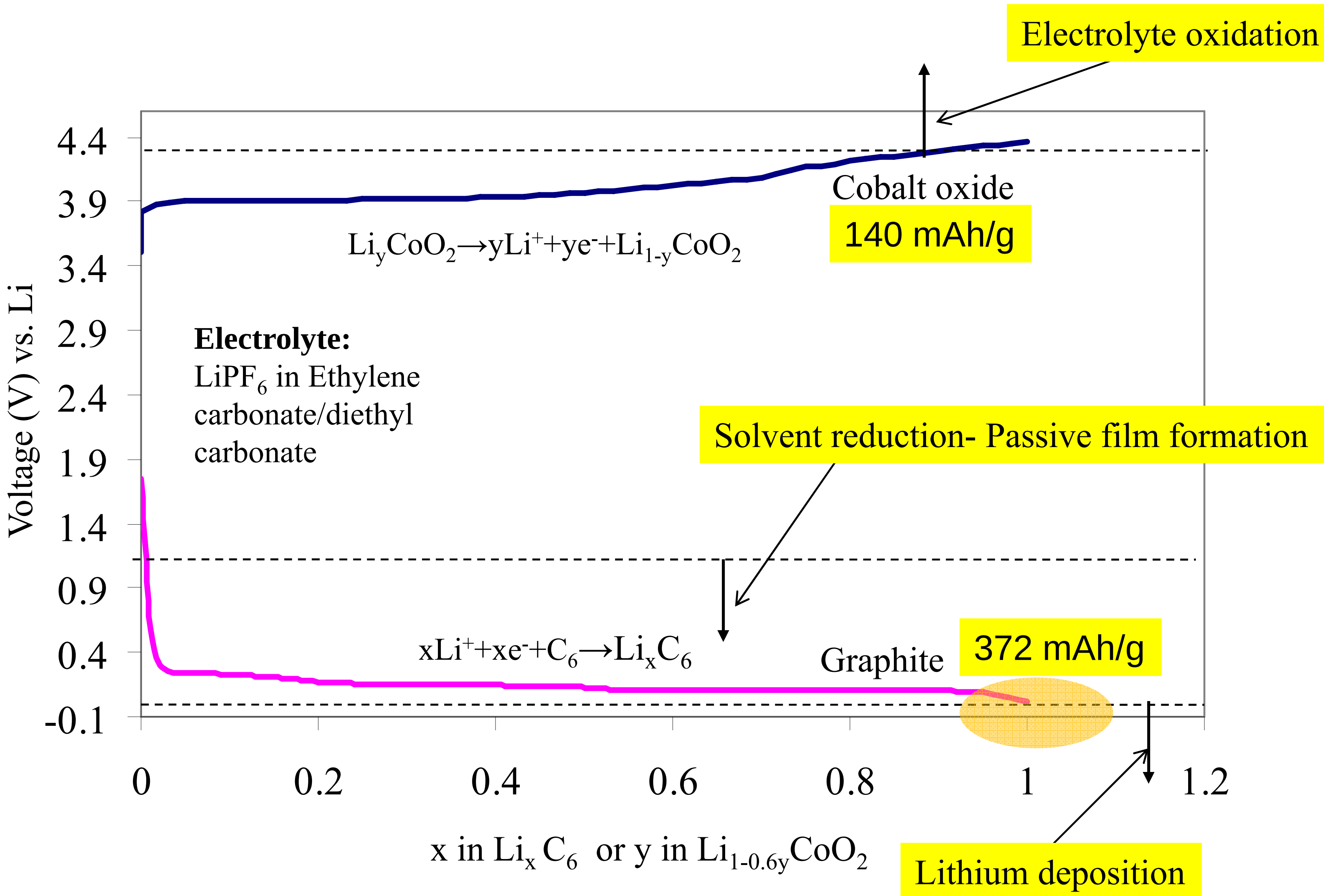
Lithium-ion battery



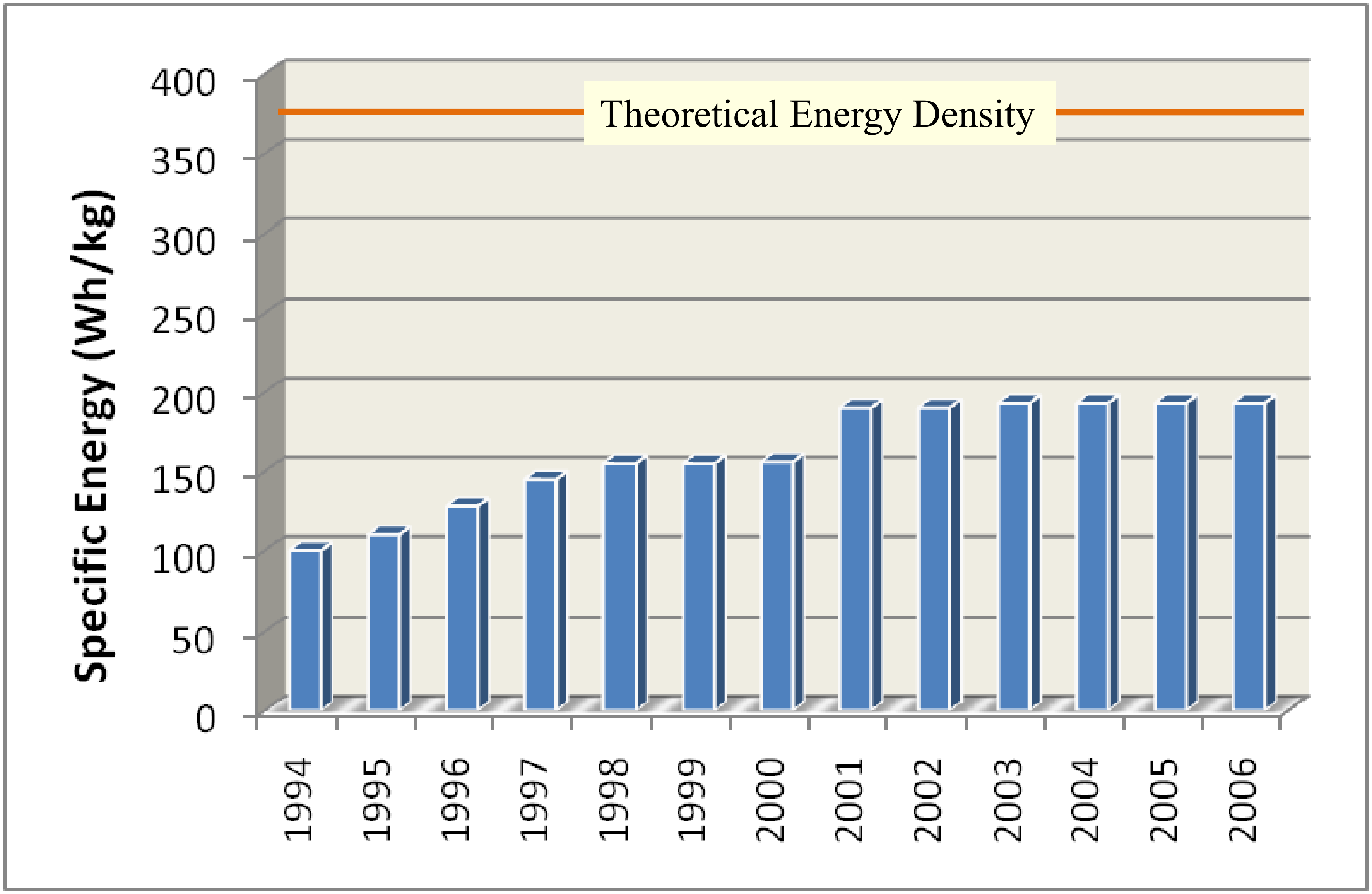


Improvements can occur via new material development, or by better engineering

Cycling of a Graphite-CoO_2 Cell



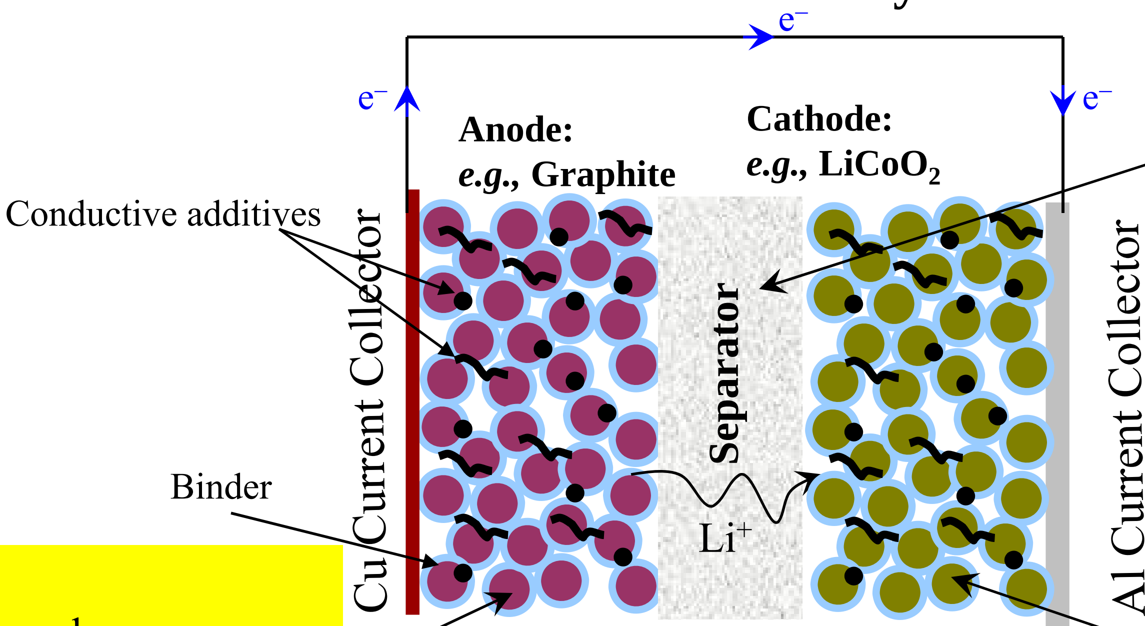
Energy Density Increase of Consumer Electronic Li-ion Batteries



Source: TIAX, LLC

Battery Technology

Lithium-ion battery



Electrolyte:
- Liquid organic solvents
- Polymers
- Gels
- Ionic liquids

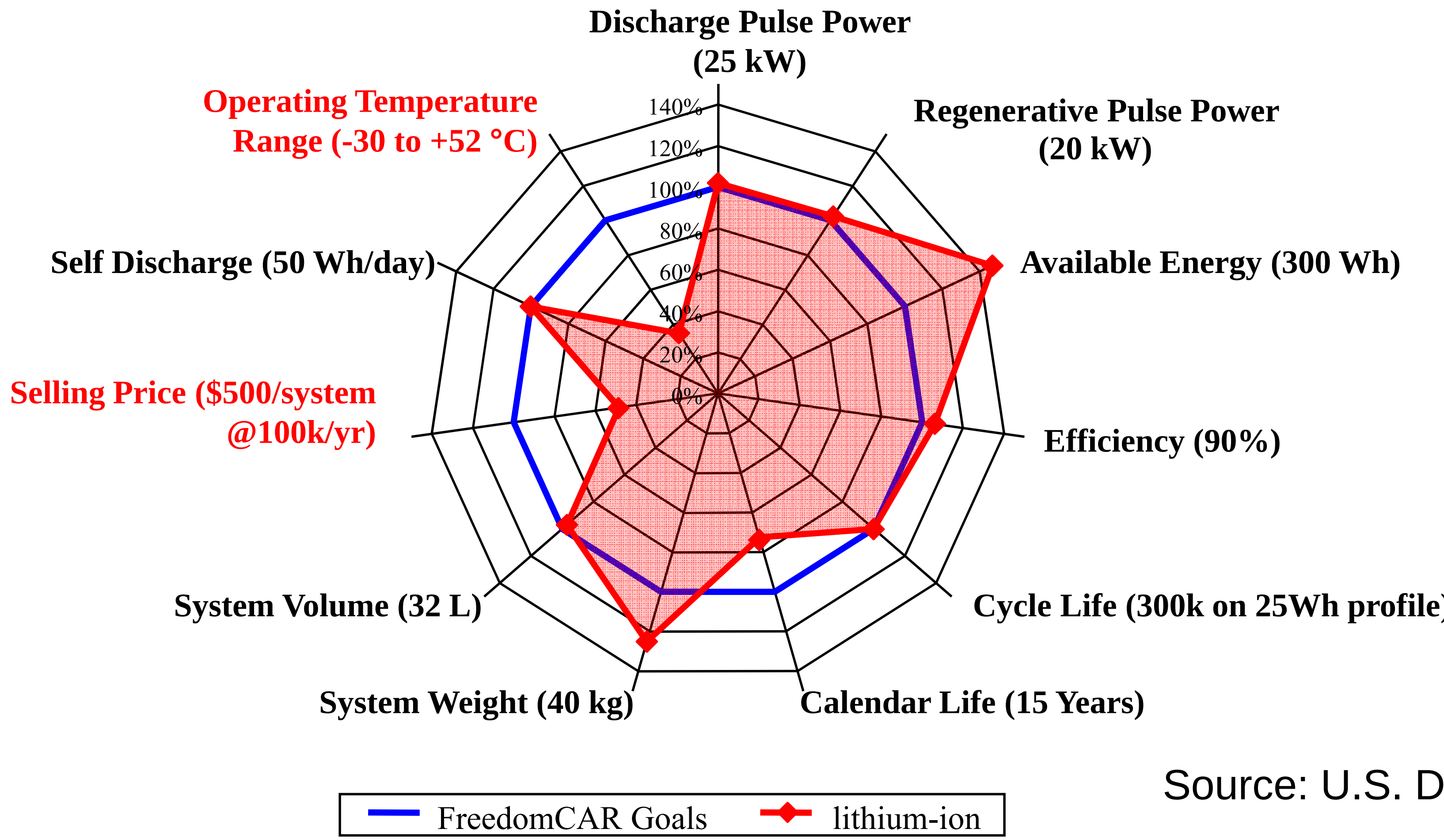
Anode:
- Carbon-based
- Alloys and intermetallics
- Oxides
- Lithium-metal

Cathode:
- Layered transition-metal oxides
- Spinel-based compositions
- Olivine-based compositions

- Presently three classes of cathodes, four classes of anodes, and four classes of electrolytes under consideration for Li-ion cells
- Four important criteria for selection of a battery chemistry: Cost, life, abuse tolerance, and performance
- None of the presently-studied chemistries appear to satisfy all four criteria

Comparison of Present-day Li-ion Batteries *vs.* HEV Goals

Anode: Graphite, Cathode: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, Electrolyte: $LiPF_6$ in PC:EC:DEC



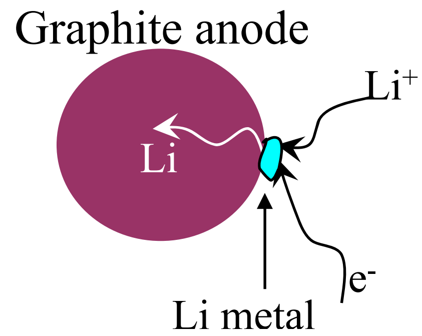
Source: U.S. DOE

- Safety, not included in the plot, is an issue.

Technical Challenges

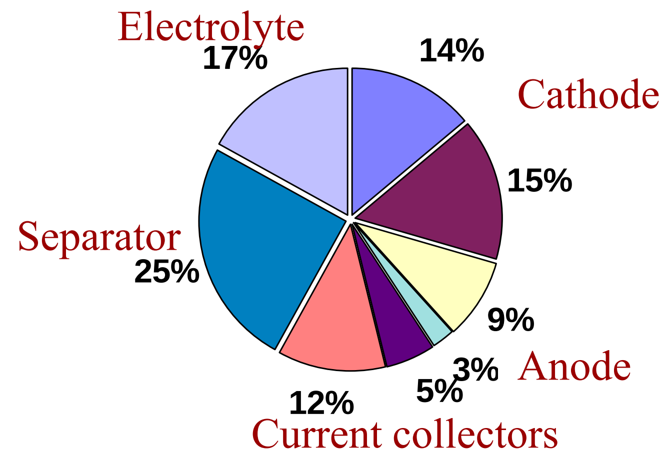
Operating Temperature:

- Batteries in HEV's are subject to high-current charging during regenerative braking
- At low temperatures (below 0º C) the Li plates on the anode surface instead of intercalating



Cost:

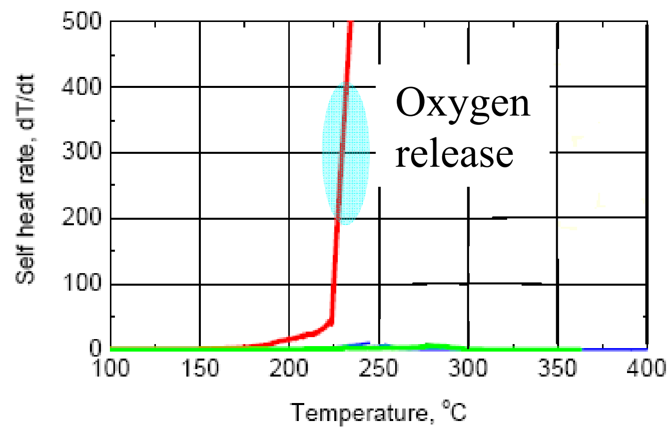
- Cell-level cost account for 50% of battery cost (rest is for packaging etc)
- Separator accounts for as much as 25% of cell cost



Source: ANL cost model

Safety (abuse tolerance):

- When overcharged, Li-ion cells can go into thermal runaway leading to fires *etc.*
- Runaway reaction caused by release of oxygen from the lattice of the cathode materials (*e.g.*, $LiCoO_2$)



Source: ATD Review, Feb. 2005

Anodes

Ideal Anode: Low-cost, good performance (including at low temperatures), and long cycle life

- Choices include
  - Carbon-based materials
    - » Graphite, in particular, has demonstrated high cycleability
      - However, low-temperature performance is poor
  - $Li_4Ti_5O_{12}$ is very stable, but the voltage is high for a negative electrode (1.5 V vs. 0.2 V for graphite)
    - » Results in lower cell voltage (2.4 V *vs.* 3.7 V) and hence lower energy
    - » However, higher voltage means no lithium deposition

Toshiba Supercharge

Low-temperature performance remains a stumbling block
However, a second battery can be used to circumvent this problem

Electrolytes

Ideal Electrolyte: Low-cost, good transport properties over wide temperature range, stable over wide voltage, and low flammability

- Organic electrolytes: wide voltage window (~4 V)
- Choices
  - Liquid systems: higher transport properties
  - Gel systems: flexible packaging, lower cost, and improved abuse tolerance

Most common electrolytes for propulsion: liquid systems

- While gels can decrease cost significantly, there has been little progress in making a gel-cell

- Few reports are emerging on the use of ionic liquids in these applications.
  - However, no clear indications of enhanced performance or lowered cost

Cost remains a stumbling block

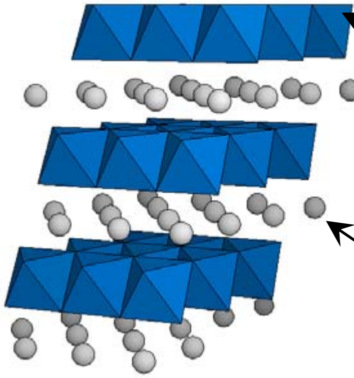
Cathodes

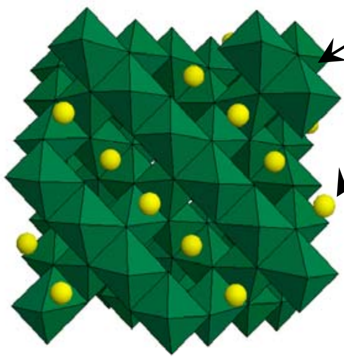
Ideal Cathode: low-cost, abuse tolerant, good performance, and long cycle life

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Layered)

Advantages: Good cycle life
High capacity

Disadvantages: Higher cost, but better than present baseline
Oxygen releases during abuse → Safety concerns





$LiMn_2O_4$ (Spinel)

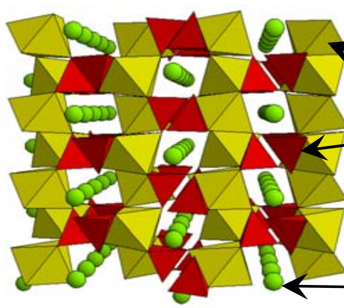
Advantages: 3-D transport through material → High power
Low cost
Reasonable abuse tolerance

Disadvantages: Low capacity
Manganese dissolves → Low cycle life

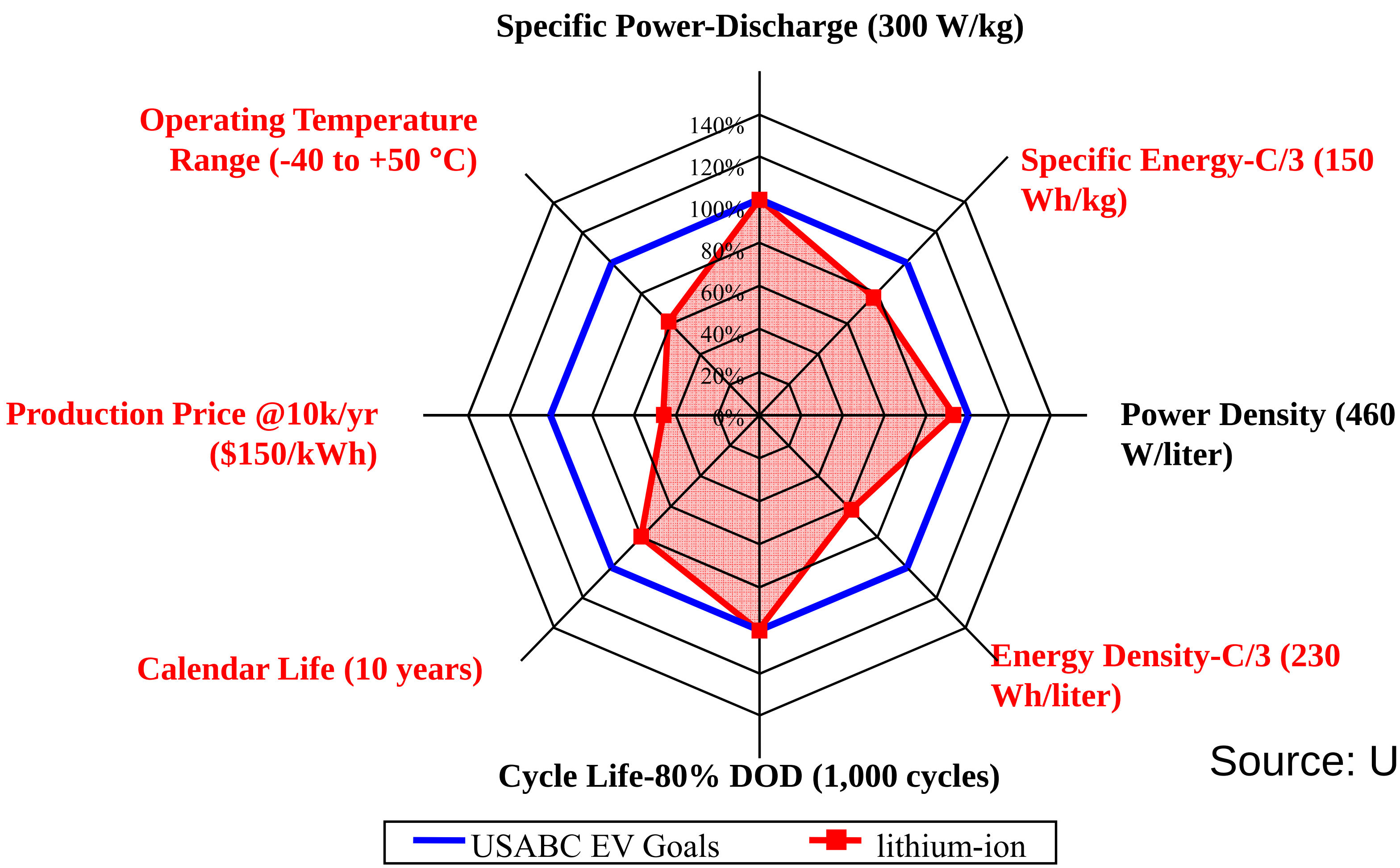
$LiFePO_4$ (Olivine)

Advantages: Oxygen strongly bound → Excellent safety
Excellent power
Reasonable capacity → Reasonable energy
Good cycle life

Disadvantages: Very high cost



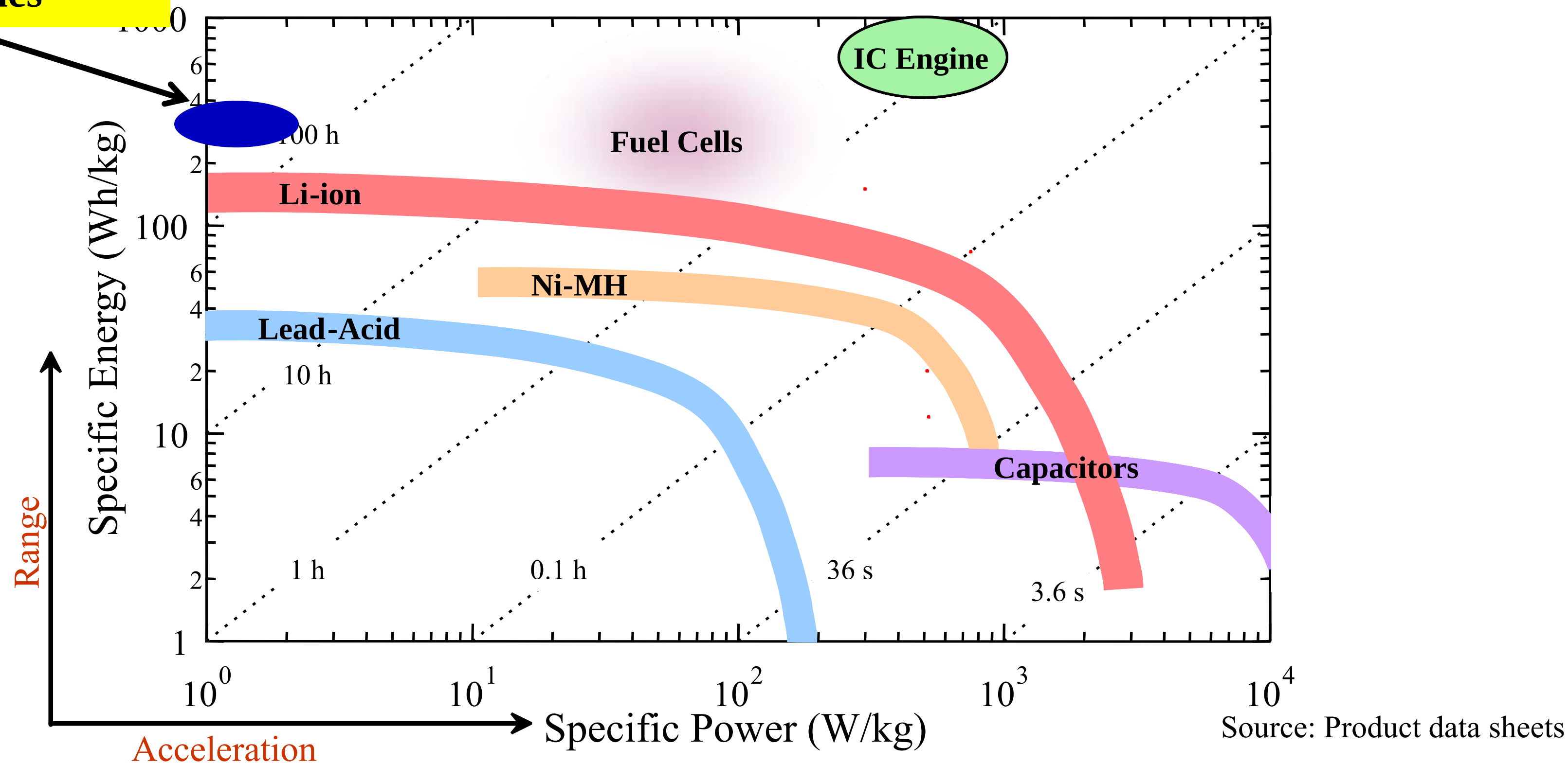
Comparison of Present-day Li-ion Batteries *vs.* EV Goals



Source: U.S. DOE

Electric-Vehicle Batteries

High voltage cathodes
Alloy anodes
Li-metal anodes



Source: Product literature

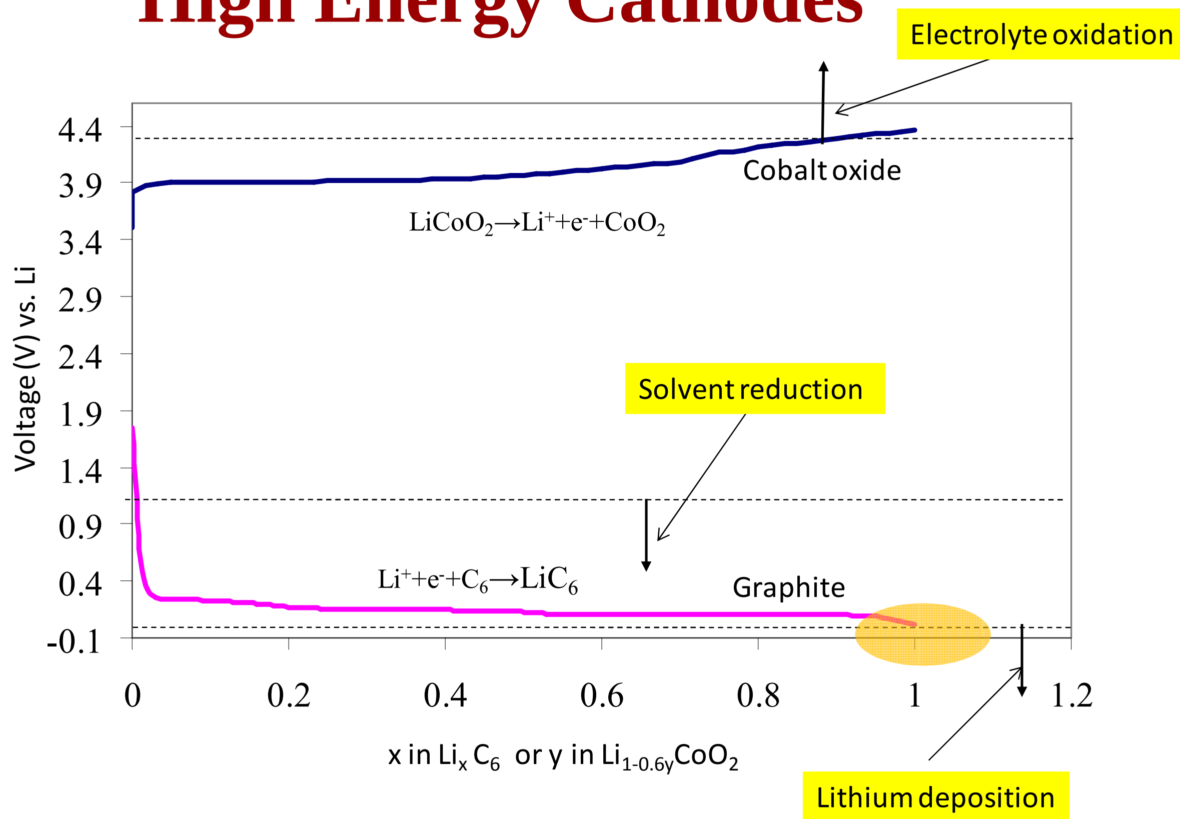
• Significant improvements are possible if high voltage cathodes can be used or if the anode can be substituted to an alloy or intermetallic

– Capacity of graphite is 372 mAh/g (operating at 0.15 V)

– Capacity of alloys range from 1000 to 3000 mAh/g, but voltage is higher (0.5 V)

– Capacity of Li-metal is 3860 mAh/g at 0.0 V

High Energy Cathodes

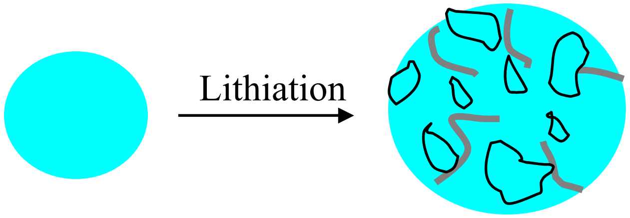


- Theoretical capacity of typical cathodes=280 mAh/g.
- Practical capacity limited by solvent oxidation reactions to 140-180 mAh/g.

- Recent reports suggest that coatings cathodes with a protective layer improves energy without sacrificing life and safety

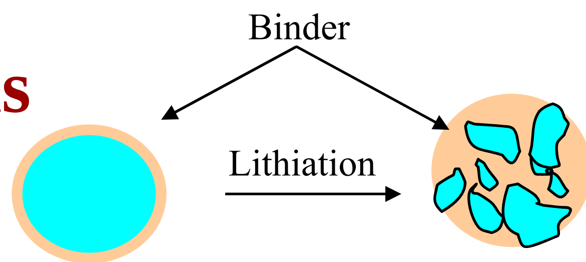
Alloy Anodes

- Alloys, like Li-silicon and Li-aluminum, can intercalate upto 4 lithium per lattice site (graphite intercalates 1 Li for every 6 lattice sites)
- However, to accommodate these lithium ions volume expands more than 300% (graphite expands 10%)

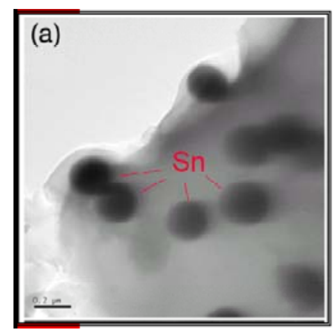


Possible Solutions

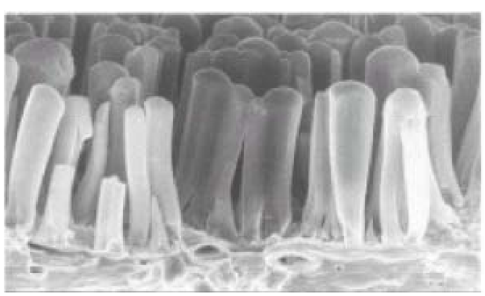
1. Use an elastic binder to accommodate the volume change



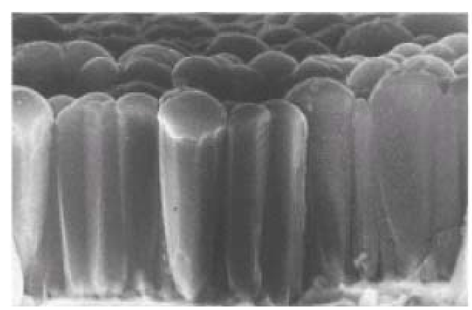
2. Reduce particle size to prevent cracking during expansion
   - However, smaller particles tend to agglomerate
   - Approach 1: Embed smaller particles in an inactive matrix (*e.g.*, Sony "Nexelion" battery)
   - Approach 2: Form microstructures



ESL, 7, A44 (2004)



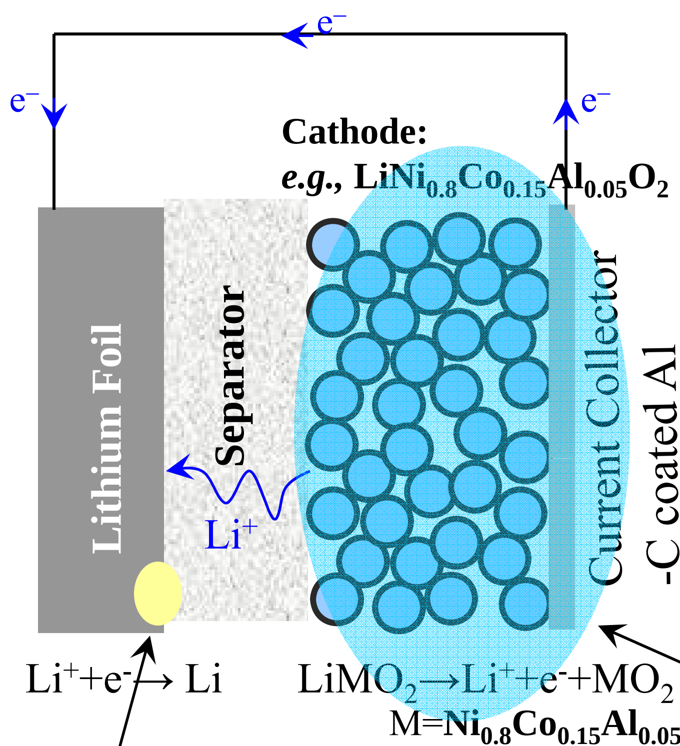
(a)Discharged-state
10μm



(b)Charged-state
10μm

Source: Sanyo

Lithium-metal Batteries



The interface, where Li deposition occurs, is the issue

Cathodes similar to those used in Li-ion systems (*e.g.*, metal oxides). Improved cathodes in the HEV research will lead to higher energy density EV materials.

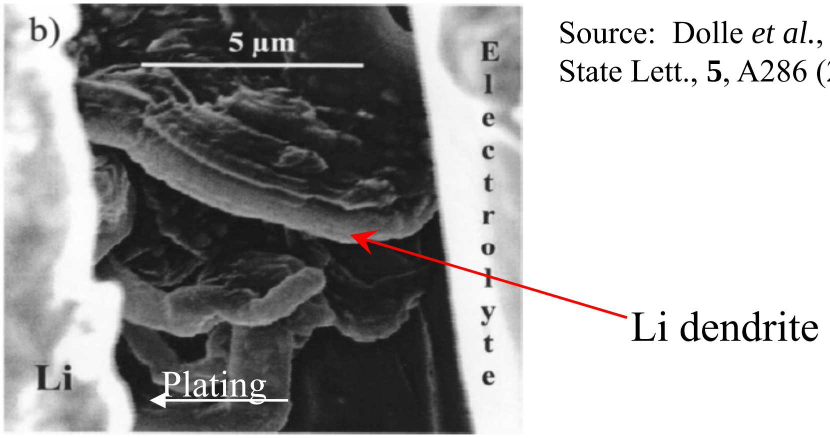
Problems with Li-metal-based Batteries

• During charge, Li plates on the anode

• The surface of the anode has irregularities on a nanometer scale

• It has been seen that the plating is not uniform (deposition occurs on protrusions) and leads to formation of dendrites

- This leads to cell shorting and failure
- In addition, the growth can break from the surface, thereby isolating material, leading to capacity fade

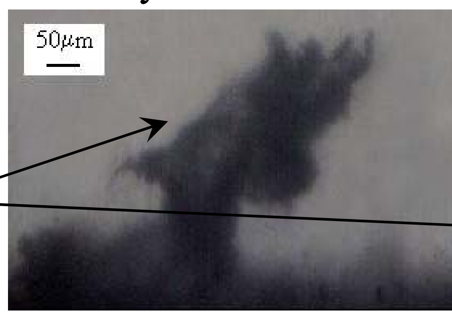


Source: Dolle *et al.*, Electrochem. Solid State Lett., **5**, A286 (2002)

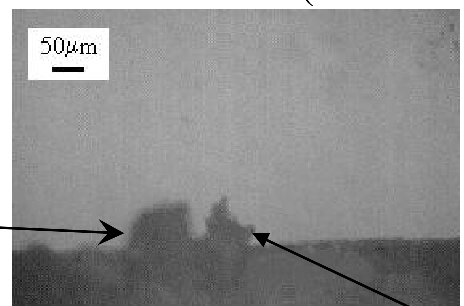
Possible Solution

- The initiation and propagation of dendrites is caused by an interplay of mechanical, kinetic, and thermodynamic behaviors at the Li-metal/electrolyte interface
- Dendrites could be prevented if an electrolyte with "stiffness" is used adjacent to the metal (*i.e.*, a solid polymer electrolyte)
  - Material would flatten any sharp dendrite growth
  - However, stiffer materials tend to have lower conductivity, leading to lower power

Poly-ethylene oxide (PEO) electrolyte



PEO with 10% silica filler (a stiffening agent)



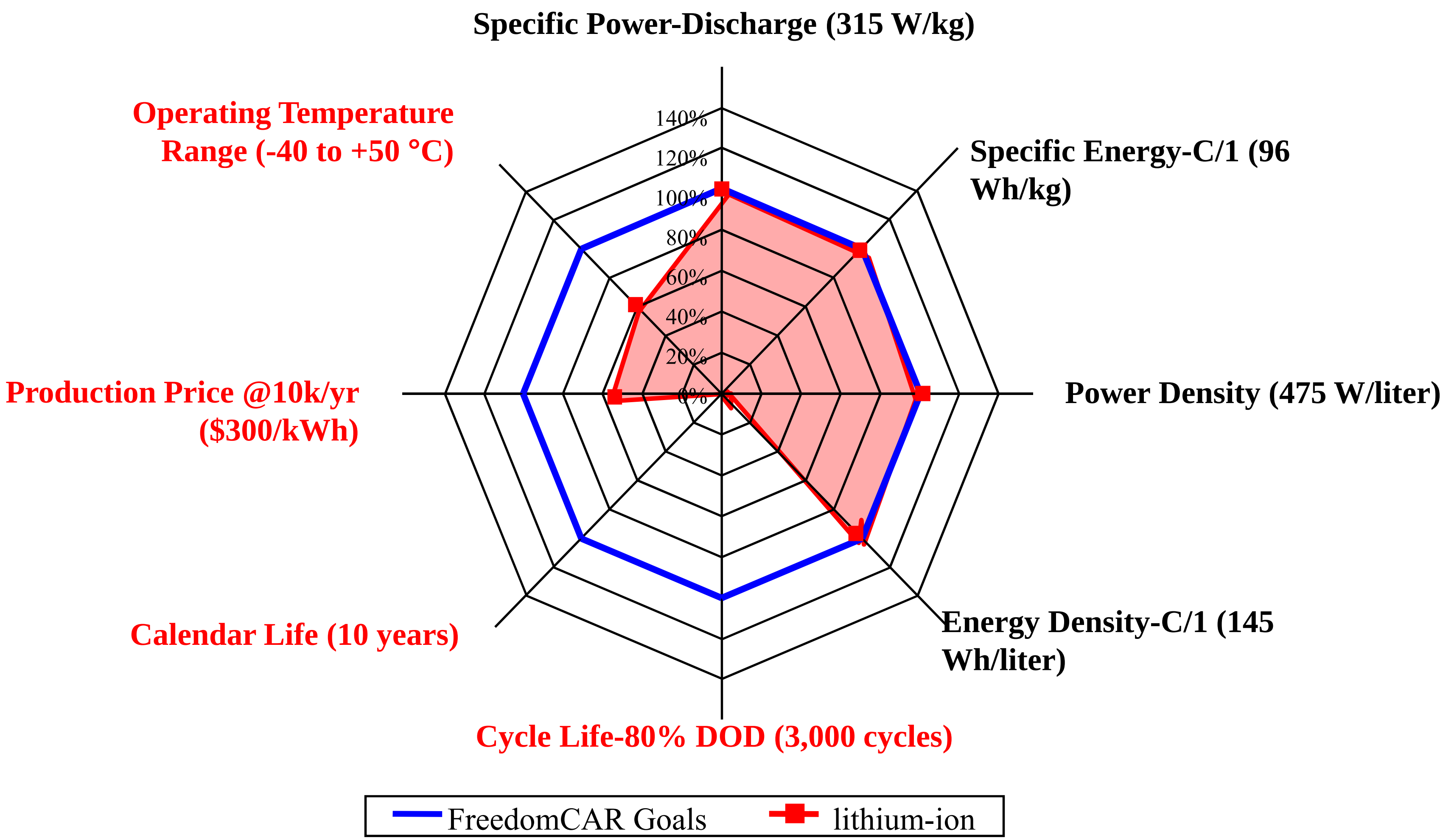
Source: Khan, Fedkiw, and Baker, BATT program annual review, May 2004

Dendrite

Growth is slower as material is stiffer. However, dendrites still grow, as it is not stiff enough

Present focus is on finding means of protecting the interface using a sufficiently stiff, conductive material (*e.g.*, block copolymers, conductive glasses)

Comparison of Present-day Li-ion Batteries *vs.* 40 mile PHEV Goals



- Safety, not included in the plot, is an issue

PHEVs offer an elegant means of solving the range issue

Challenges with PHEVs

Cost:

- Prius conversion cost $9000 for a 5 kWh battery (40 mile PHEV requires 15-20 kWh battery)
- Expectations are that battery costs would be greater than $10,000

Life:

- Batteries need to cycle upwards of 3500 times
- Also have to last 15 years.

Possible Approaches

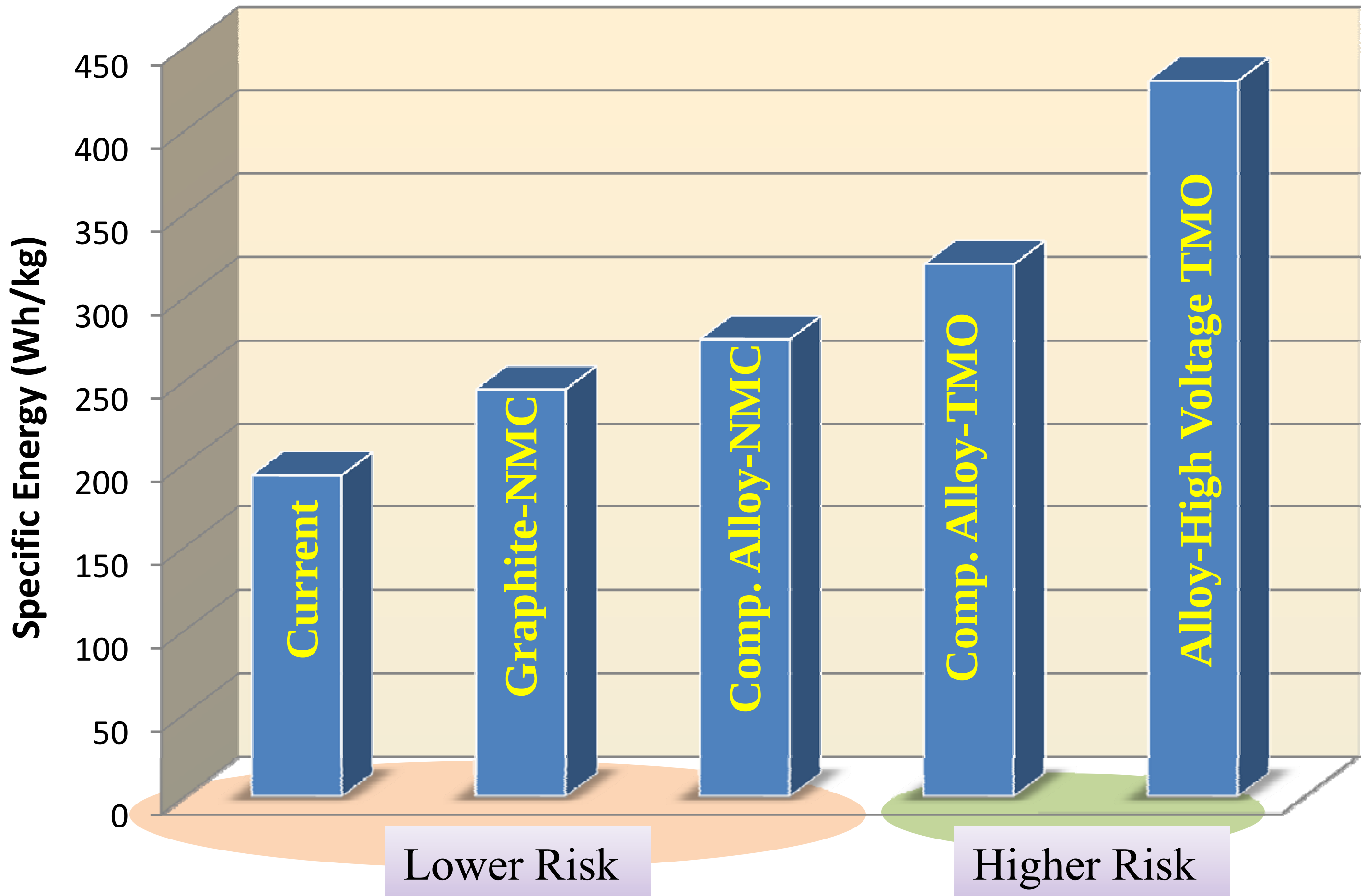
Cost:

- Volume manufacturing
- Development of higher energy cells (more energy means less battery can be used, thereby decreasing cost)
  - Improvements in alloy anodes and/or high-voltage cathodes would allow for higher energy

Life:

- Li-ion manufacturers now claims upwards of 3000 cycles
- However, challenge is calendar life

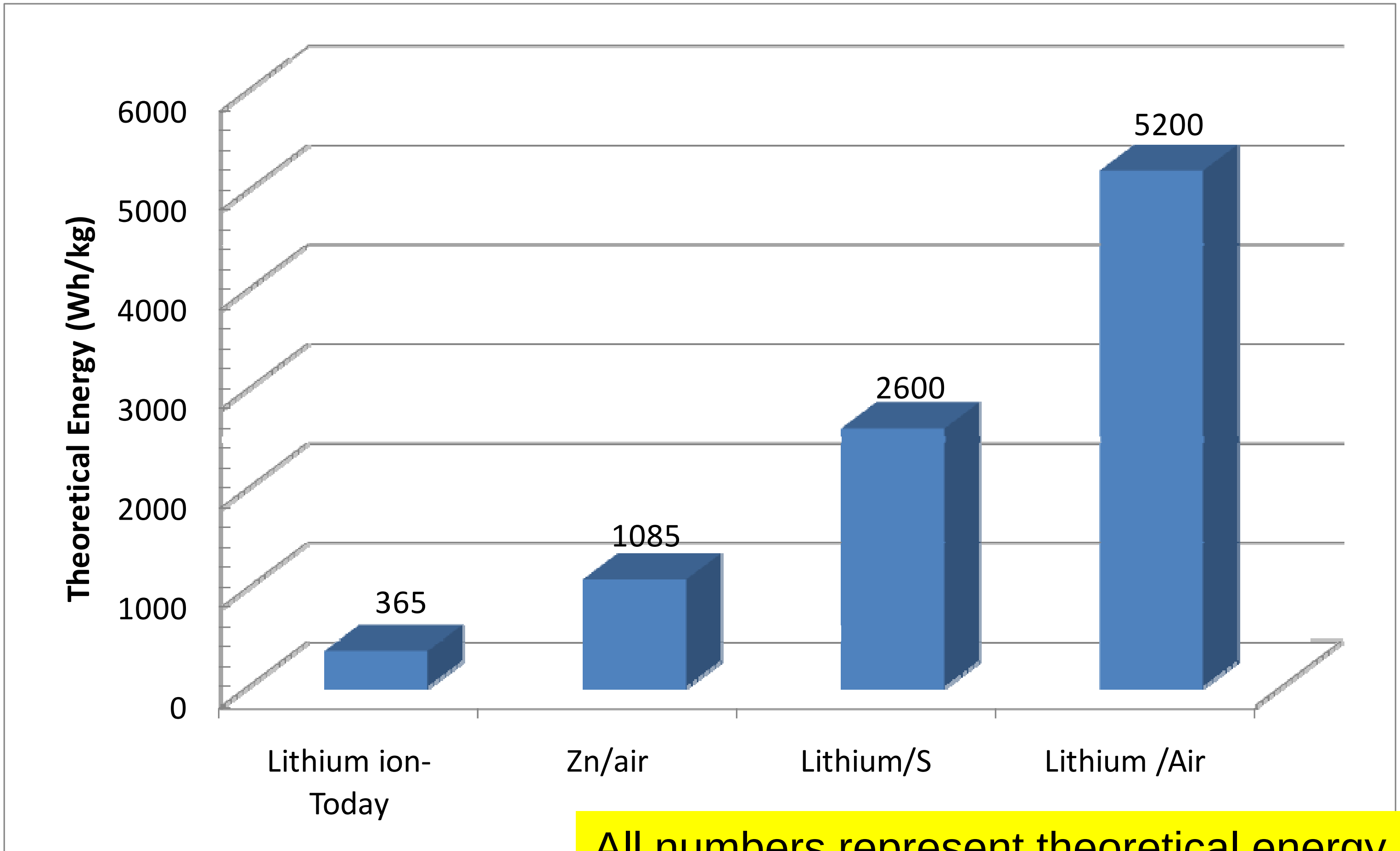
Future of Batteries



Based on: Draft of FreedomCAR PHEV R&D Plan:
http://www1.eere.energy.gov/vehiclesandfuels/features/phev_plan.html

- New materials in the research stage promise to improve energy density by a factor of two.

Future of Batteries- Longer Term



All numbers represent theoretical energy densities

- Systems exist that promise very high theoretical energy
- However challenges are daunting
- Efforts are underway to perform the long term research to solve these problems

Summary

- Li-ion, unlike lead-acid batteries, are not limited to one anode and cathode material
  - Depending on the combination of anode cathode and electrolyte, one can get different energy, power, life, cost, and safety.

- HEVs with Li-ion batteries expected to be a reality in the near future.

- The problem of range makes a pure EV problematic

- PHEVs offer an ideal alternative, however cost and life remain problems
  - Battery technology expected to improve to meet the needs

- Li-ion batteries have a very bright future. Improvements will be incremental, but expect them to be fast paced.

Thank you