

Electric Vehicle Technologies

Workshop Session EV-04

Electric Vehicle Battery Technologies

Anthony Burrell

Department Head: Electrochemical Energy Storage

Principle Investigator: Multivalent Intercalation – JCESR

Joint Center for Energy Storage Research

Chemical Sciences and Engineering Division

Argonne National Laboratory

9700 South Cass Ave.

Argonne, IL 60439-4854

630 252 2629 office

603 995 5272 mobile

Acknowledgements

Argonne National Laboratory:

Electrochemical Energy Storage Department.



U.S. Department of Energy

- Vehicle Technologies Program, EERE
- Basic Energy Sciences, Office of Science



- The Center for Electrical Energy Storage (CEES) - *Tailored Interfaces*
- The Joint Center for Energy Storage Research (JCESR)

This presentation has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne").

Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC0206CH1125.

The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license

in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display

publicly, by or on behalf of the Government.



Argonne's Energy Storage Mission

Matches DOE's Discovery Deployment Spectrum

GRAND CHALLENGES

DISCOVERY SCIENCE

USE-INSPIRED BASIC RESEARCH

APPLIED RESEARCH

TECHNOLOGY MATURATION AND DEPLOYMENT



APPLIED RESEARCH
EERE, OE, DoD
BATTERY DEPARTMENT (85)



BASIC RESEARCH
OS, BES
EFRC – CEES (60)
Universities
LDRD funding

ES HUB
OS, BES
JCESR (120)
Energy, Safety,
Life, Cost

TECHNOLOGY TRANSFER
IP Generation, Scale up



Argonne
Transport.
Center

CONTRACT RESEARCH
Industry

KY-ANL
Battery Mfg
R&D



Argonne's Electrochemical Energy Storage Department

Primary Mission:

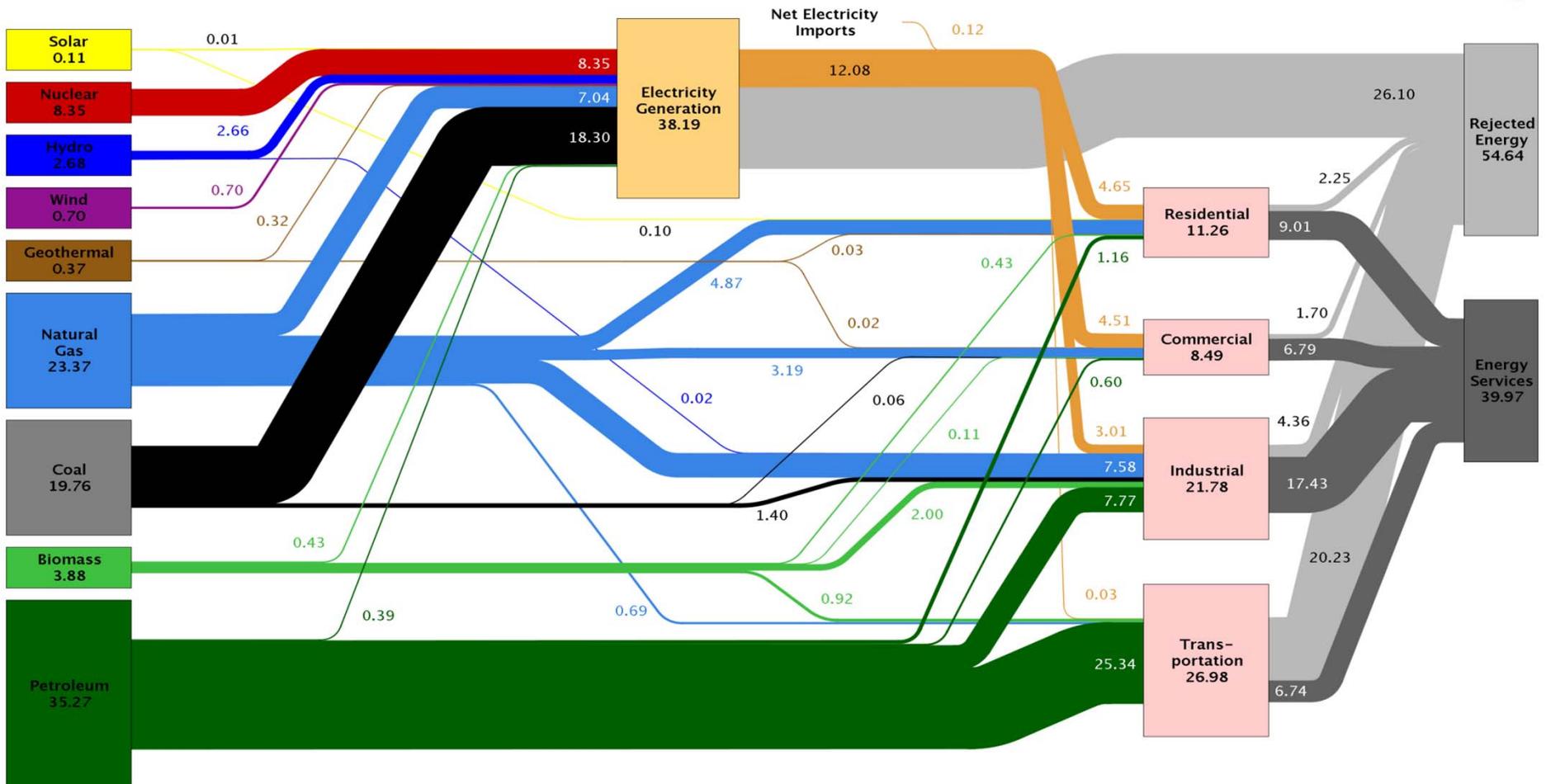
To undertake applied, performance-driven research and development of advanced battery materials and systems for the U.S. Department of Energy through the Office of Vehicle Technologies and for U.S. industry.

Current Major Focus:

1) To study and find solutions to the voltage-fade phenomenon in high-capacity lithium- and manganese-rich composite electrode structures, and 2) to find new advanced materials for the next generation of advanced lithium-ion batteries and those 'beyond lithium-ion'.

Energy flow chart shows relative size of primary energy resources and end uses in U.S.

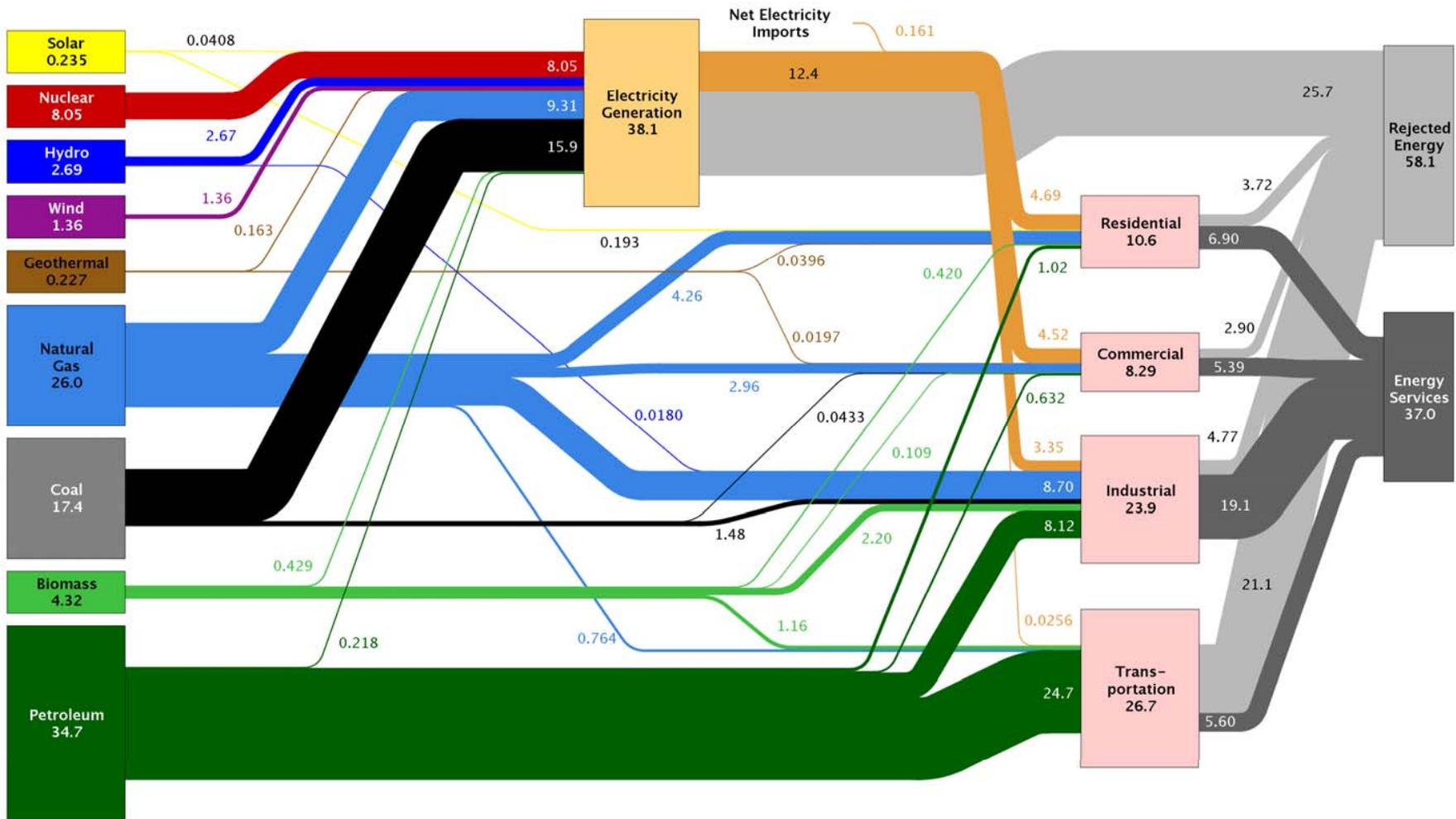
Estimated U.S. Energy Use in 2009: ~94.6 Quads



Source: LLNL 2010. Data is based on DOE/EIA-0384(2009), August 2010. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports flows for non-thermal resources (i.e., hydro, wind and solar) in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Energy flow chart shows relative size of primary energy resources and end uses in U.S.

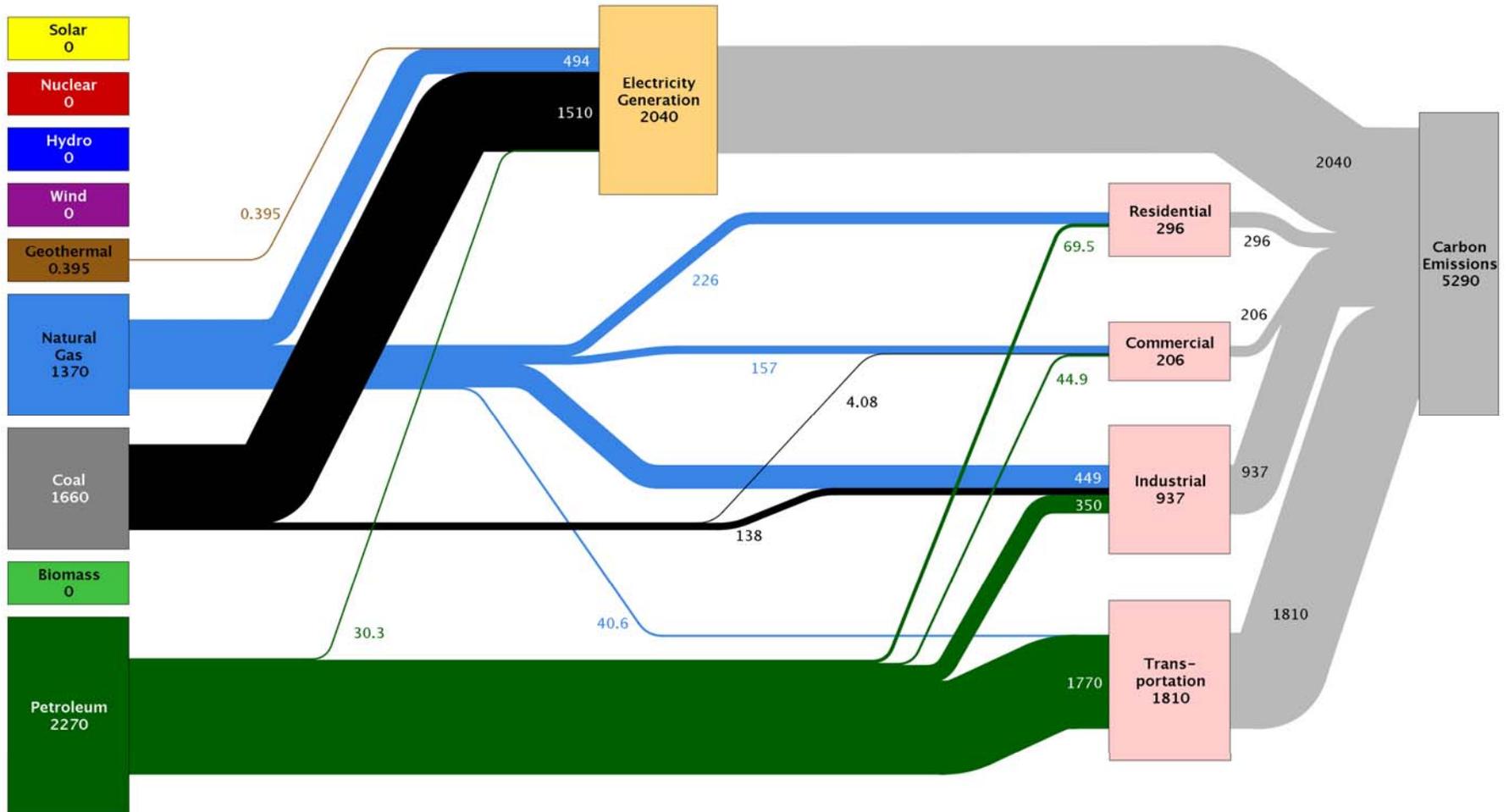
Estimated U.S. Energy Use in 2012: ~95.1 Quads



Source: LLNL 2013. Data is based on DOE/EIA-0035(2013-05), May, 2013. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

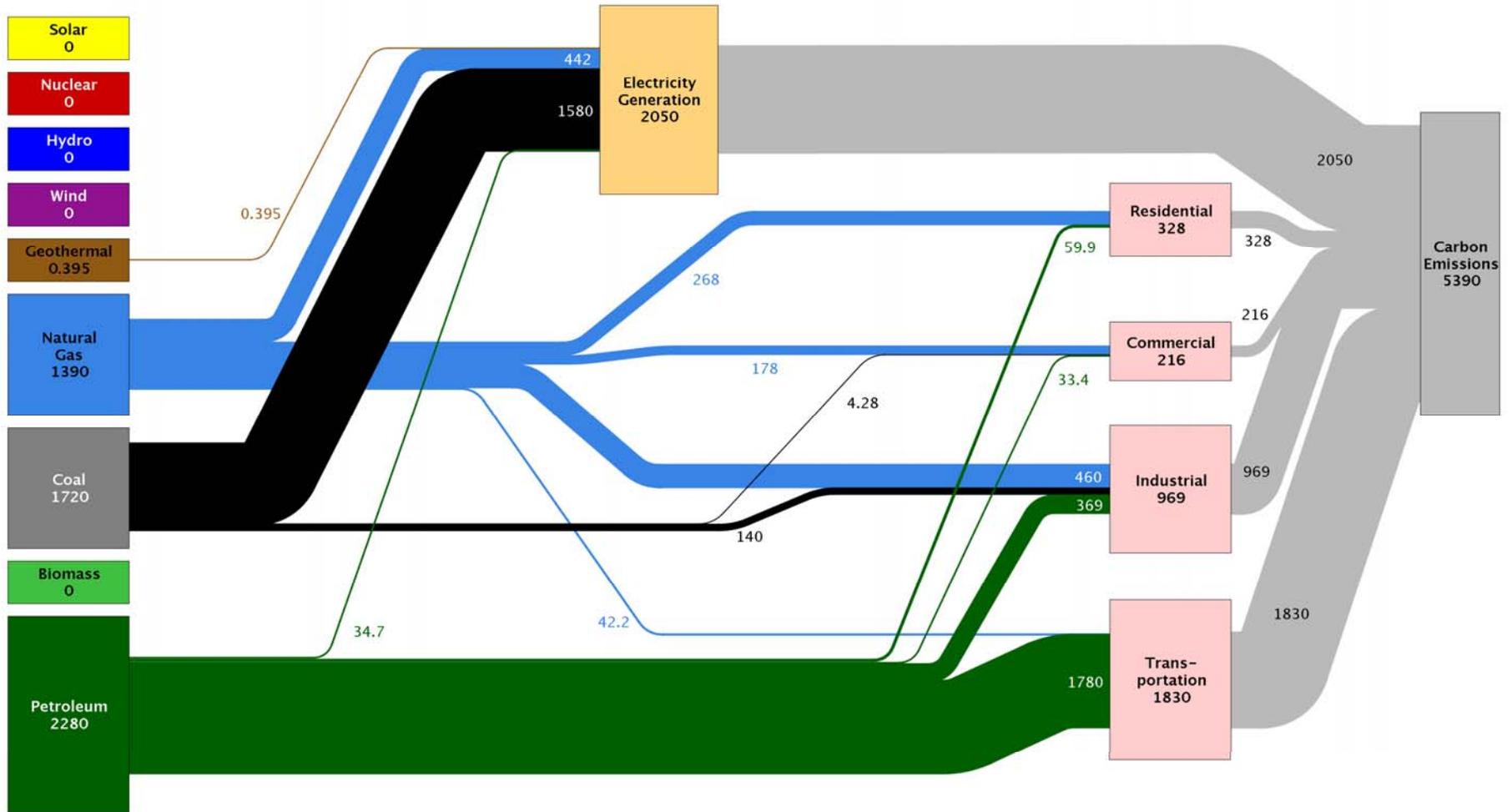
3,120,755,000 barrels 880 M US production 2,373,373,000

Estimated U.S. Energy-Related Carbon Dioxide Emissions in 2012: ~5,290 Million Metric Tons



Source: LLNL 2013. Data is based on DOE/EIA-0035(2013-05), May, 2013. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Carbon emissions are attributed to their physical source, and are not allocated to end use for electricity consumption in the residential, commercial, industrial and transportation sectors. Petroleum consumption in the electric power sector includes the non-renewable portion of municipal solid waste. Combustion of biologically derived fuels is assumed to have zero net carbon emissions - the lifecycle emissions associated with producing biofuels are included in commercial and industrial emissions. Totals may not equal sum of components due to independent rounding errors. LLNL-MI-410527

Estimated U.S. Carbon Emissions in 2013: ~5,390 Million Metric Tons



Source: LLNL 2014. Data is based on DOE/EIA-0035(2014-03), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Carbon emissions are attributed to their physical source, and are not allocated to end use for electricity consumption in the residential, commercial, industrial and transportation sectors. Petroleum consumption in the electric power sector includes the non-renewable portion of municipal solid waste. Combustion of biologically derived fuels is assumed to have zero net carbon emissions - the lifecycle emissions associated with producing biofuels are included in commercial and industrial emissions. Totals may not equal sum of components due to independent rounding errors. LLNL-MI-410527

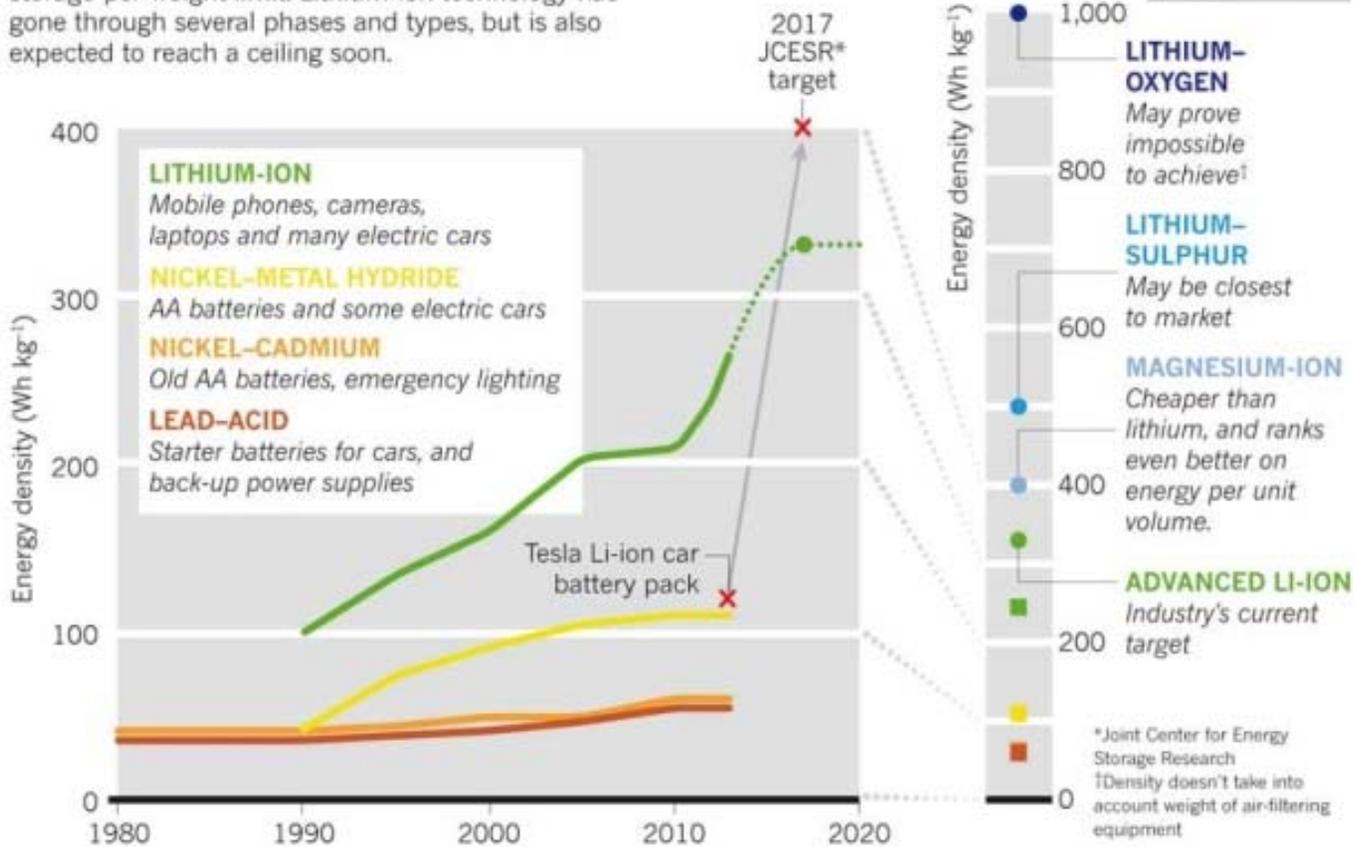


“The rechargeable revolution: A better battery”

Van Noorden, Nature; **March 5, 2014**

POWERING UP

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



OEMs around the world have plans for vehicles with electric drive trains



BMW Megacity



Chevy Volt



Mini E



Renault Fluence



China's BYD



Volvo V70



Mitsubishi Imiev



Toyota FT-EV



Ford Focus EV



Mercedes Bluezero

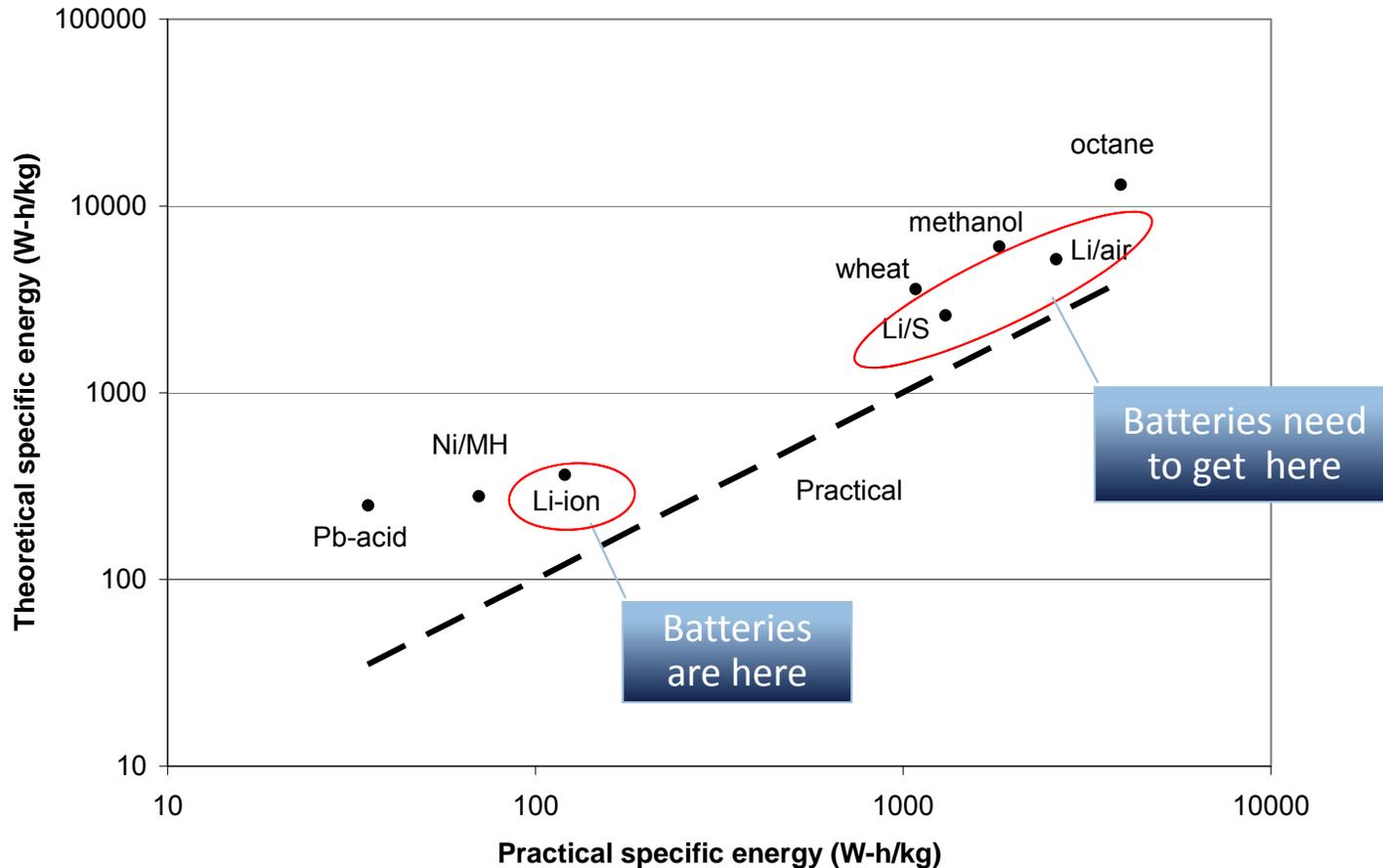


Nissan Leaf



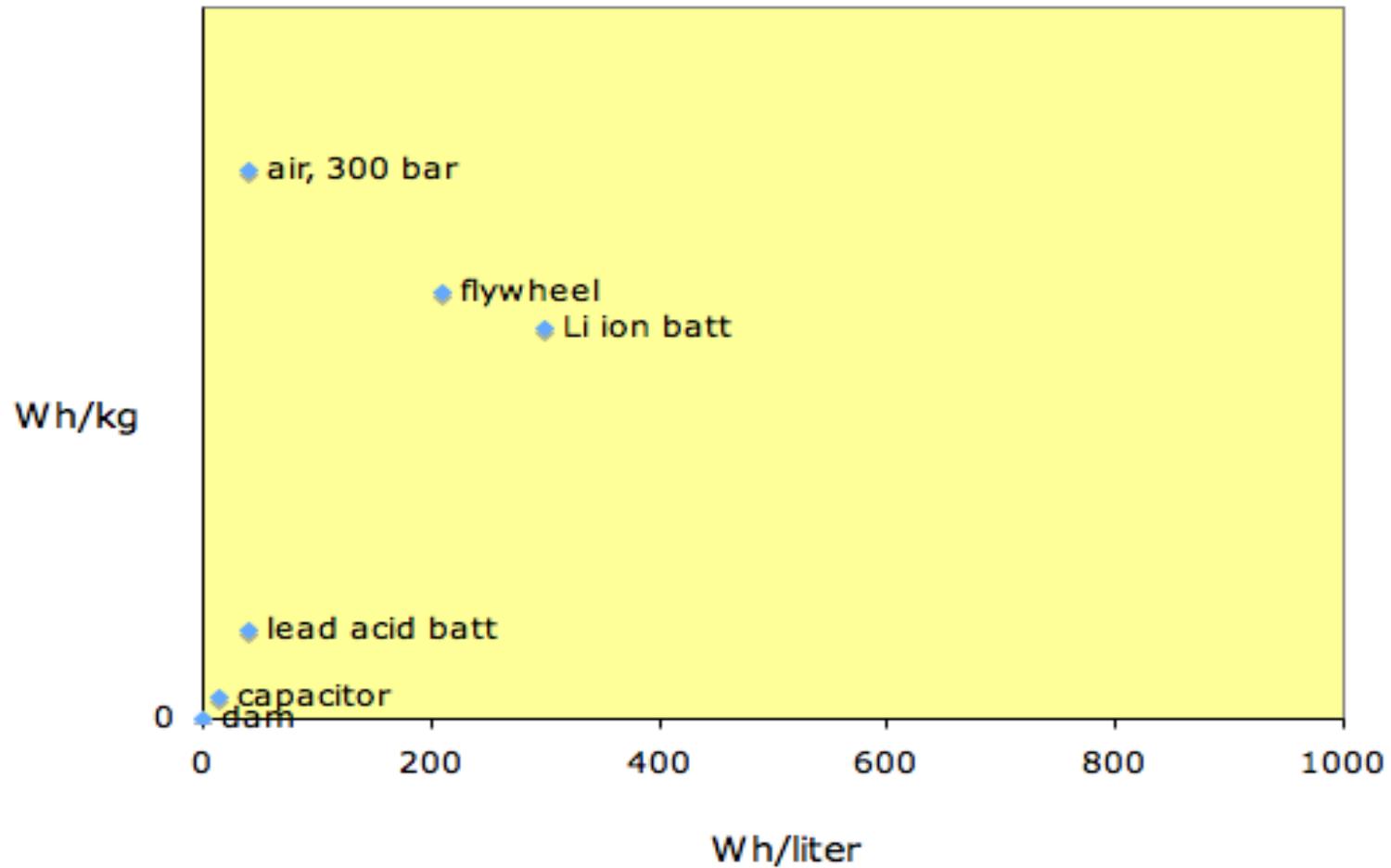
Subaru R1e

So what's the problem?



Source: Prof. J. Newman, LBNL

The Challenge



Energy Storage Basics

A Battery is a device that allows energy to be stored in a **chemical form** and to be released when needed.

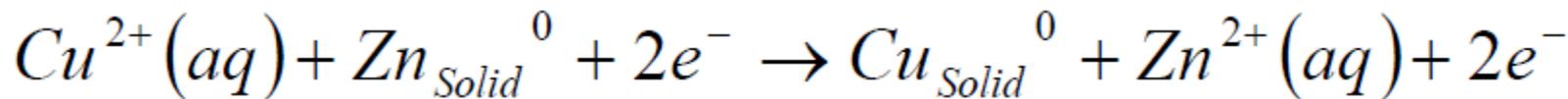
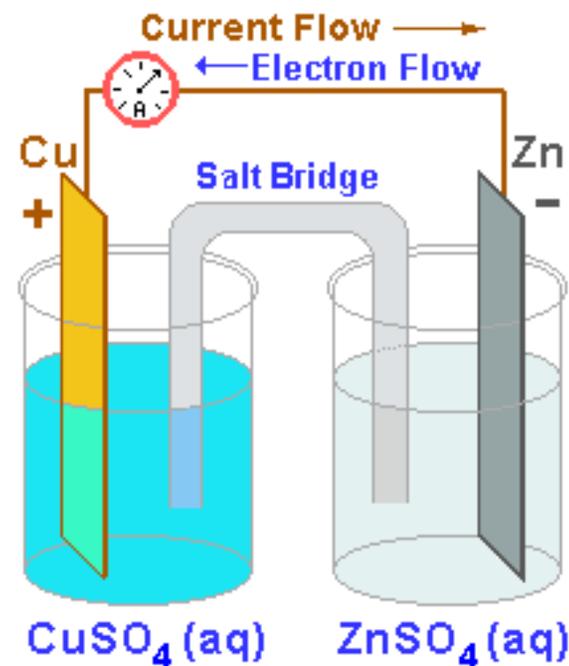
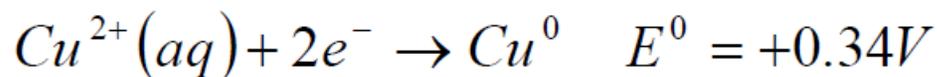
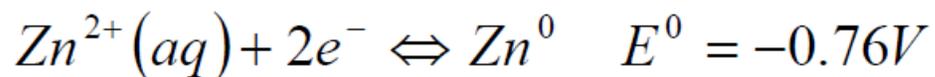
Primary Batteries: only store energy and cannot be recharged.

Secondary Batteries: can be “re-charged” by forcing the discharge reaction to be reversed

A Battery consists of at least three regions:

- Cathode: Negative potential lead
- Anode: Positive potential lead
- Electrolyte: A “weak barrier” that allows ions to be

transferred from anode to cathode.



$$+0.34\text{V} - (-0.76\text{V}) = 1.10\text{V.}$$

Battery Figures of Merit

- **Cell Voltage** – the resulting potential of the combined double $\frac{1}{2}$ reactions.
- Battery Capacity - fundamental unit of battery capacity is coulombs (C) but this is normally re-written as Amp-hrs (Ah)
- Energy Capacity - Ah×Battery Voltage
- **Energy Density** - Ah/Kg Important in portable applications more so than in PV
- Cut-Off Voltage - The minimum battery voltage for which the battery can be discharged. Below this value, permanent damage may be done to the battery.
- State of Charge (SOC) – The fraction of the total energy or battery capacity that has been used over the total available from the battery.
- Depth of Discharge (DOD) - The fraction of energy that can be withdrawn from the battery without significant devaluation of the lifetime of the battery.
- **Specific Energy Density** - The capacity of the battery divided by the weight of the battery, in Wh/kg
- **Volumetric Energy Density** - The capacity of the battery divided by the volume, in Wh/m³ (or Whr/litre)

USABC Goals for Advanced Batteries for EVs

Parameter(Units) of fully burdened system	Minimum Goals for Long Term Commercialization	Long Term Goal
Power Density(W/L)	460	600
Specific Power – Discharge, 80% DOD/30 sec(W/kg)	300	400
Specific Power - Regen, 20% DOD/10 secW/kg	150	200
Energy Density - C/3 Discharge Rate(Wh/L)	230	300
Specific Energy - C/3 Discharge Rate(Wh/kg)	150	200
Specific Power/Specific Energy Ratio	2:1	2:1
Total Pack Size(kWh)	40	40
Life(Years)	10	10
Cycle Life - 80% DOD (Cycles)	1,000	1,000
Power & Capacity Degradation(% of rated spec)	20	20
Selling Price - 25,000 units @ 40 kWh(\$/kWh)	<150	100
Operating Environment(°C)	-40 to +50 20% Performance Loss (10% Desired)	-40 to +85
Normal Recharge Time	6 hours (4 hours Desired)	3 to 6 hours
High Rate Charge	20-70% SOC in <30 minutes @ 150W/kg (<20min @ 270W/kg Desired)	40-80% SOC in 15 minutes
Continuous discharge in 1 hour - No Failure(% of rated energy capacity)	75	75

USABC BEV targets are for low P/E (2) systems which can be sized by energy – at least as a first estimate.

Energy Targets (Pack Level):

- 300 Wh/L
- 200 Wh/kg

Practical Cell Chemistries

Primary Cells

- Leclanché Cells
- Alkaline Cells
- Silver Oxide Cells
- Zinc Air Cells

Secondary Cells

- Lead Acid
- Nickel Cadmium
- Nickel Metal Hydride
- Nickel Zinc
- Nickel Hydrogen
- Lithium Secondary Cells



Leclanché Cells (Zinc- Carbon Cells or Dry Cells)

- Primary cell with a nominal open circuit voltage of 1.5 Volts.
- Produced in very high volumes.
- Chemistry based on a zinc anode and a cathode of manganese dioxide. It uses a carbon rod as the cathode current collector with an electrolyte of ammonium chloride. Over 100 years of development time.

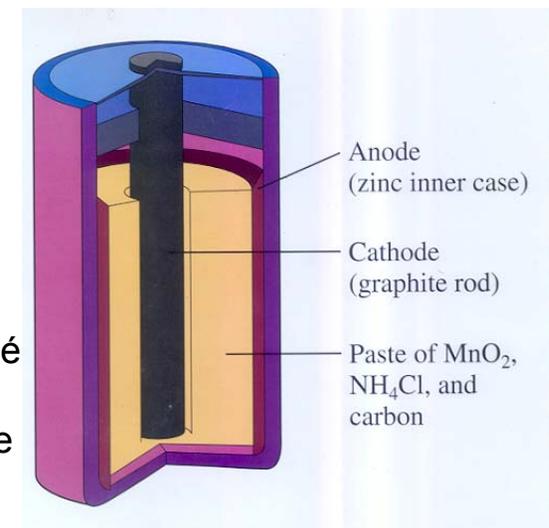
Advantages

- Inexpensive materials
- Low cost

Shortcomings

- Propensity to leak

The **Alkaline** Manganese Dioxide battery is a variant on the Leclanché cell. As with the [Leclanché cell](#) the electrodes are zinc and manganese dioxide but the electrolyte is Potassium hydroxide (KOH).



Zinc/Silver Oxide Batteries

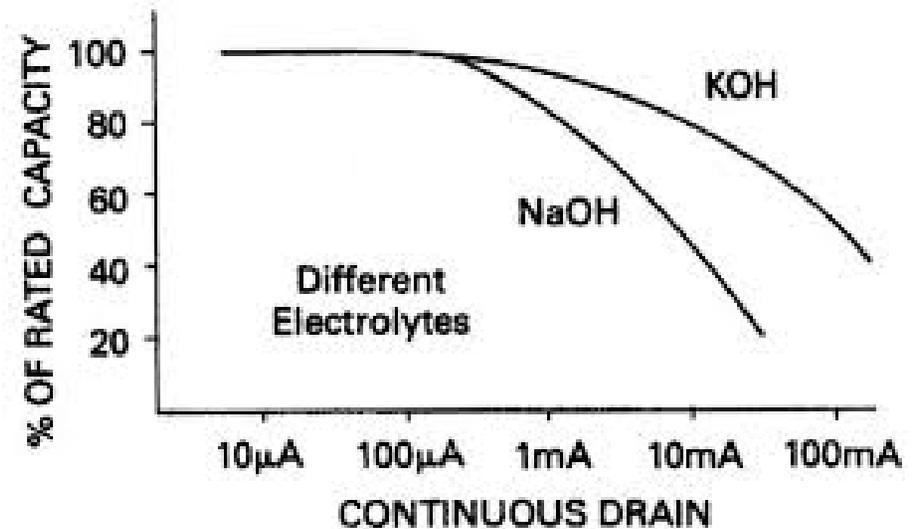
- Common low capacity primary button cell versions are typically called **Silver Oxide** batteries.
- Open circuit voltage of 1.6 Volts.

Advantages

- High capacity per unit weight.
- Long operating life.
- Low self discharge

Shortcomings

- Uses expensive materials.
- Lower energy density than zinc air.



Zinc Air Batteries

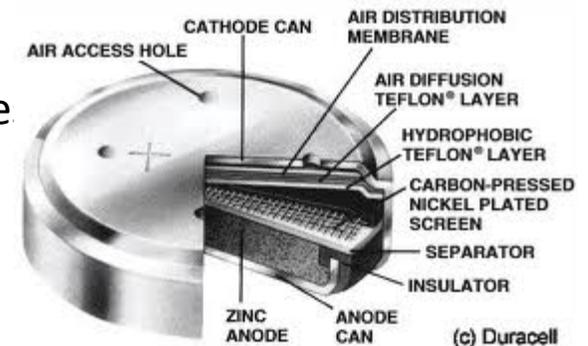
An example of Metal Air batteries, cells using zinc-air technology are energized only when atmospheric oxygen is absorbed into the electrolyte through a gas-permeable, liquid-tight membrane.

Advantages

- High energy density but low power
- Inexpensive materials
- The zinc-air system, when sealed, has excellent shelf life.
- In relation to their physical size, Zinc/Air batteries store more energy per unit of weight (in terms of 220 Wh/kg) than almost any other primary type.

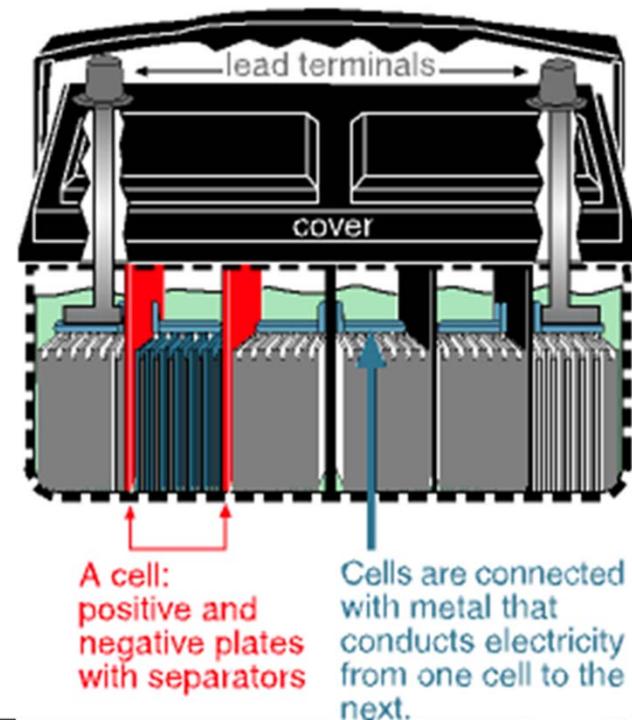
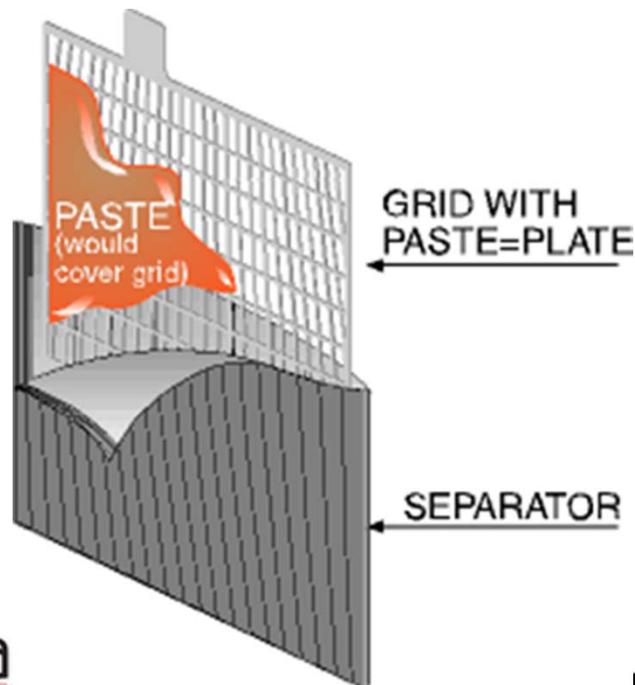
Shortcomings

- Sensitive to extreme temperature and humid conditions.
- Carbon dioxide from the air forms carbonate which reduce conductivity.



Lead Acid Batteries

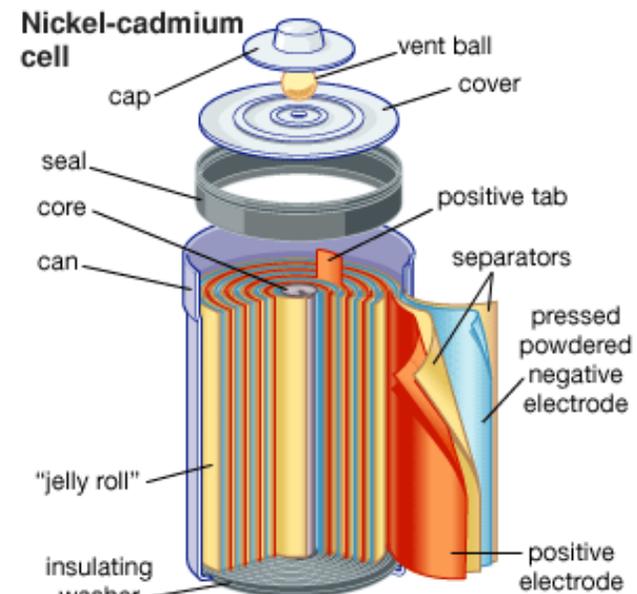
- Lead acid batteries were invented in 1859 by Gaston Planté and first demonstrated to the French Academy of Sciences in 1860.
- Lead-acid batteries are composed of a Lead-dioxide cathode, a sponge metallic Lead anode and a Sulphuric acid solution electrolyte.
- The cell voltage is 2 Volts



Nickel Cadmium Batteries

- 1.2 Volt secondary cells using an alkaline chemistry with energy density about double that of lead acid batteries.

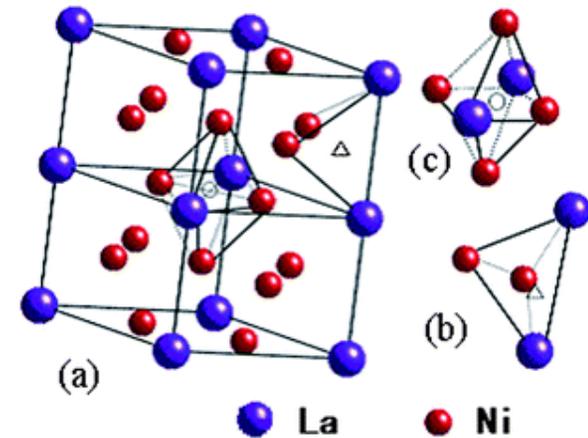
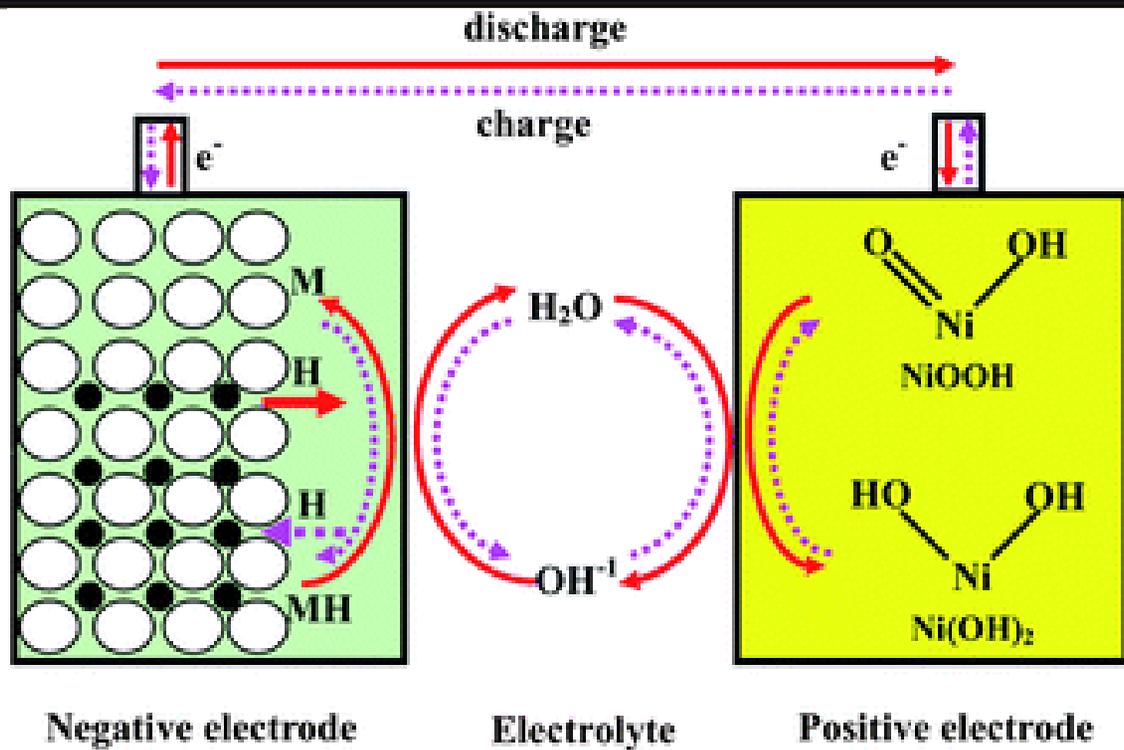
nickel hydroxide $\text{Ni}(\text{OH})_2$ for the positive electrode (cathode), cadmium Cd as the negative electrode (anode) and an alkaline potassium hydroxide KOH electrolyte



© 2007 Encyclopædia Britannica, Inc.

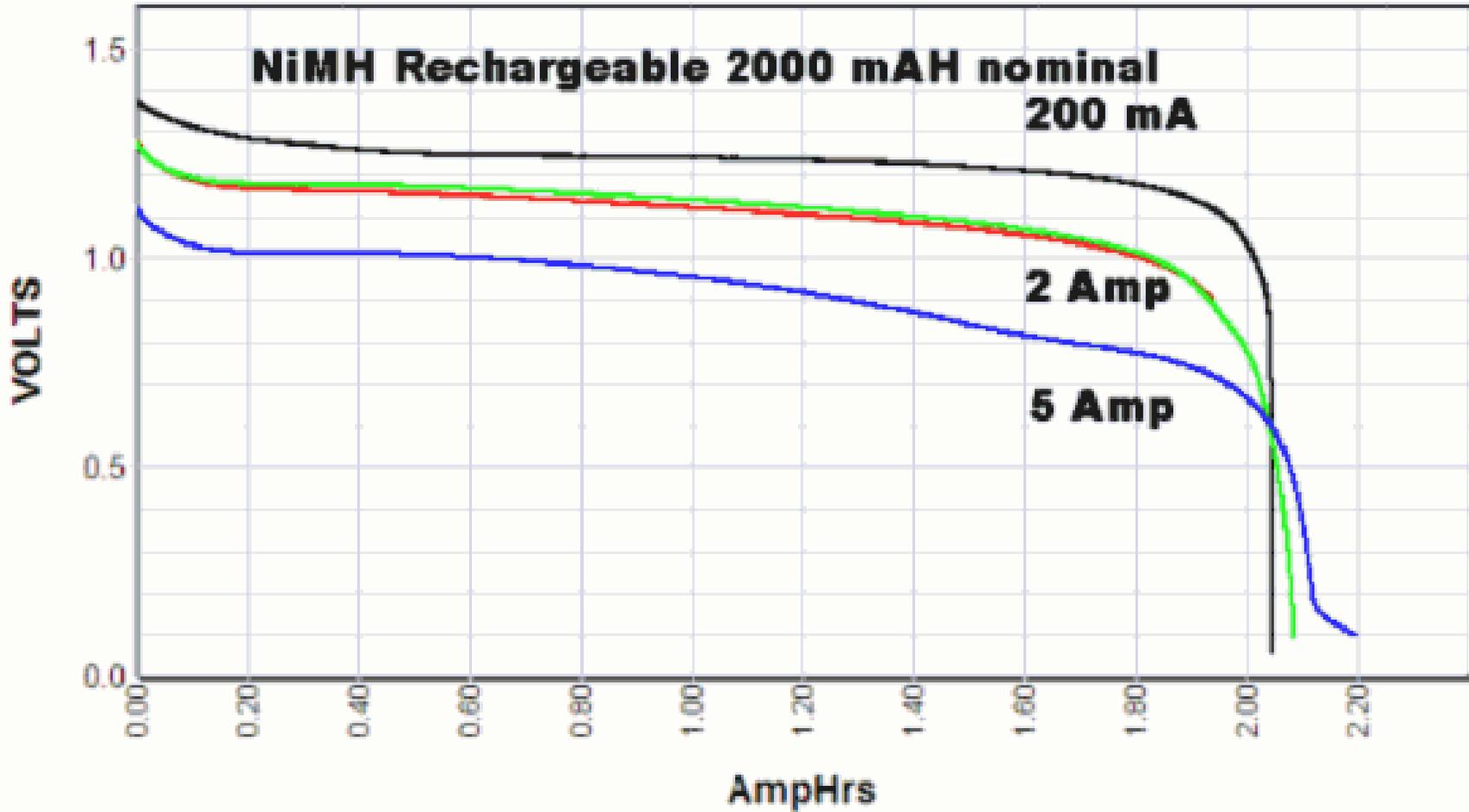
Nickel Metal Hydride Batteries

- Nickel-metal-hydride batteries are related to sealed nickel-cadmium batteries and only differ from them in that instead of cadmium, hydrogen is used as the active element at a hydrogen-absorbing negative electrode (anode). This electrode is made from a metal hydride usually alloys of Lanthanum and related metals that serve as a solid source of reduced hydrogen.
- Cell voltage is 1.2 Volts
- The NiMH battery was patented in 1986 by Stanford Ovshinsky, founder of Ovonics.
- The energy density is more than double that of Lead acid and 40% higher than that of NiCads
- They accept both higher charge and discharge rates and micro-cycles thus enabling applications which were previously not practical



$\text{LaNi}_5 \rightarrow \text{LaNi}_5\text{H}_6$,
 $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ (Mm = misch-metal with the composition $\text{La}_{0.62}\text{Ce}_{0.27}\text{Pr}_{0.03}\text{Nd}_{0.08}$)

• J. Mater. Chem., 2011, 21, 4743-4755



Advantages

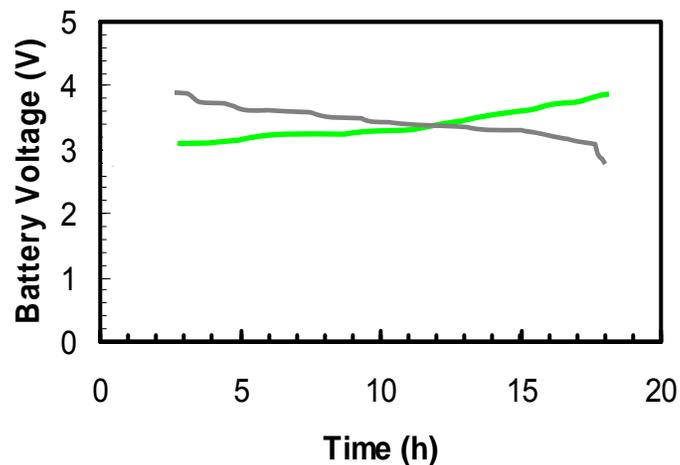
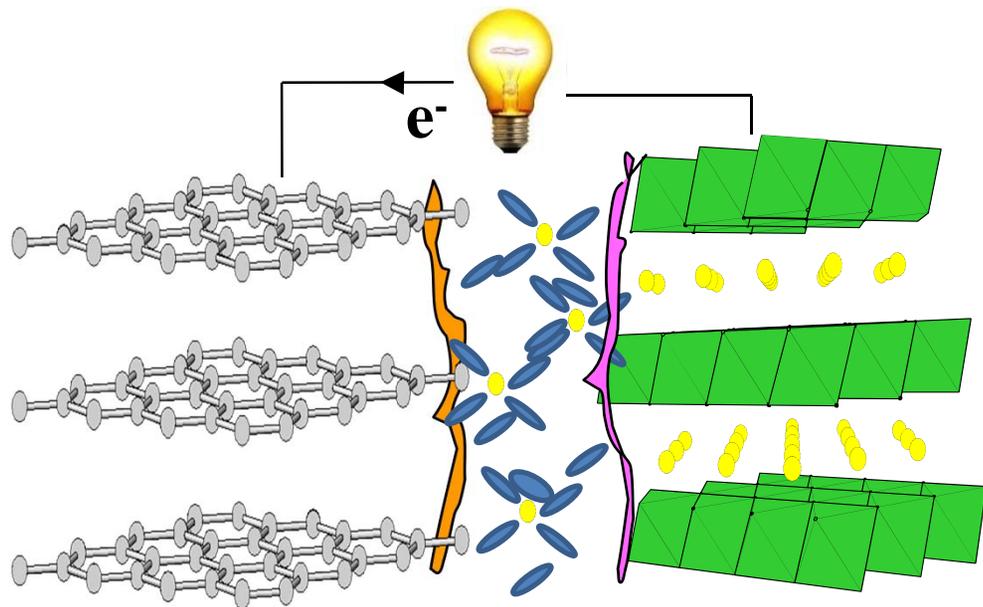
- High energy density (W/kg), about 50% better than Nicads, but only about 60% of Lithium ion.
- Low internal impedance though not as low as NiCads
- Typical cycle life is 3000 cycles.
- Can be deep cycled. (80% to 100% DOD)
- Robust - NiMH batteries also tolerate over charge and over discharge conditions and this simplifies the battery management requirements.
- Flat discharge characteristic (but falls off rapidly at the end of the cycle)
- Wide operating temperature range
- Rapid charge possible in 1 hour
- Environmentally friendly (No Cadmium, Mercury or Lead)
- Much safer than Lithium based cells in case of an accident or abuse due to the use of more benign active chemicals, a particularly important property in high power and automotive applications.



Shortcomings

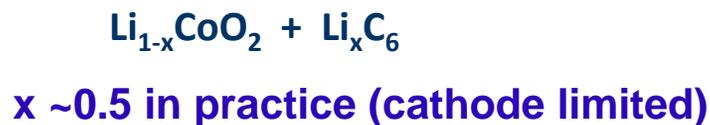
- High self discharge rate.
- Cell voltage is only 1.2 Volts.
- Lower capacity and cell voltage than alkaline primary cells.
- Limited supplies of rare earth element Lanthanum. Mostly in China.

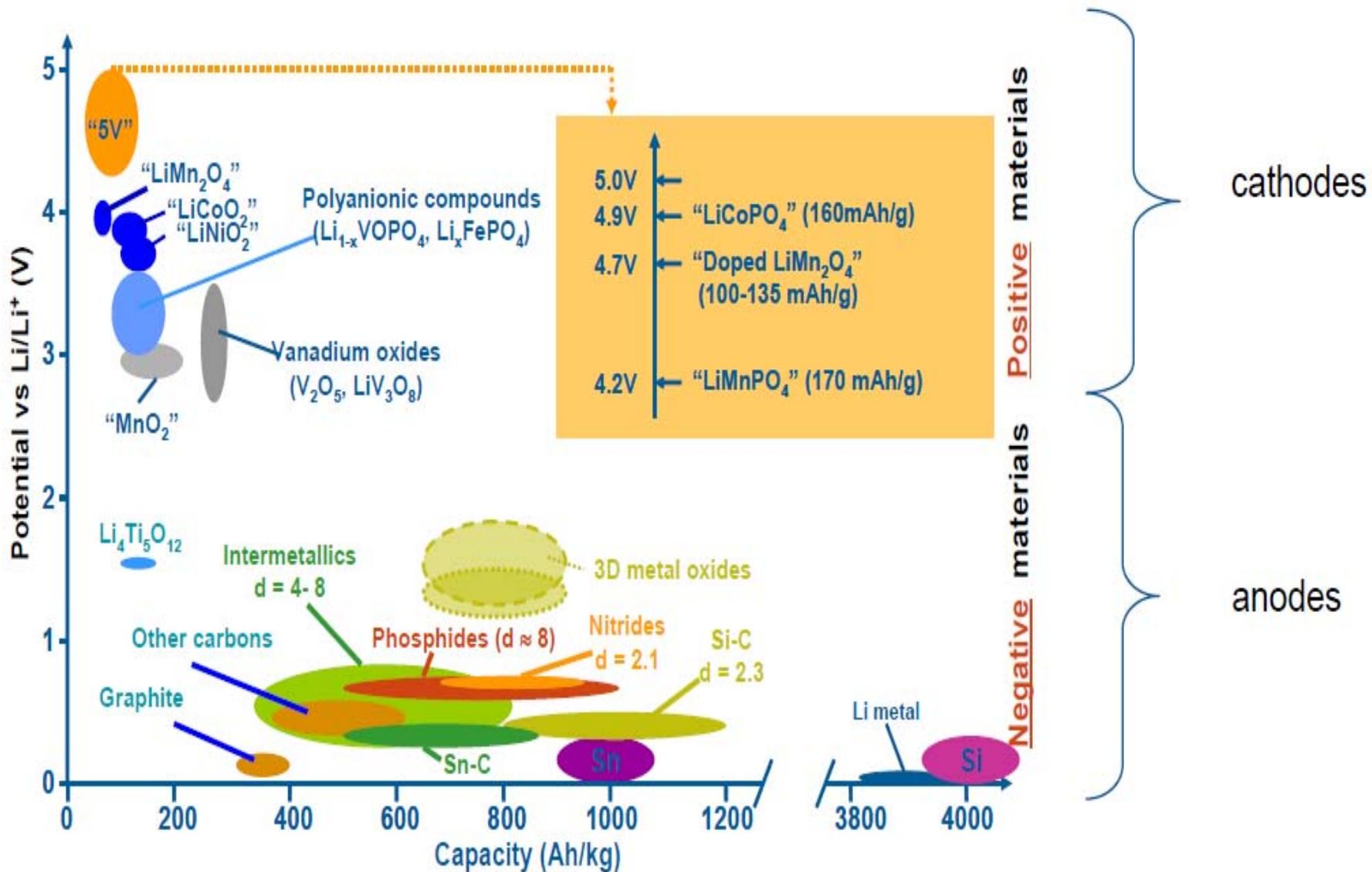
Schematic of a $\text{Li}_x\text{C}_6/\text{Li}_{1-x}\text{CoO}_2$ Li-Ion Cell Commercialized by Sony in 1991



Li_xC_6 (Anode)

LiCoO_2 (Cathode)





Acc. To Prof. J. M. Tarascon (Amiens)

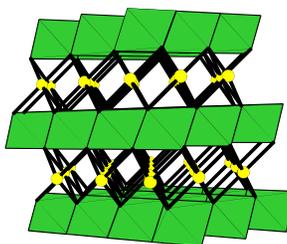
Cathodes

- Improve safety (oxygen loss at full charge)
- Increase Power (HEVs) and Energy (PHEVs & PEV-EVs)
- Increase Long-term life and material stability
- Decrease Cost! –
 - Replace the costly $\text{Li}_{1-x}\text{CoO}_2$ (or doped $\text{Li}_{1-x}\text{Co}_{1-y}\text{M}_y\text{O}_2$) with a Mn or Fe-based cathode. Cell phone battery contains ~\$2.50 of cobalt (by weight)
 - ~ 8% cost battery pack is cathode
 - Co metal cathode cost in battery pack is \$640
 - Mn < 5% cost of Co
 - Fe ~ 1/3 cost of Mn (July '08; scrap iron \$0.40/lb)*



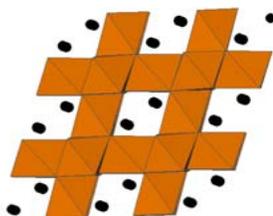
Li-Ion Batteries: 3.5 - 4 V Cathode Materials Limitations

**Ordered
Rocksalt
Layered**
 LiMO_2
(**M=Co, Ni, Mn**)



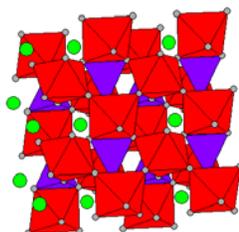
- **Capacity limited** to ~ 0.5 Li per M atom (i.e., **~ 140 mAh/g**)
- Co^{4+} and Ni^{4+} unstable/highly oxidizing
- Structure destabilized at low Li content
- Layered LiMnO_2 transforms to spinel

Spinel
 LiM_2O_4
(**M=Mn**)



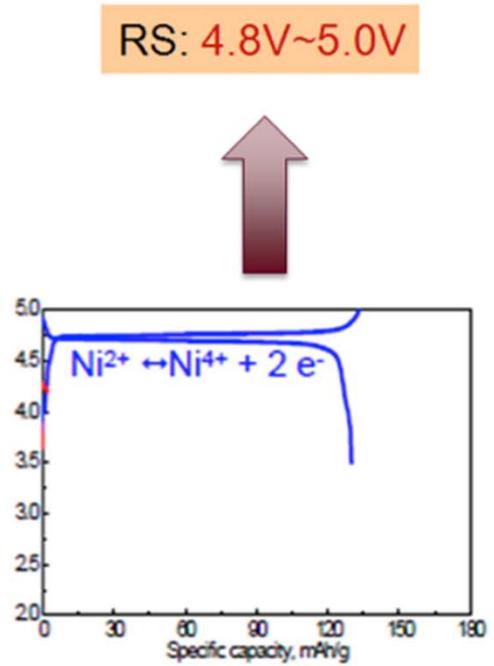
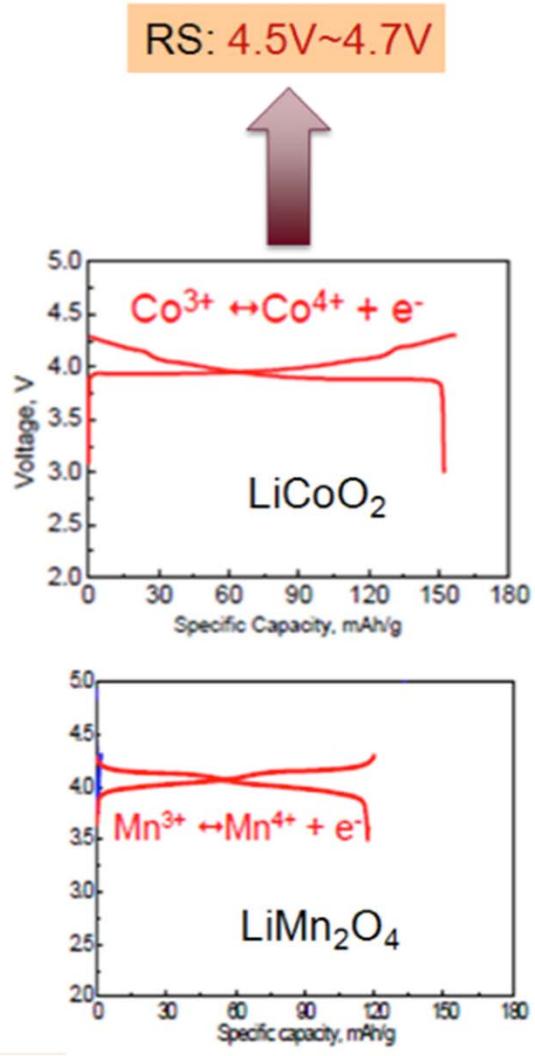
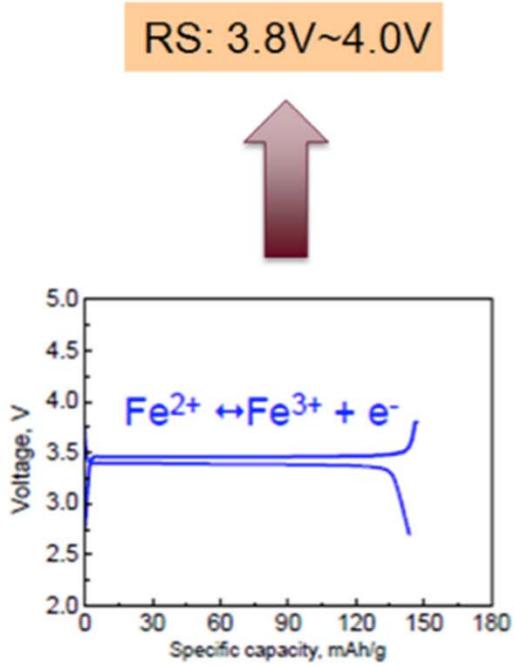
- **Capacity limited** to < 0.5 Li/Mn at 4 V
- Robust M_2O_4 spinel framework; 3-D channels
- **High rate capability**
- Jahn-Teller (Mn^{3+}) distortion at 3 V
- Solubility problems at high potentials

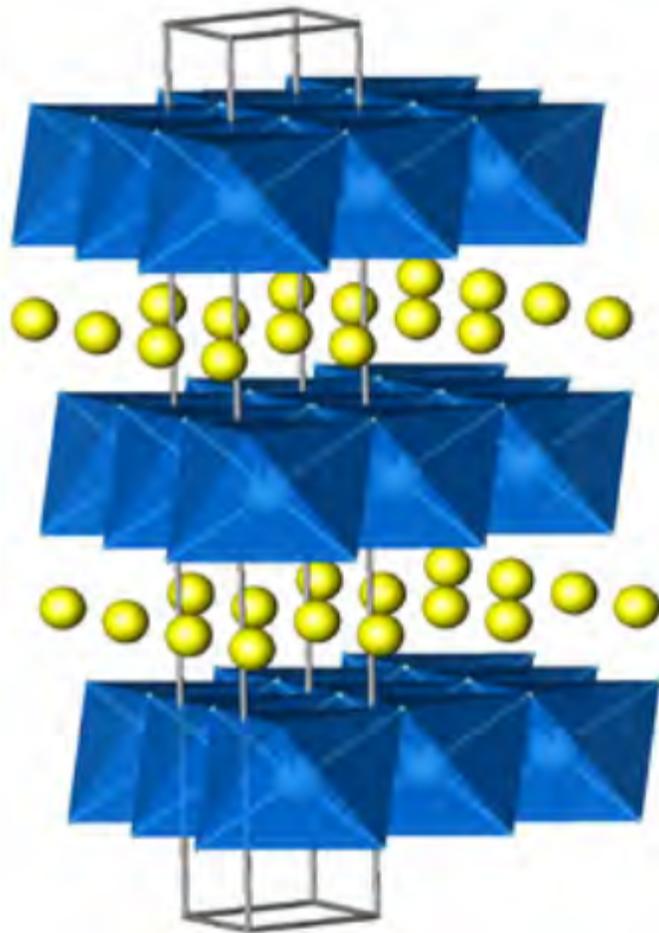
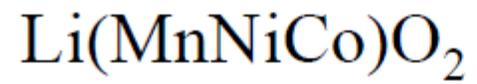
Olivine
 LiMPO_4
(**M=Fe, Mn**)



- **Capacity limited** to 1 Li/Fe; P inactive
- Excellent structural stability; 1-D channels
- Poor electronic and Li-ion conductivity
- Poor packing density



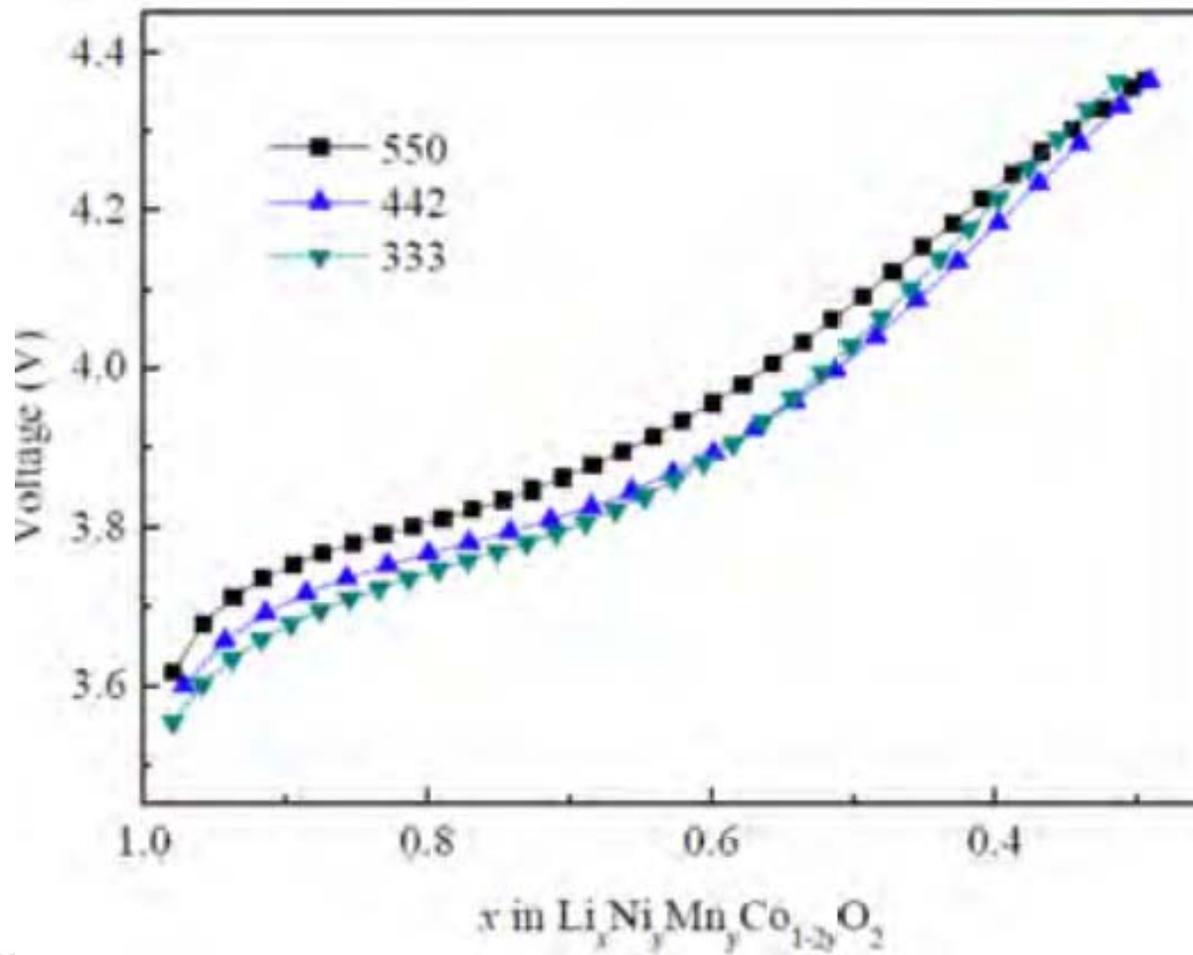




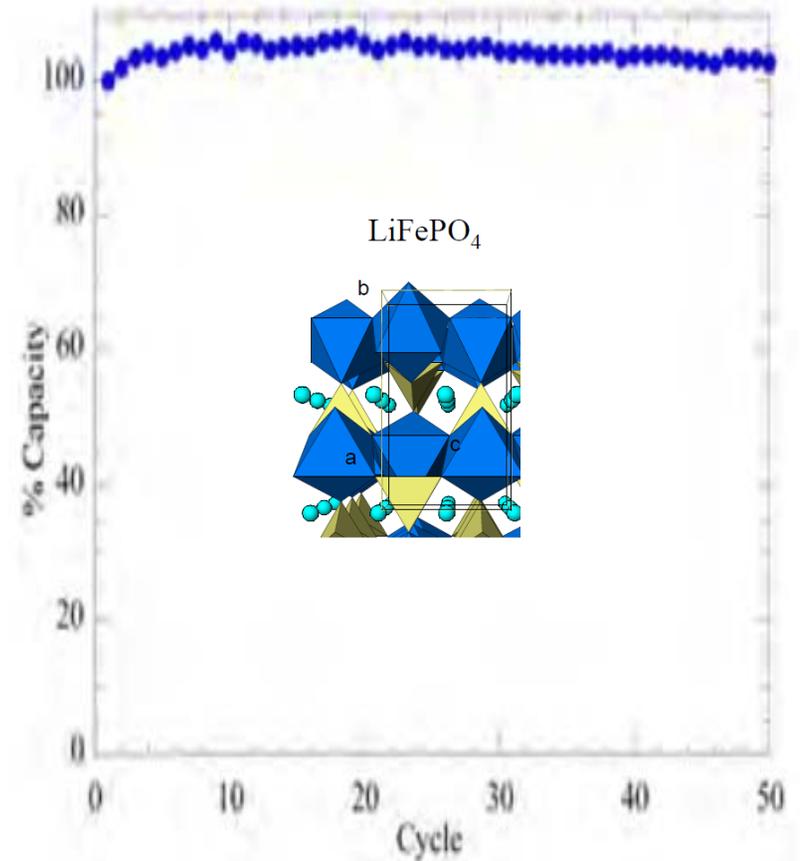
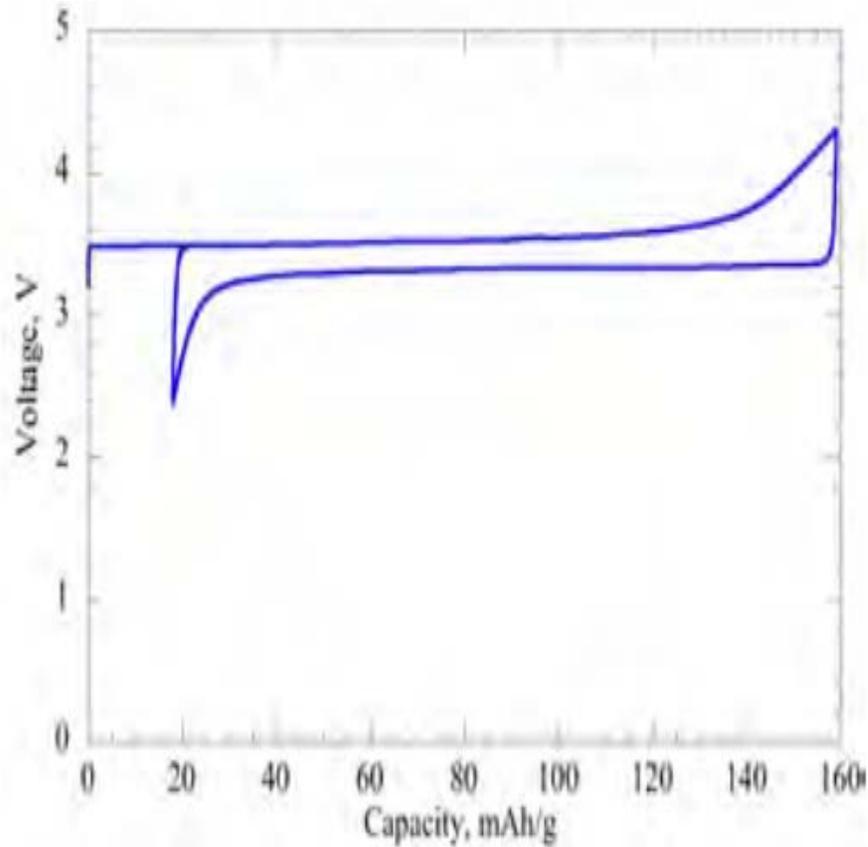
MO_6 octahedra

LiO_6 octahedra

Composition can be adjusted for optimal performance



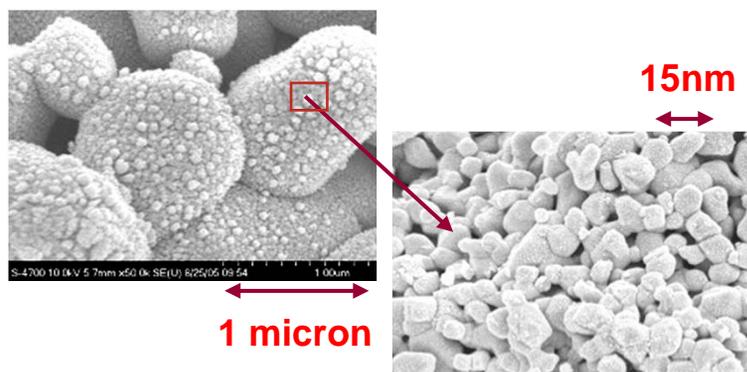
Lithium Iron Phosphate



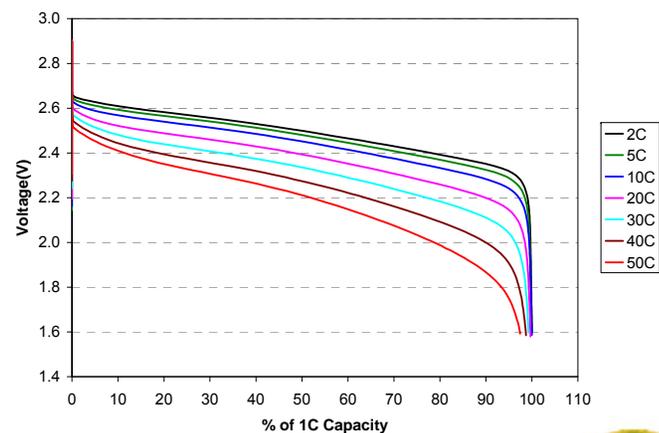
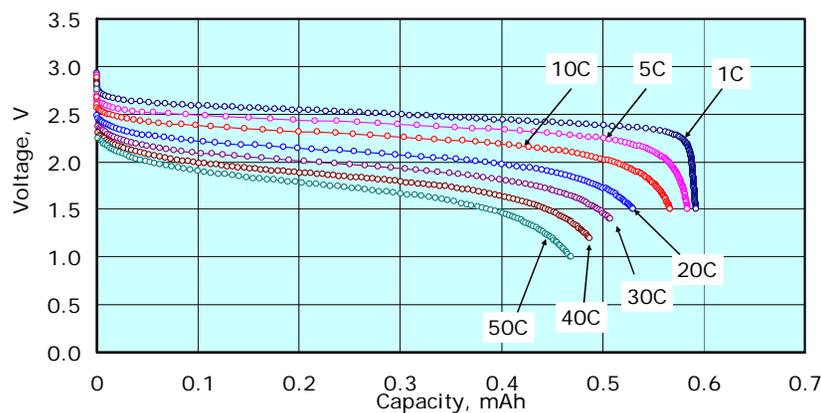
High-Power Cell Chemistry for HEV Applications

Nano-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_{1.06}\text{Mn}_{1.94}\text{O}_4$ spinel

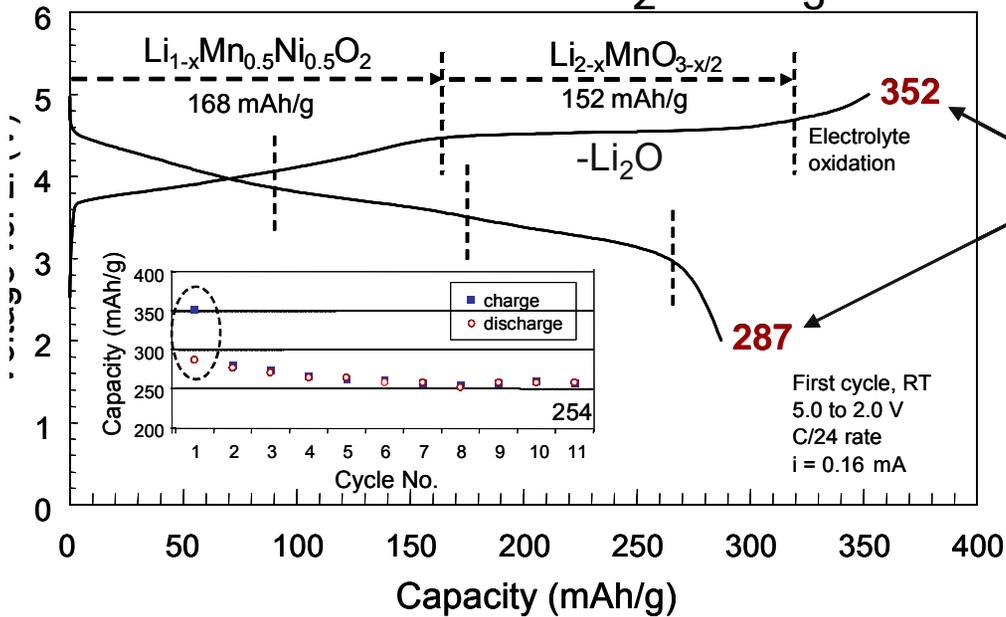
Argonne's nano-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$



- Very high rate capability
- No lithium plating during regen at low temperature
- No SEI & resulting heat from decomposition
- Limited surface reactivity with electrolyte
- Zero volume change—no structural stress



Electrochemistry of a Li/0.3Li₂MnO₃•0.7LiMn_{0.5}Ni_{0.5}O₂ Cell



1st cycle
irreversible
capacity loss



- Theoretical capacity of LiMn_{0.5}Ni_{0.5}O₂ Component: 184 mAh/g
- Theoretical capacity of Li₂MnO₃ Component: 158 mAh/g
- Theoretical charge capacity (total): 342 mAh/g
- Coulombic efficiency: 82% (1st cycle); >99% (10th cycle)
- Capacity (10th cycle): 254 mAh/g

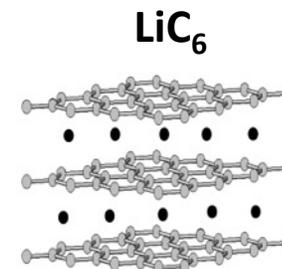
<http://www.anl.gov/articles/gm-argonne-sign-licensing-deal-advanced-battery-chemistry>

http://web.anl.gov/pse/Publications/success_stories/cathode_tech_licensing.html

Alternative Anodes

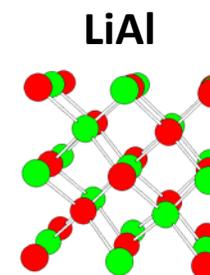
Carbon

- **Graphite:** <100 mV vs. Li^0
- Moderate capacity (372 mAh/g)
- Highly reactive, surface protection necessary



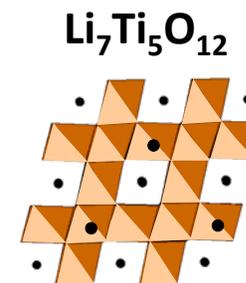
Metals, Semi-metals and Intermetallic Compounds

- Al, Si, CoSn, Cu_6Sn_5 : <0.5 V vs. Li^0
- High gravimetric/volumetric capacities (1000-4000 mAh/g)
- Large volume expansion on reaction with lithium
- Reactive, surface protection required
- **Greatest opportunity and challenge**



Metal Oxides

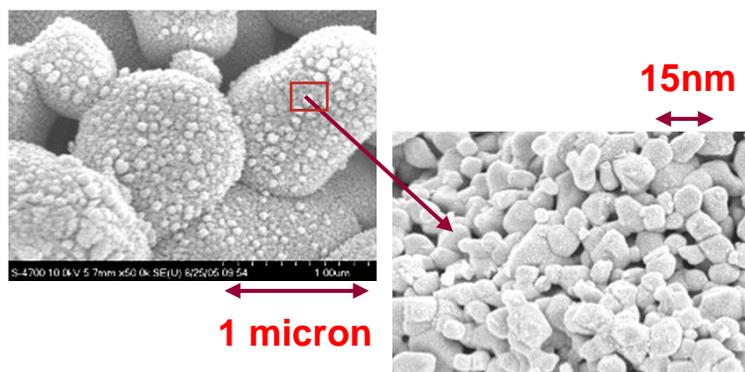
- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$) Spinel: 1.5 V vs. Li^0
- Low capacity (175 mAh/g)
- Very high rate capability
- Stable in nanoparticulate form



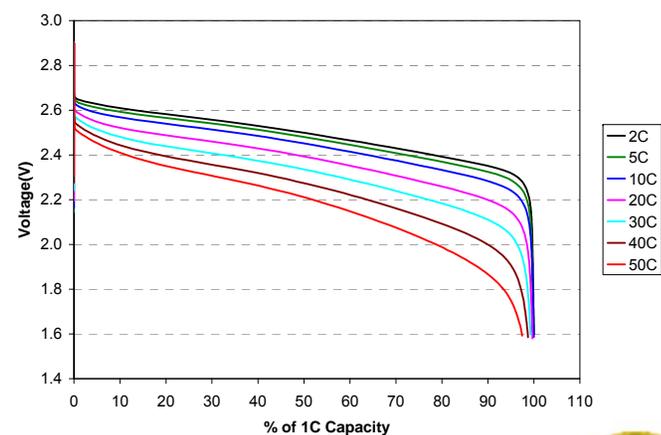
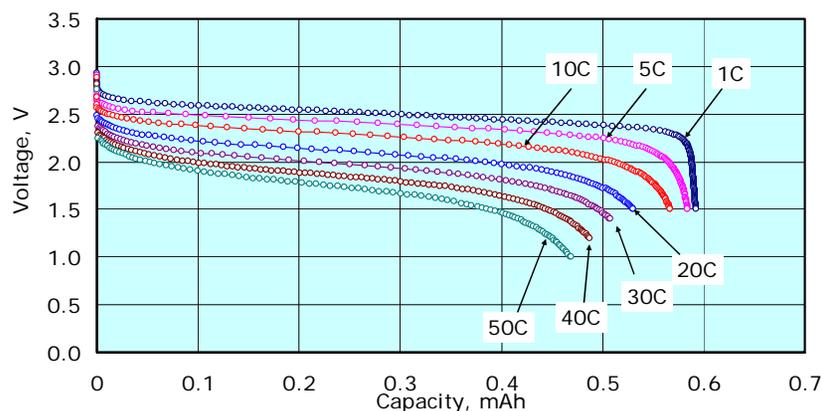
High-Power Cell Chemistry for HEV Applications

Nano-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_{1.06}\text{Mn}_{1.94}\text{O}_4$ spinel

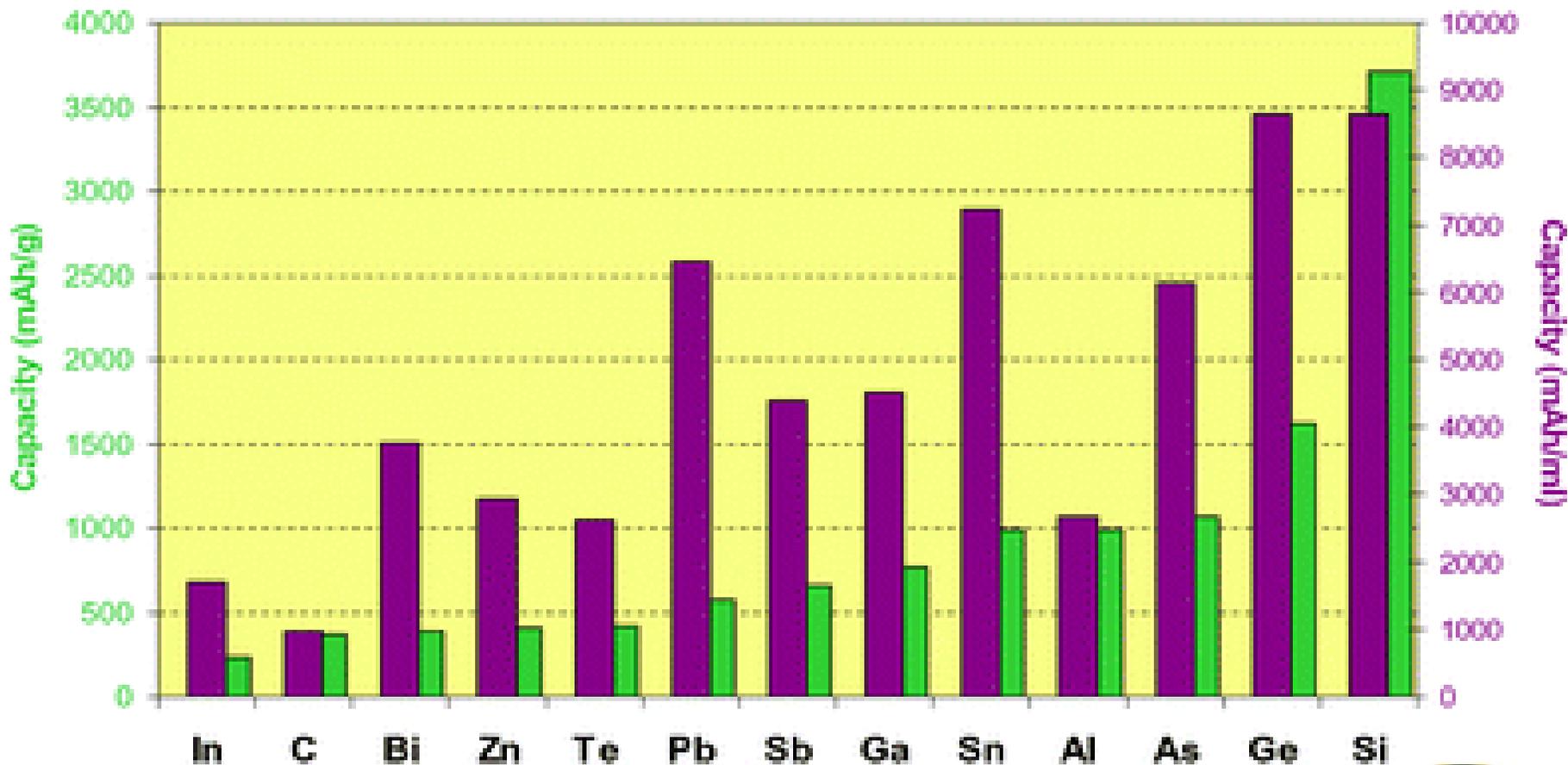
Argonne's nano-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$



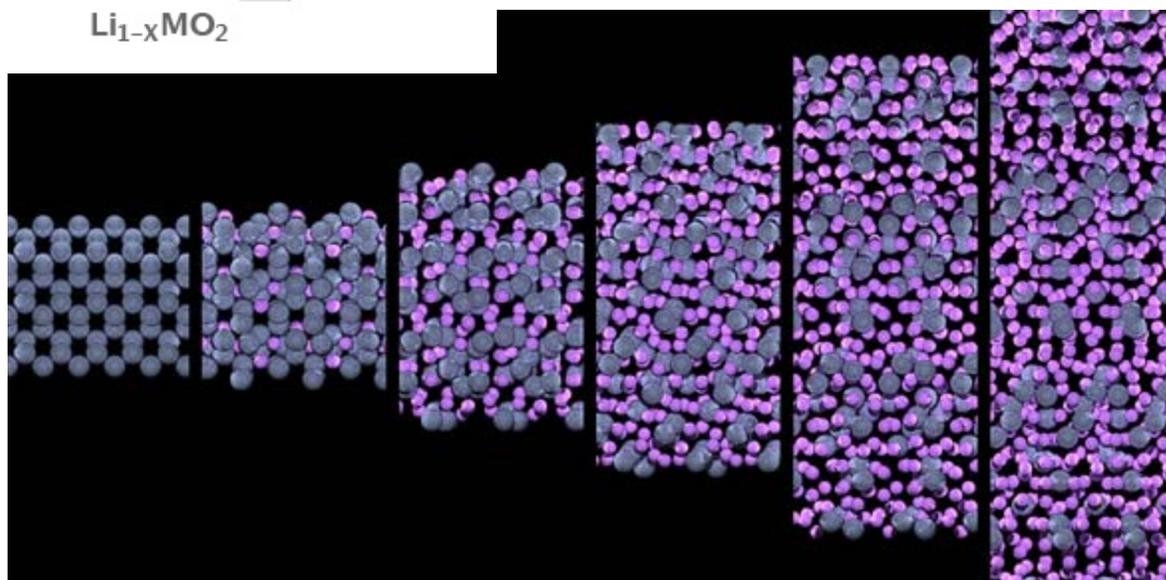
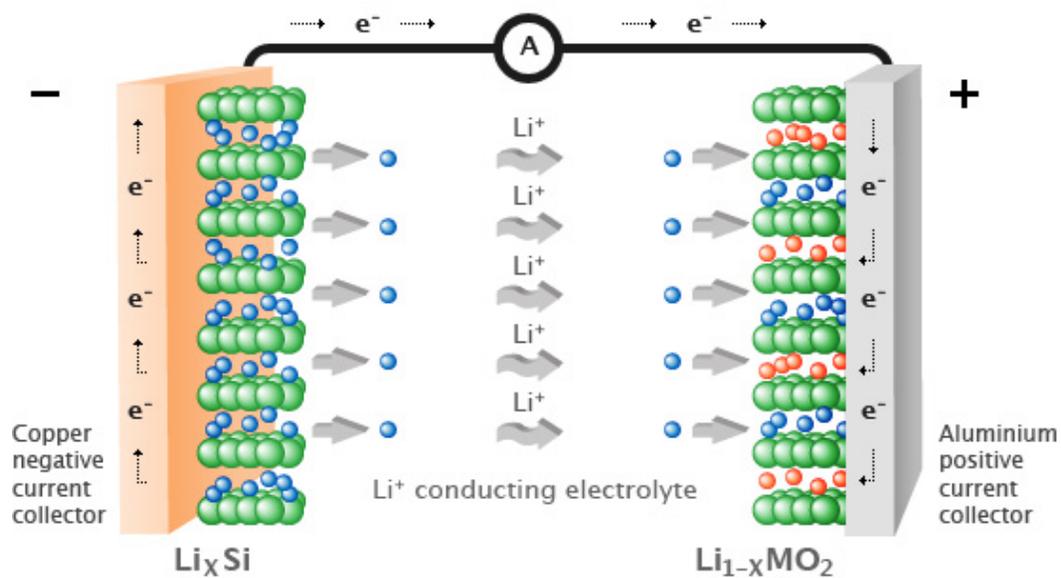
- Very high rate capability
- No lithium plating during regen at low temperature
- No SEI & resulting heat from decomposition
- Limited surface reactivity with electrolyte
- Zero volume change—no structural stress

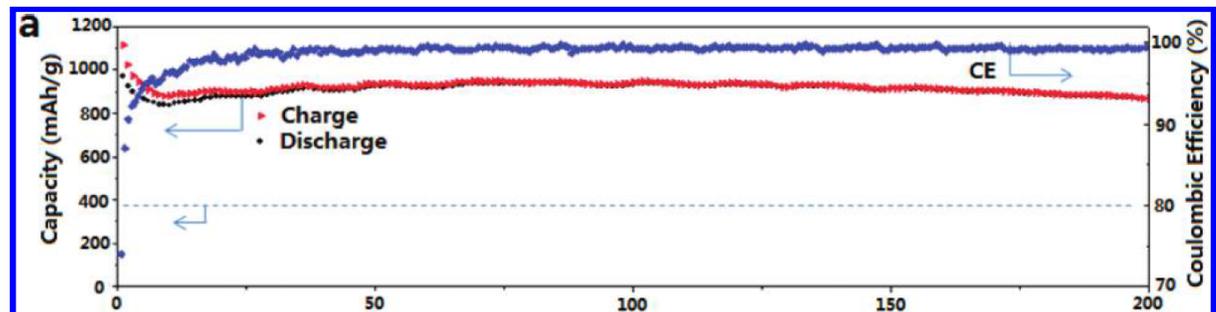
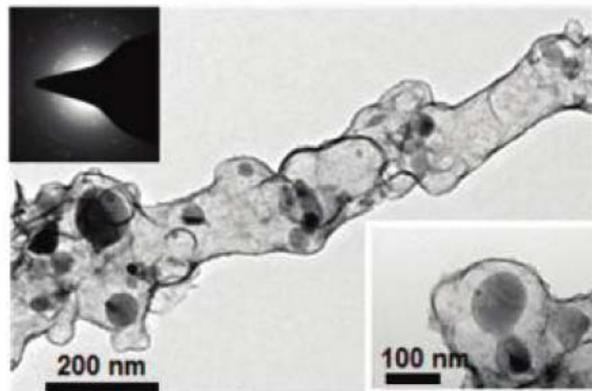
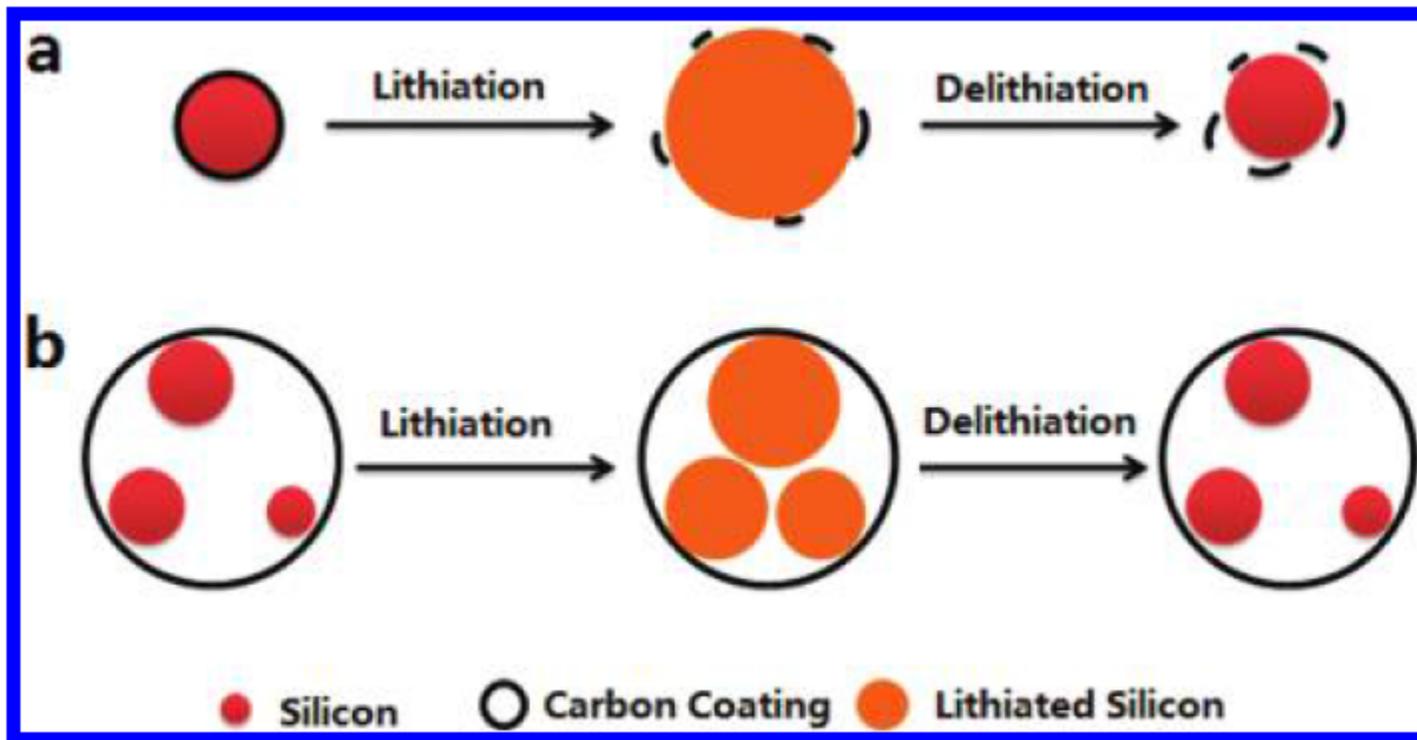


Capacities of Alternative Anodes



Silicon Anodes

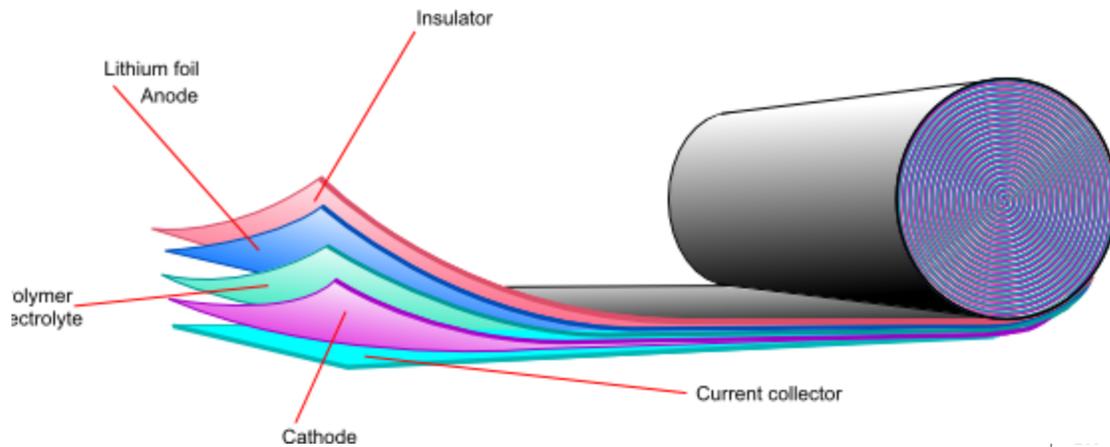




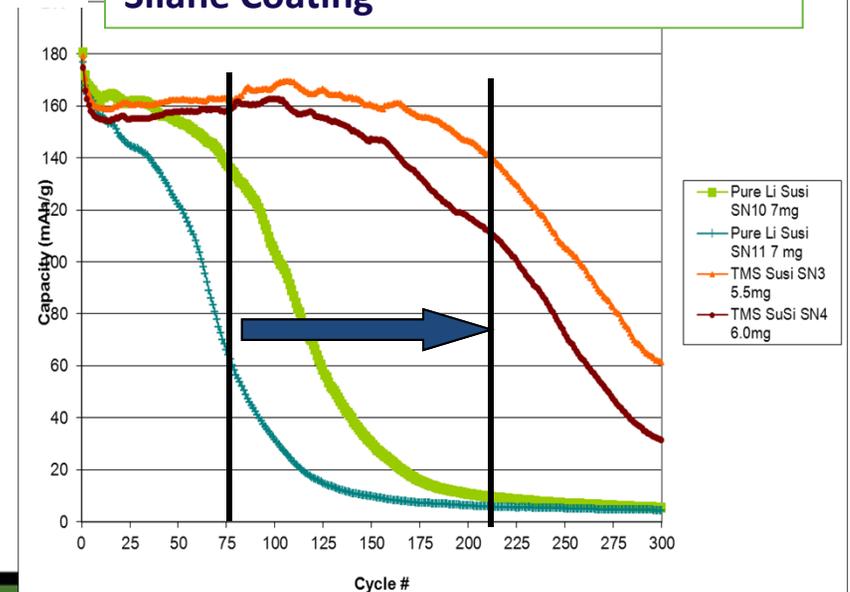
Nano Lett. 2012, 12, 904–909



Lithium Metal – The Ultimate Anode



Electrochemical Cycling using a Silane Coating





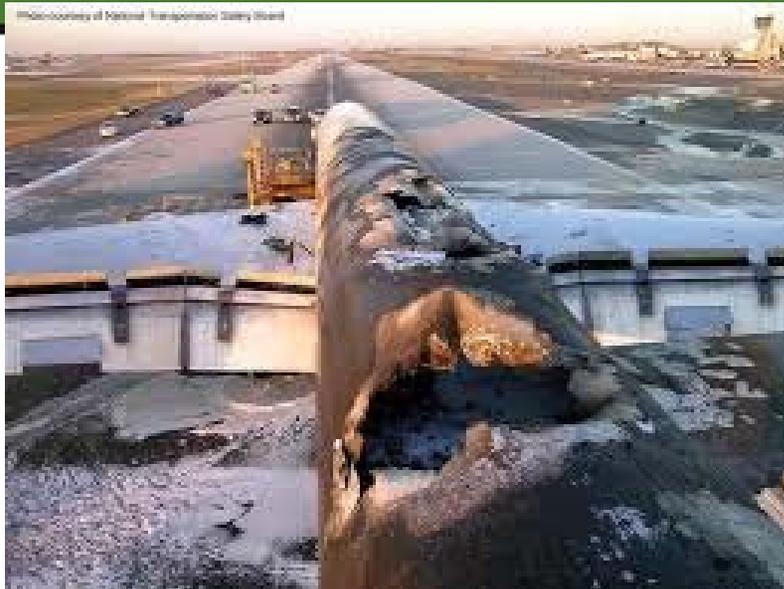
Russ Chianelli -
Exxon



AT&T U-verse batteries going supernova
BY [Steven Kim](#) January 16th 2008, at
8:51:00 am ET

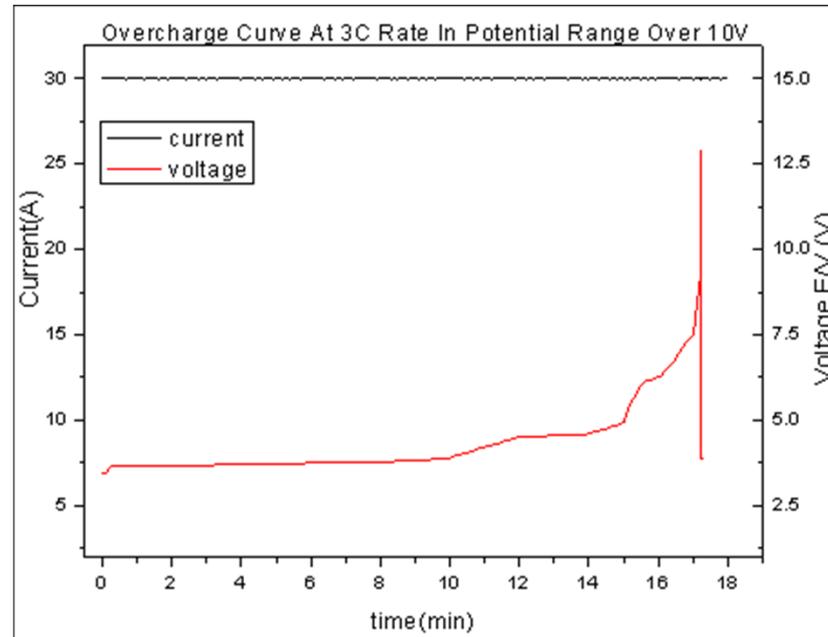


Photo courtesy of National Transportation Safety Board





Safety Issues: Overcharge Abuse and Preventions



Overcharge Protection Methods:

Typical charging voltage profile of a lithium ion cell during overcharge.

1. Electronic circuit:
2. Electrolyte Additives - redox shuttles
3. Electroactive polymer

Low Voltage Redox Shuttle for LiFePO₄ Cathode

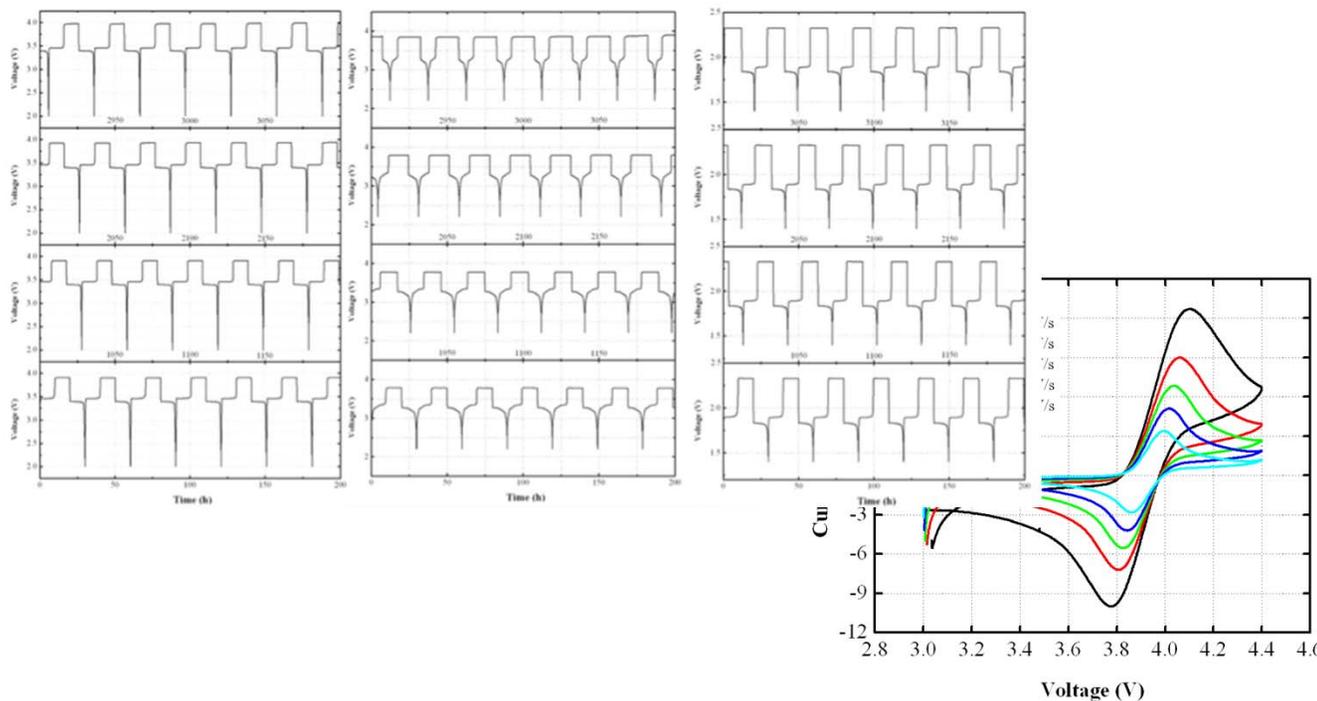
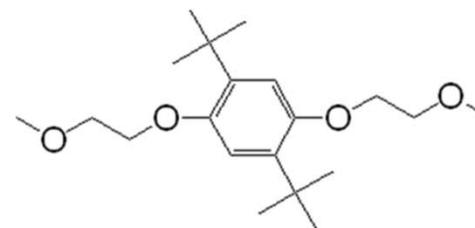
ANL-RS-2 Overcharge Protection for Li/LiFePO₄,
MCMB/LiFePO₄, Li₄Ti₅O₁₂/LiFePO₄ Cells

Li/LiFePO₄

MCMB/LiFePO₄

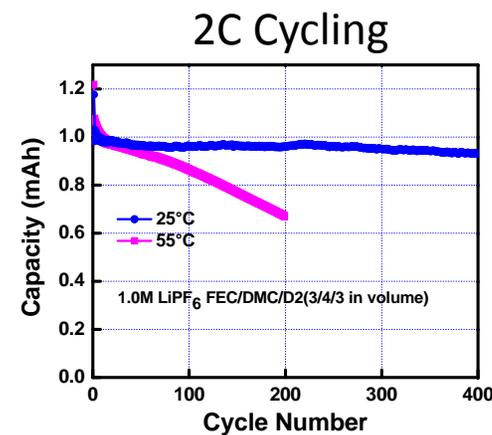
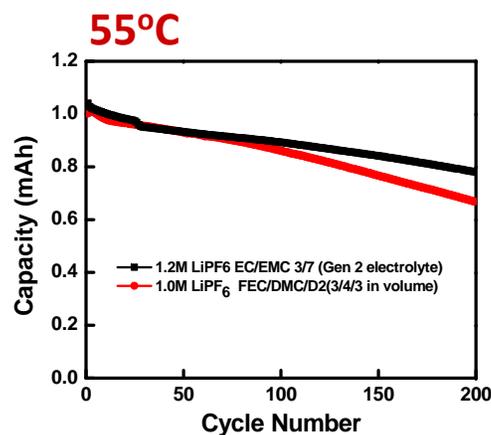
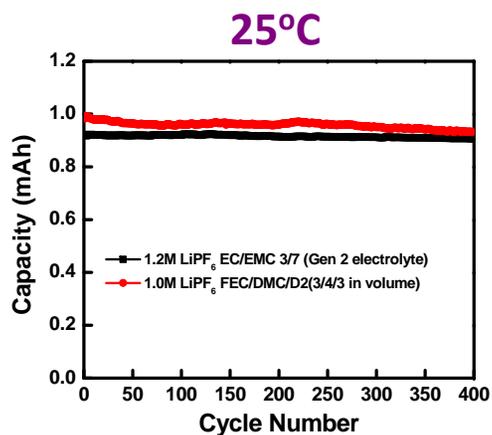
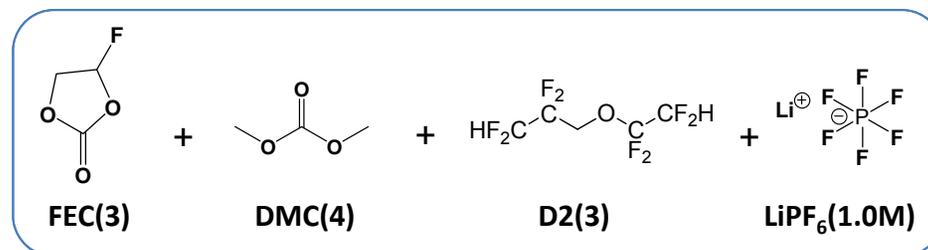
Li₄Ti₅O₁₂/LiFePO₄

(10h charging + 10h overcharging + 10h discharging → 30h for one overcharging cycle)



Increase the carbon number between the two oxygen atoms significantly improve the electrochemical stability, as a result ANL-2 exhibits perfectly reversible redox peaks at 3.9 V vs Li/Li⁺

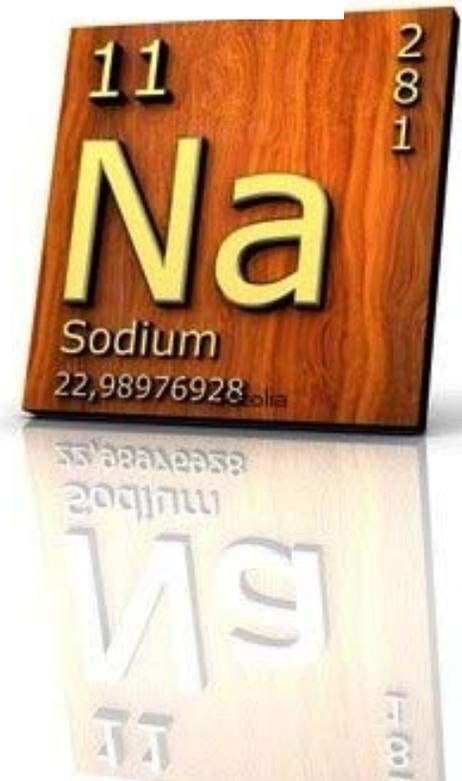
Electrolyte Performance in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ~5 Volt Cell at Elevated Temperature



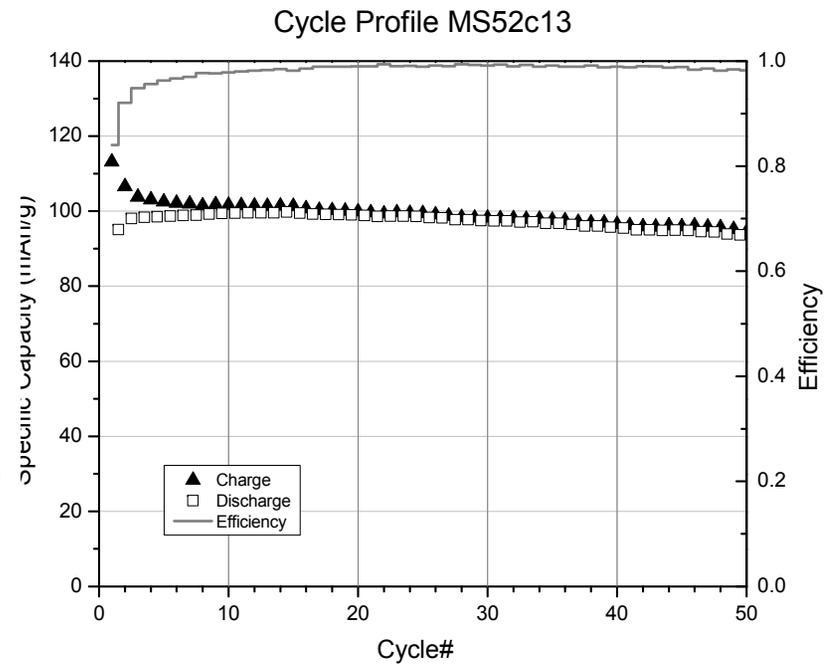
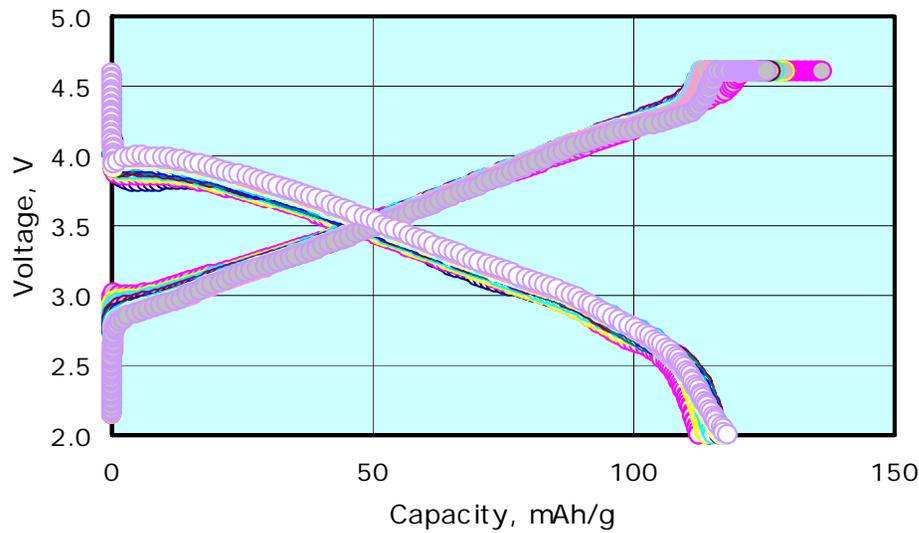
BEYOND TRADITIONAL LITHIUM ION

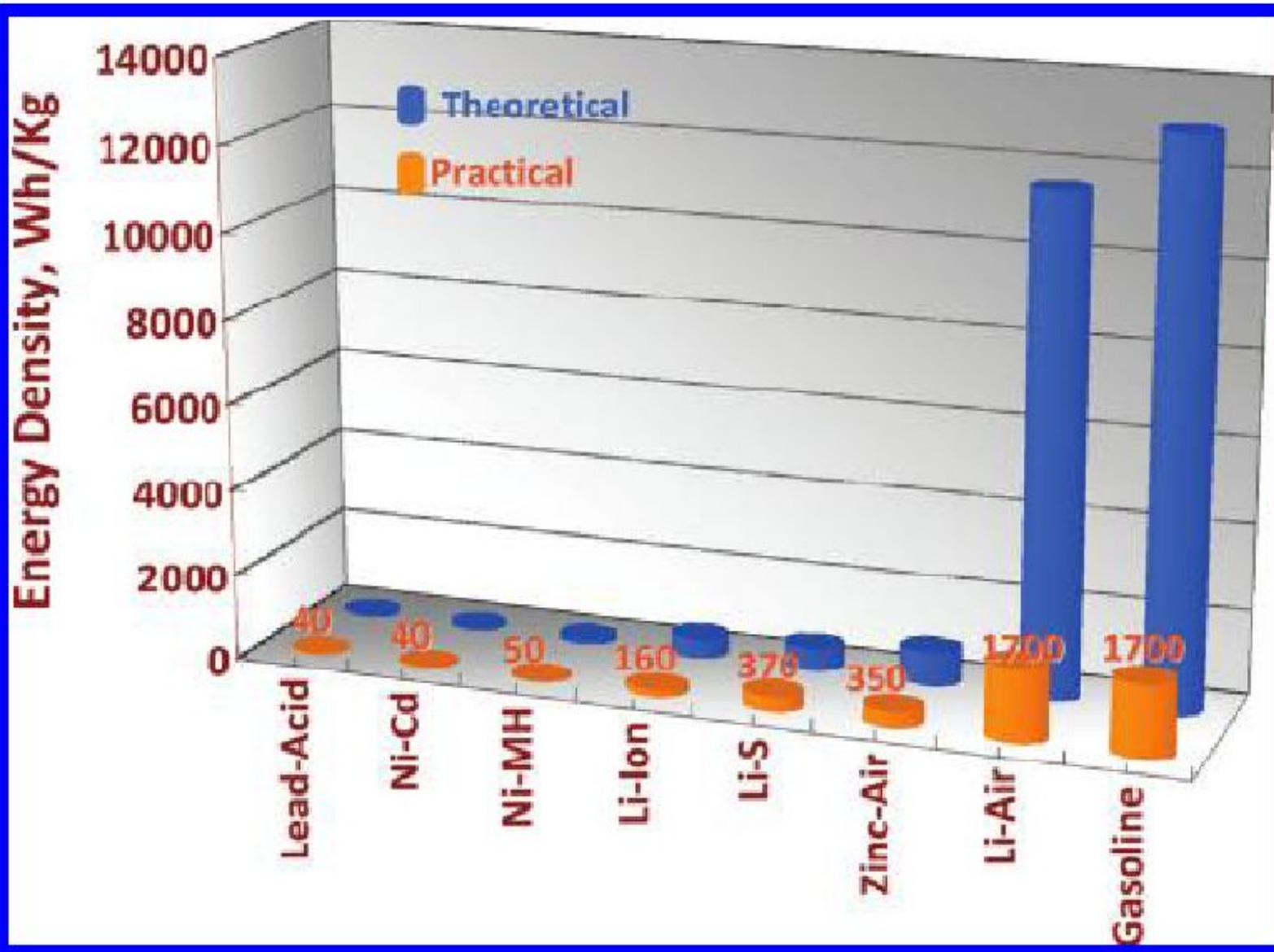
Why Na-ion and where are we going?

- On the surface Na-ion is compared to Li-ion –is this fair?
- Is this...and do we need... a backup technology to Li-ion?
- Driver(?) – Cost and abundance; Na is an insurance to lithium price fluctuation, availability
- Na-ion ?....just beginning...

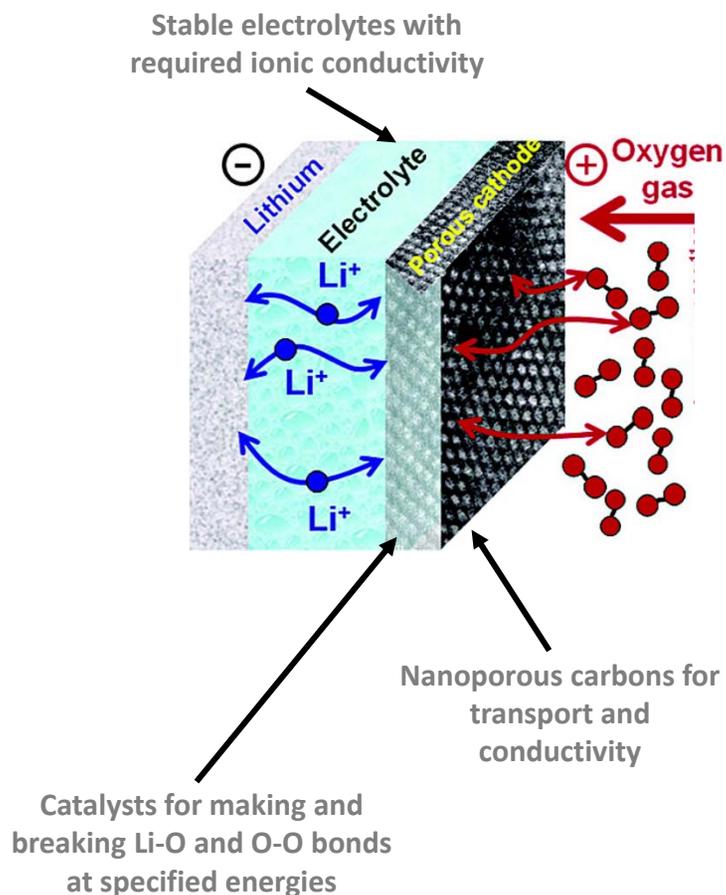


Cycling performance - Na half cell





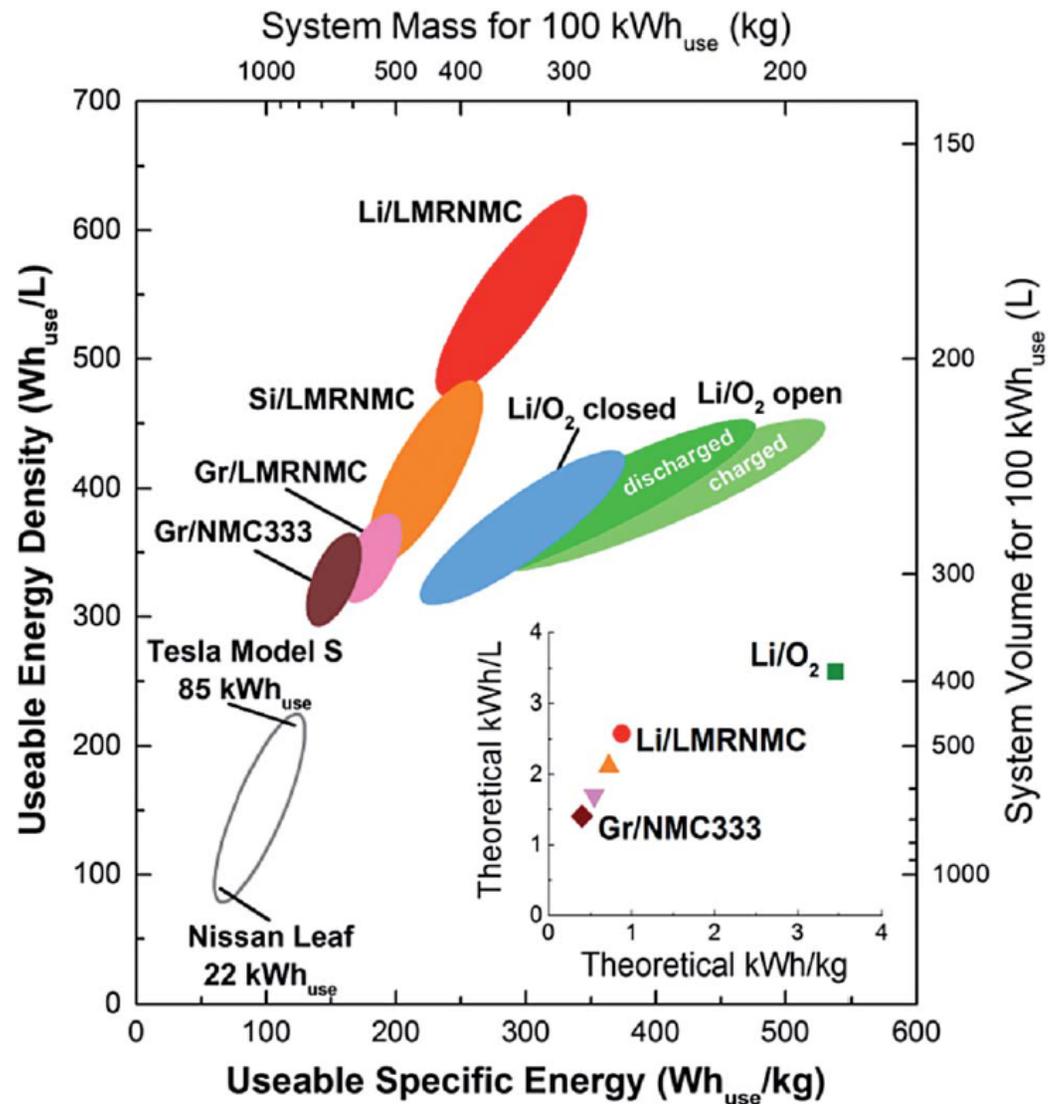
Li-Air Battery



High-Risk High-Reward R&D Project

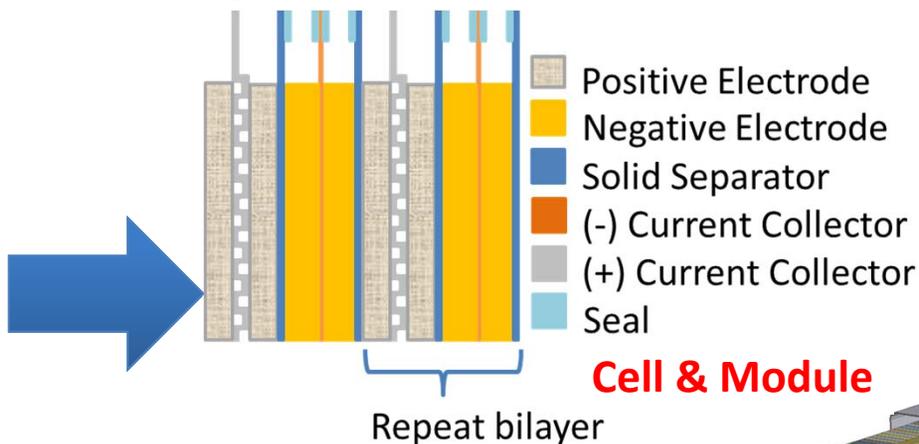
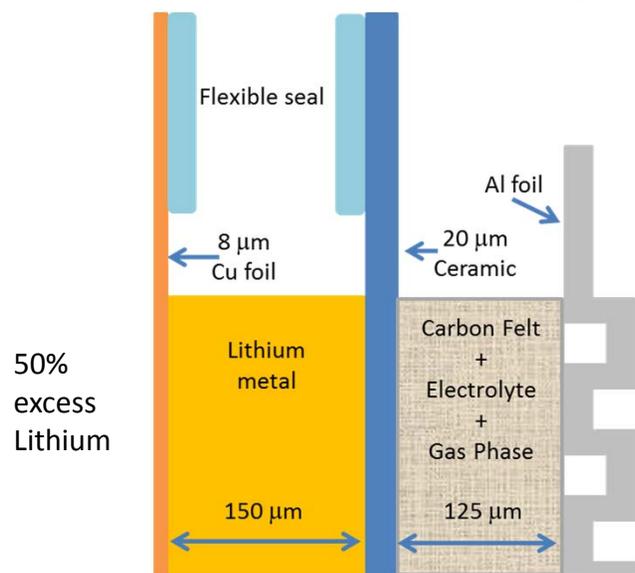
- Offers **10-fold increase in specific energy** over Li-ion
- Possesses several extremely challenging barriers:
 - Li metal dendrite formation at anode
 - Lithium peroxide formation & plugging of cathode pores
 - Flooding of cathode with electrolyte & leakage
 - Low power & poor efficiency

Li – Oxygen not much better than Li-ion



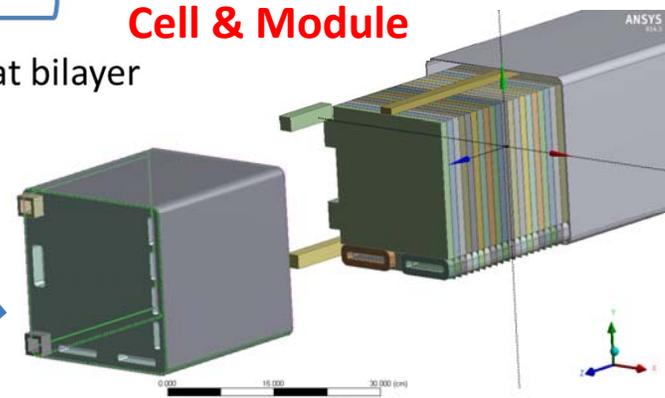
Multiple scales and approaches to design

Electrode Sizing



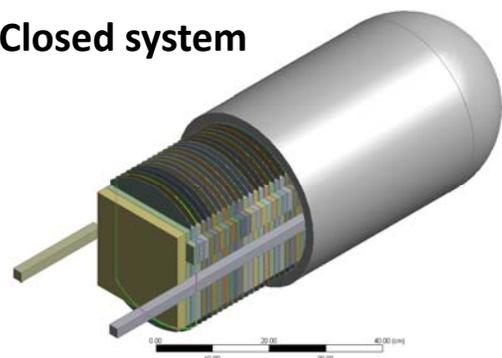
Li-O₂ Chemistry

Cell & Module

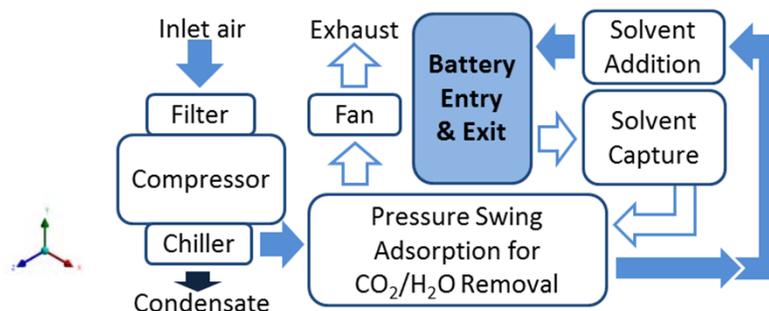


Pack & System

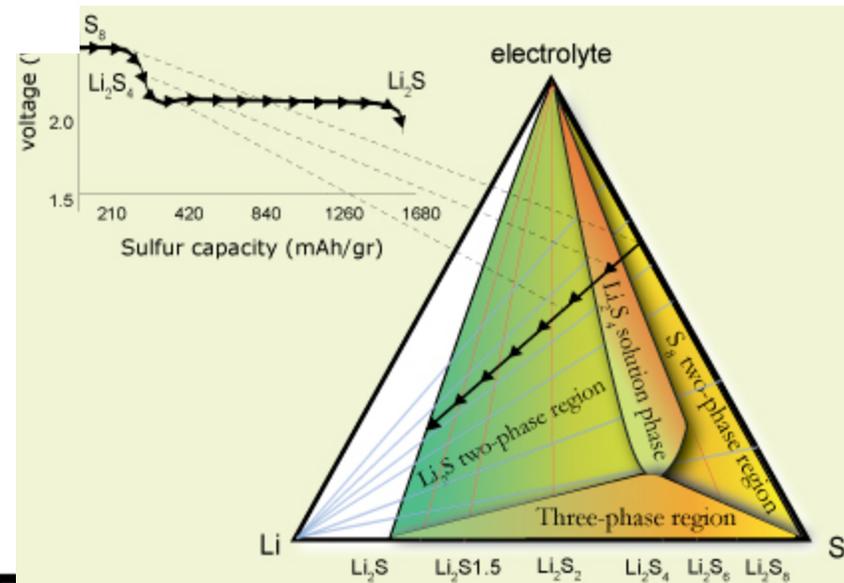
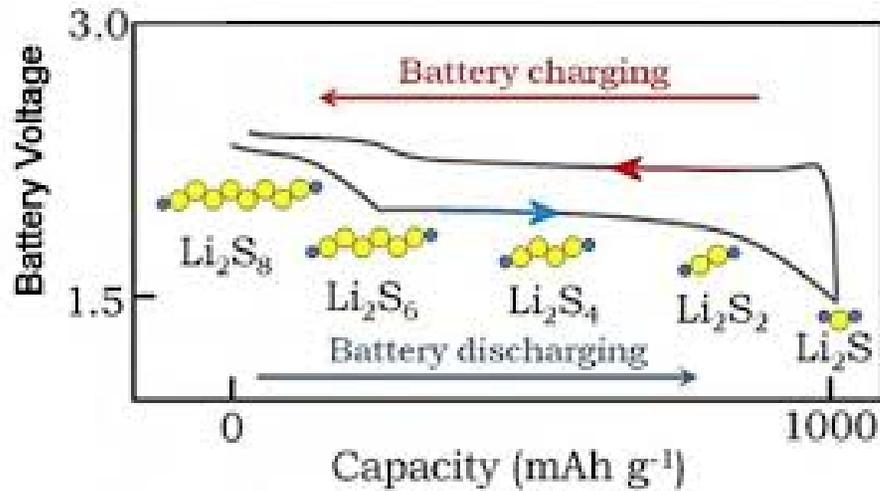
Closed system



Open system



Li - Sulfur

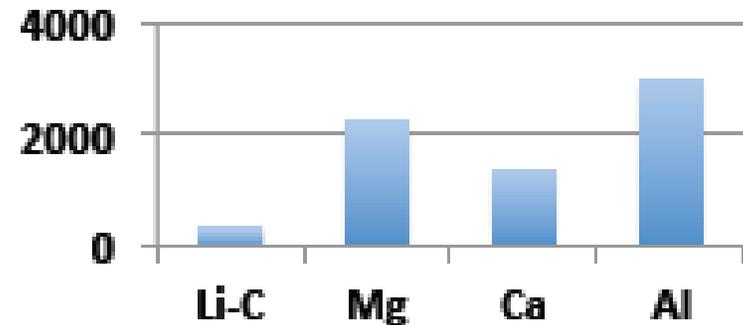


Could Mg²⁺ batteries be better than Li⁺?

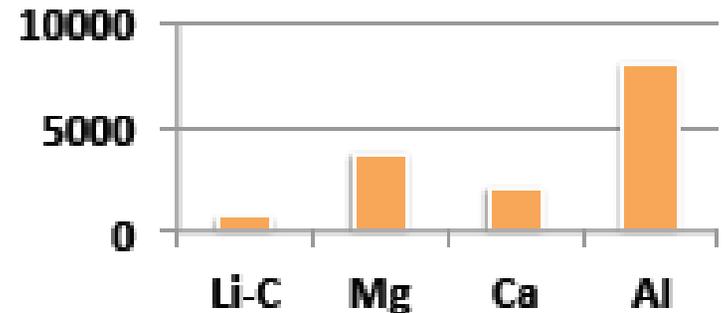
Advantages of Mg²⁺:

- 2 electrons per cation
Higher theoretical volumetric capacity:
3800 mAh/cm³
- Mg metal anode can be used
- Mg may be safer than Li

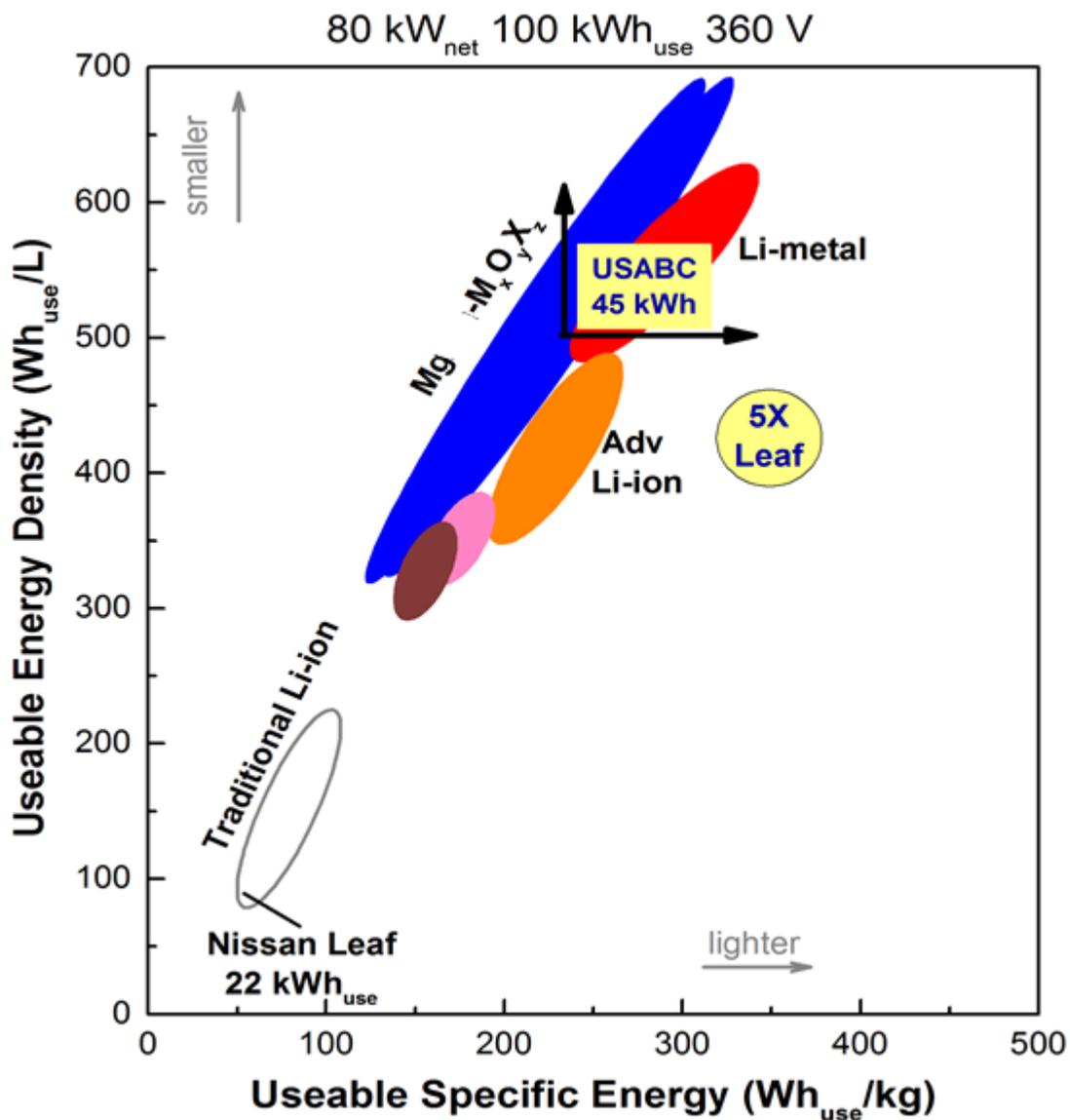
Specific Capacity (Ah/kg)



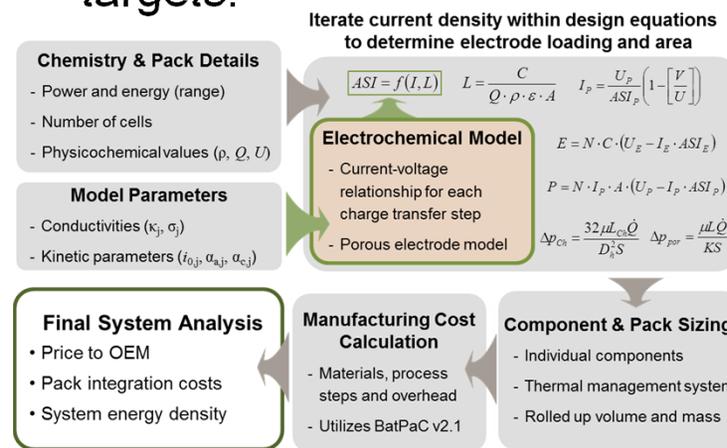
Capacity Density (Ah/l)



Yoo, H. D. *et al. Energy Environ. Sci.*, **2013**, 6, 2265.



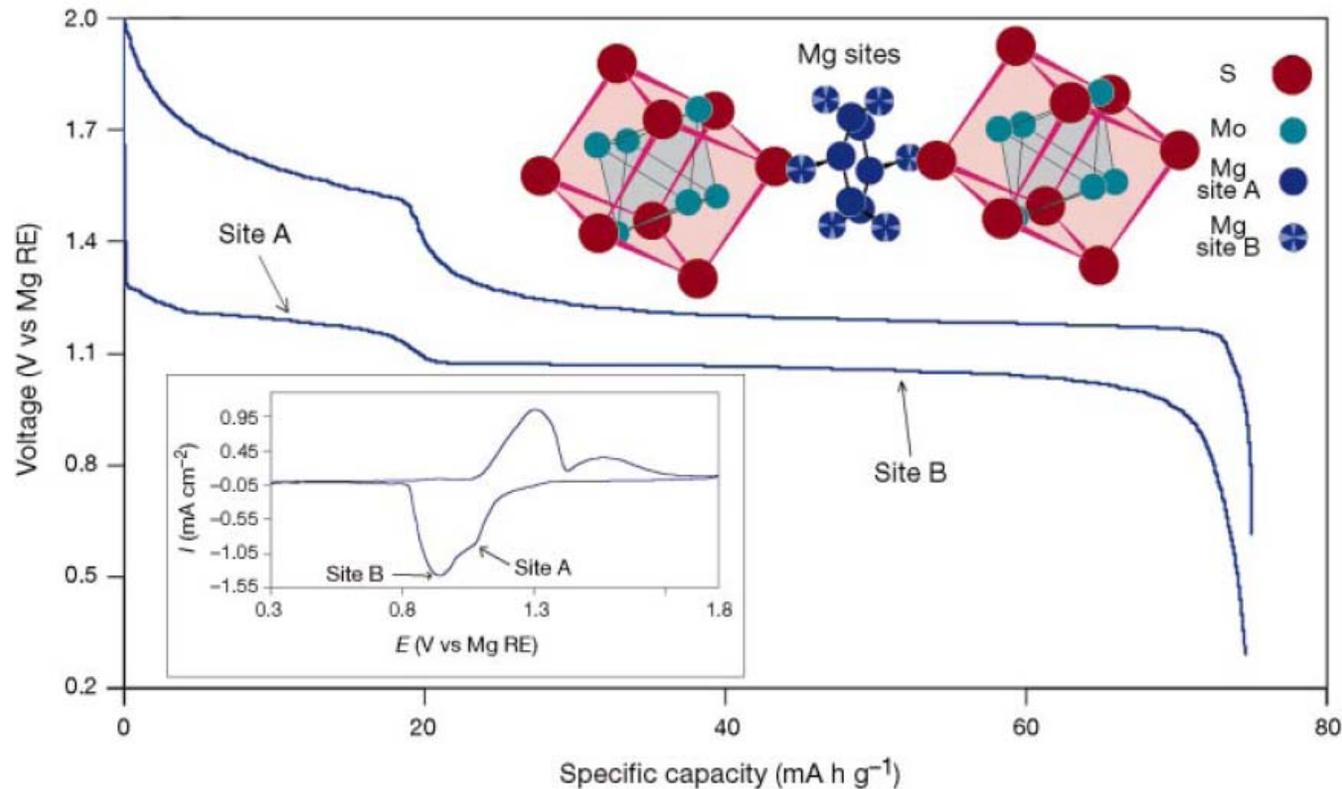
Based upon Systems Analysis and Translation analysis of full cells using metal electrodes MV can make the 5x energy density targets.



•Builds upon BatPaC: Peer-reviewed Li-ion model

www.cse.anl.gov/batpac

History



D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, and E. Levi. Prototype systems for rechargeable magnesium batteries. *Nature*, 407(6805):724–727, October 2000.

Our Team

5

National
Laboratories

ANL, LBNL,
Sandia,
PNNL, SLAC

5

Universities

UIC, UC, NU,
UIUC, UM

4

Private-
Sector
Partners

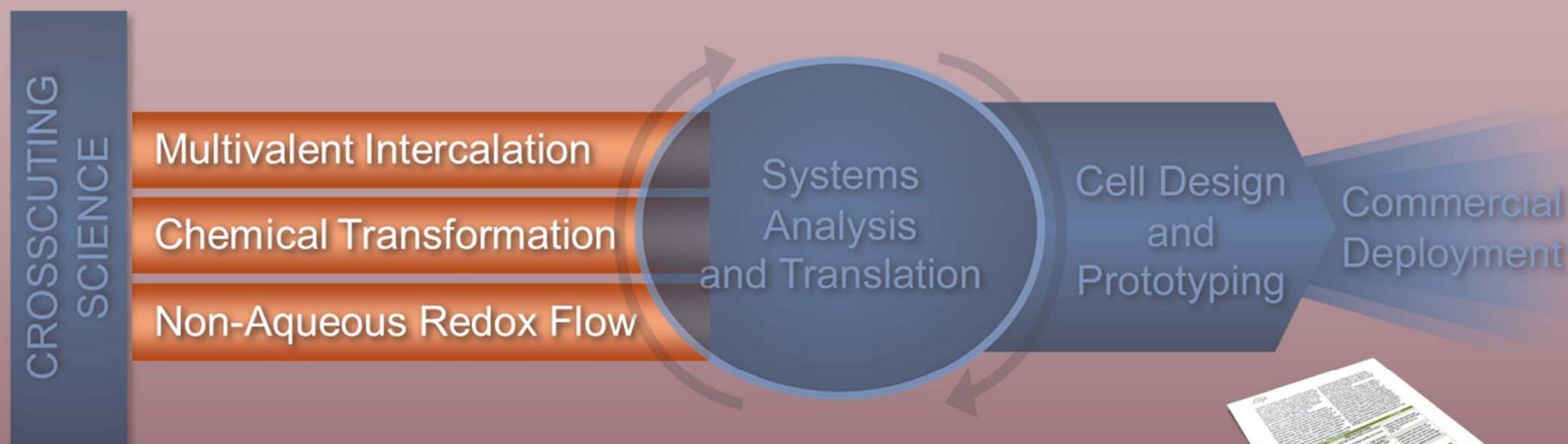
Dow, JCI,
AMAT,
CET





JCESR Distinguishing Approach

CONCEPTS NOT TECHNOLOGIES



FUNDAMENTAL SCIENCE CHALLENGES

Multivalent Intercalation

- *Mobility in host structures*
- *Mobility across interfaces*
- *Stable and selective interfaces*

Chemical Transformation

- *Phase transformation and juxtaposition*
- *Functional electrolytes*
- *Stable and selective interfaces*

Non-Aqueous Redox Flow

- *Novel redox species*
- *Ionic mobility*
- *Interfacial transport*
- *Stable and selective membranes*

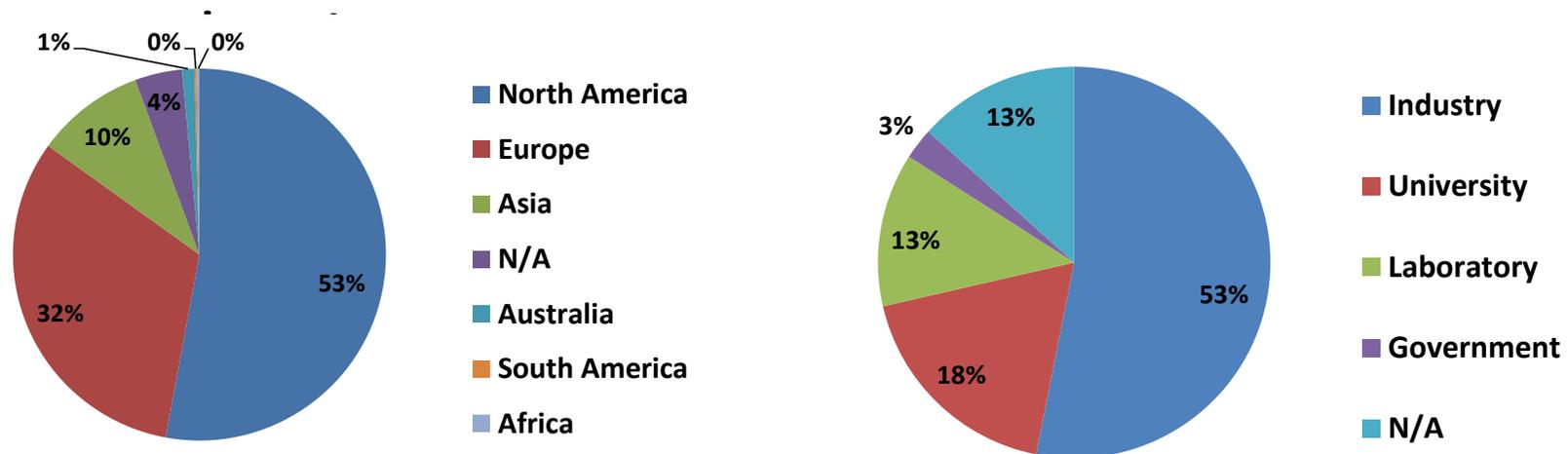
About BatPaC

- Originated from decades of battery design work by Paul Nelson
- Design work provided a “bill of materials” that then made estimating cost the obvious next step
- Argonne’s electrochemical energy storage group is largely a materials focused team – design & cost motivates materials
- The BatPaC model was developed utilizing *efficient* simulation and design tools for Li-ion batteries to predict:
 - Precise overall (and component) mass and dimensions
 - Understand how performance affects cost
 - Battery pack values from bench-scale results

www.cse.anl.gov/batpac

BatPaC Distribution

- Over 1000 unique users have downloaded the model
- Fortune 500 companies, high-profile startups,



www.cse.anl.gov/batpac

Approach to understanding cost & energy

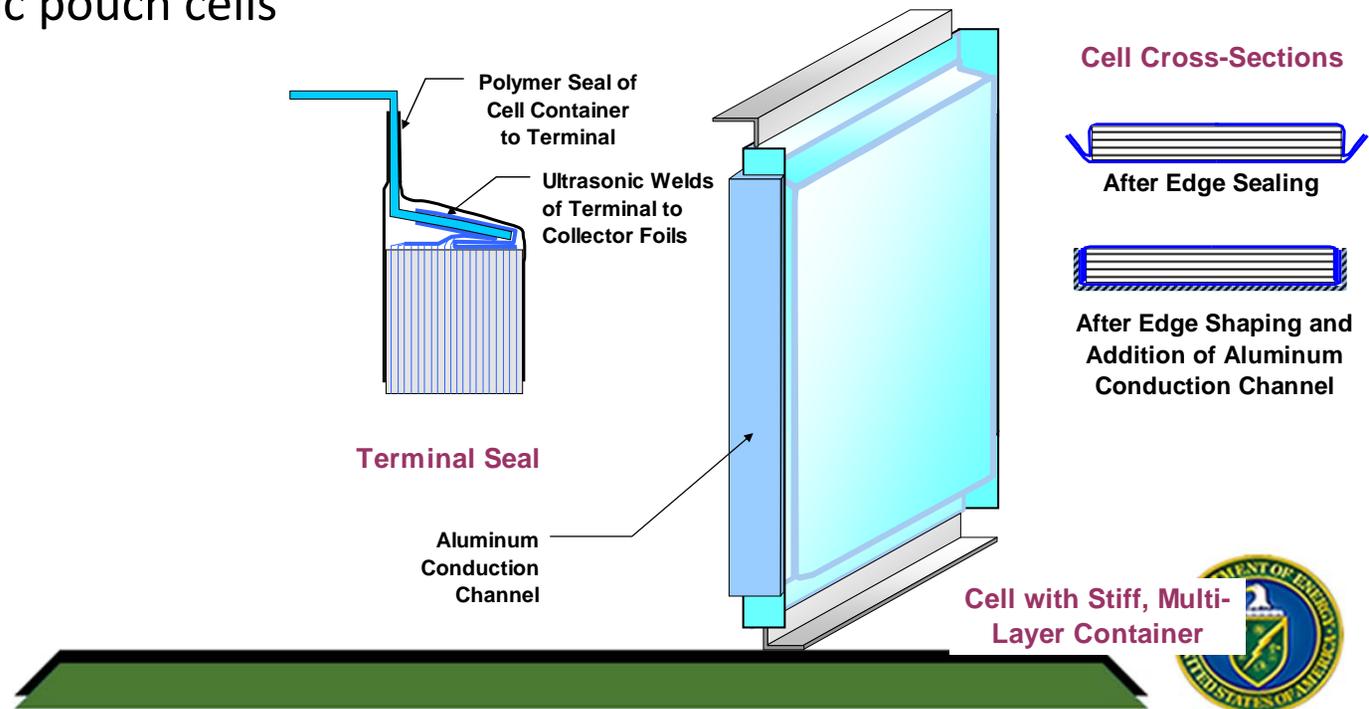
- Designs Li-ion battery and required manufacturing facility based on user defined performance specifications for an assumed cell, module, and pack format
 - Power, energy, efficiency, cell chemistry, production volume
- Calculates the total cost to original equipment manufacturer (OEM) for the battery pack produced in the year 2020
 - Not modeling the cost of today's batteries but those produced by successful companies operating in 2020
 - Some advances have been assumed while most processes are similar to well-established high-volume manufacturing practices
- Efficient calculations completed in fractions of a second

Philosophy of design and cost approach

- Defensible cell, module, and pack design (materials drive cost)
 - Account for every detail within pack (bottom-up approach)
 - Utilize charge, mass, and heat transport calculations
 - Use experimentally measured performance
 - Learn from what has been done already and analogs in other products
 - Find out what the key constraints are and if they will be there in 2020
- Manufacturing plant similar to today, but bottlenecks removed
 - Faith in the engineers
 - Account for every step in the process
- Financial structure – similar to Tier 1 auto supplier
 - No reason why margins should be higher
- Make the model as flexible and modifiable as possible
- Ask for reviews from everyone

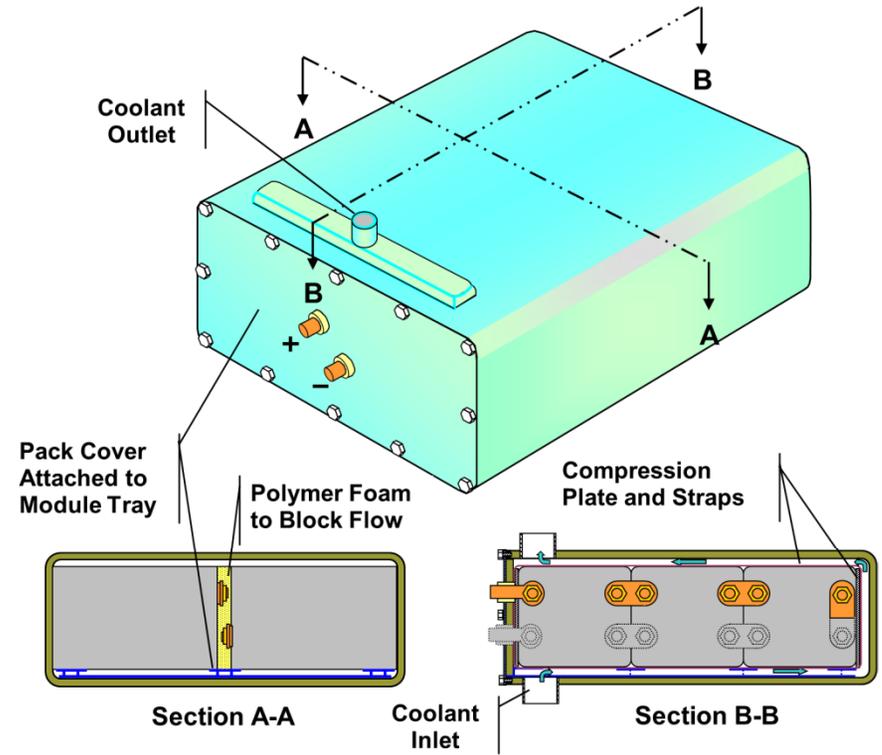
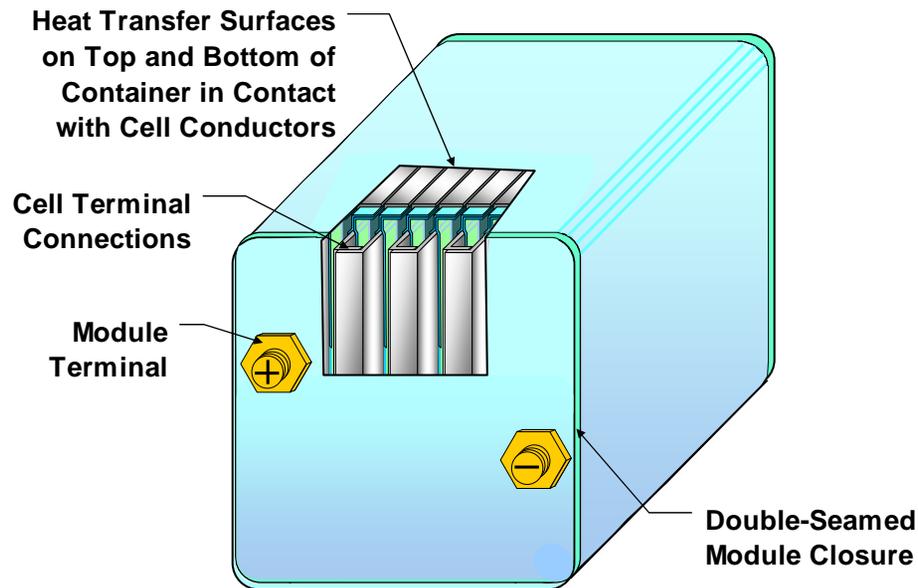
Assumed cell format

- Assuming a battery format allows for the direct calculation of all components that comprise the unit
- Previous efforts were based on flat-wound and cylindrical cells
- Our assumed format is most likely not the best design, however those successful in producing batteries in the year 2020 will reach similar energy densities and costs through other means
- Stiff prismatic pouch cells

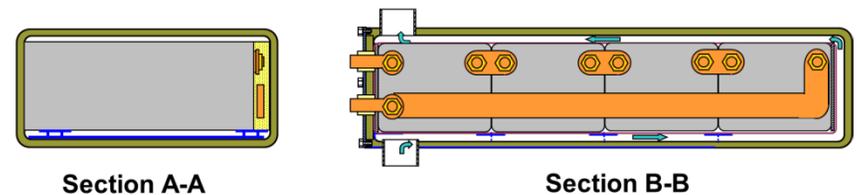


Assumed format: liquid thermal management

- Cooling of the module walls with ethylene glycol / H₂O (50:50)



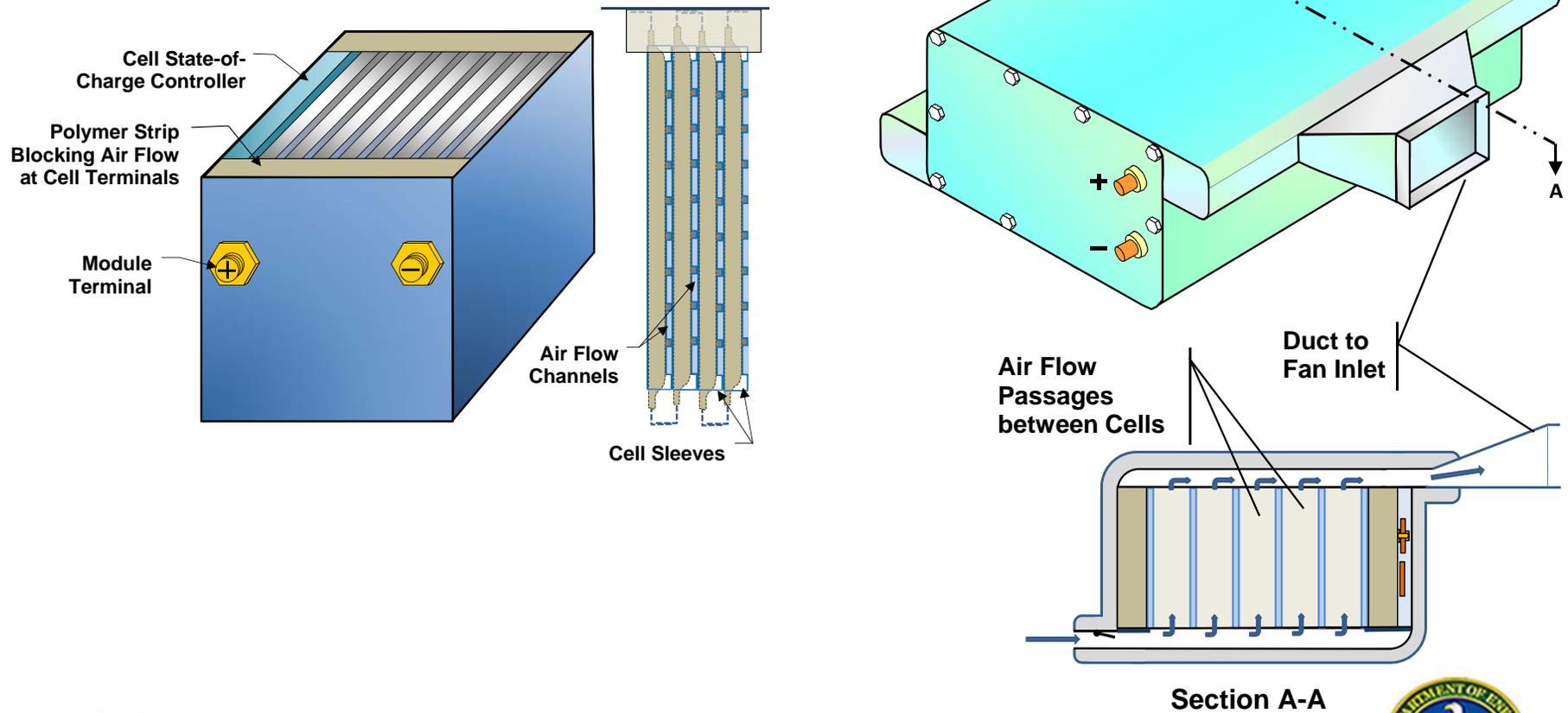
Pack with Two Rows of Modules



Pack with One Row of Modules

Assumed format: air thermal management

- Cooling of the cell containers with cabin air



BatPaC calculation methodology

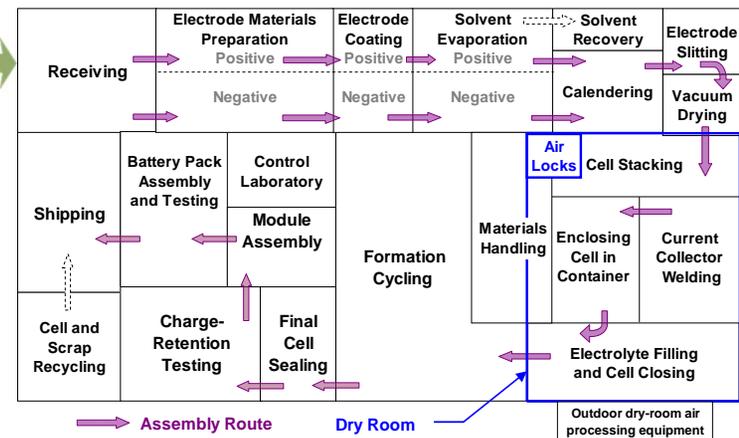
Iterate Over Governing Eqs. & Key Design Constraints

- Cell, module, & pack format
- Maximum electrode thickness
- Fraction of OCV at rated power

Battery Pack Components

- Volume
- Mass
- Materials
- Heat generation

$$\text{Process cost} = \text{Baseline cost} \cdot \left(\frac{\text{Processing rate}}{\text{Baseline processing rate}} \right)^p$$



• Pack specifications

- Power and energy (range)
- Number of cells

• Cell Chemistry

- Area-specific impedance (ASI)
- Reversible capacity $C/3$
- OCV as function of SOC
- Physical properties

Governing Equations

$$E = N \cdot C \cdot \left(U_E - \frac{C}{3} \frac{ASI_E}{A} \right)$$

$$L = \frac{C}{Q \cdot \rho \cdot \varepsilon \cdot A}$$

$$I = \frac{P}{A \cdot N \cdot U_p \left[\frac{V}{U} \right]}$$

$$A = \frac{ASI_p \cdot P}{N \cdot (U_p)^2 \left[\frac{V}{U} \right] \left(1 - \left[\frac{V}{U} \right] \right)}$$

$$ASI = \frac{\alpha + f(I)}{L} + \beta$$

Total Cost to OEM

- Materials & purchased items
- Individual process steps
- Overhead, depreciation, etc.
- Warranty

Validation of Design Calculation

- Validated design calculation for cylindrical wound cells
 - Matched measured values within 3%
- Straightforward adaption to prismatic pouch cells
 - Current collection resistance easier to calculate

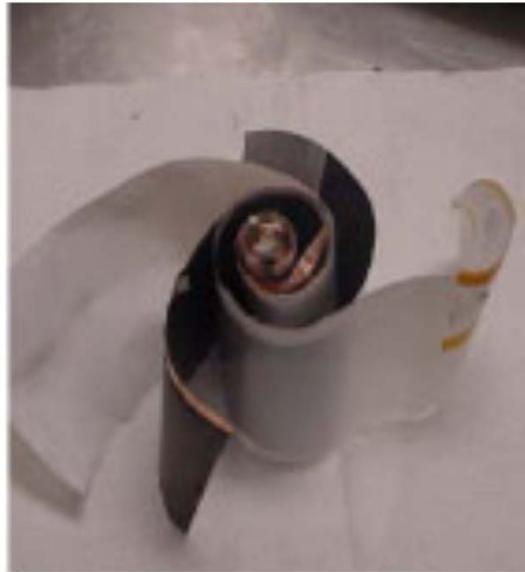


Table 2
Agreement between measured dimensions and weights of lithium-ion 18650 cells and values calculated by modeling

	Error in calculated value (%)
Lengths of winding materials (mm)	
Positive electrode	0.1
Negative electrode	-0.8
Separators	1.2
Cell area (cm ²)	0.2
Weights (g) ^a	
Positive electrode	1.0
Negative electrode	1.6
Electrolyte	-0.4
Balance of cell	2.3
Total	1.0

^a Measured weights are averages for 17 randomly selected cells.

Validation of Impedance Calculation

- Development of enhanced ASI calculation to account for

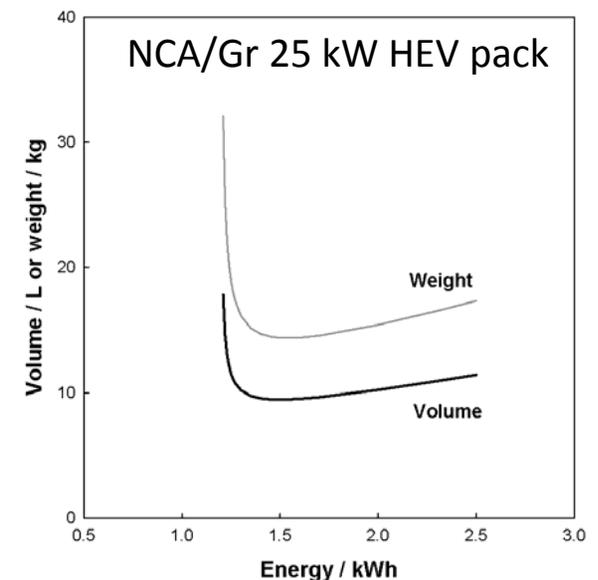
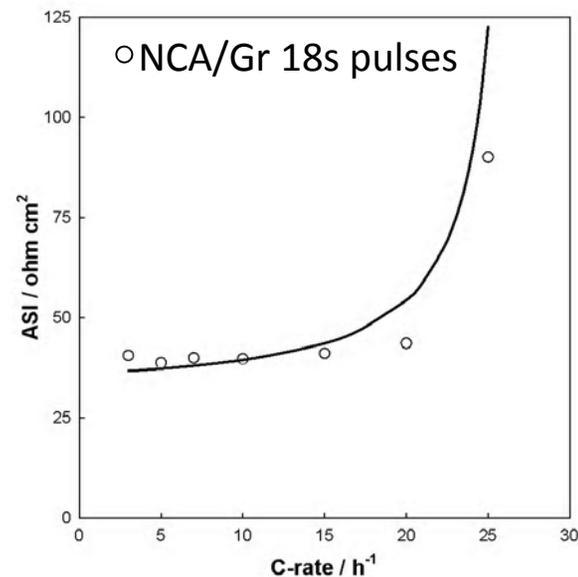
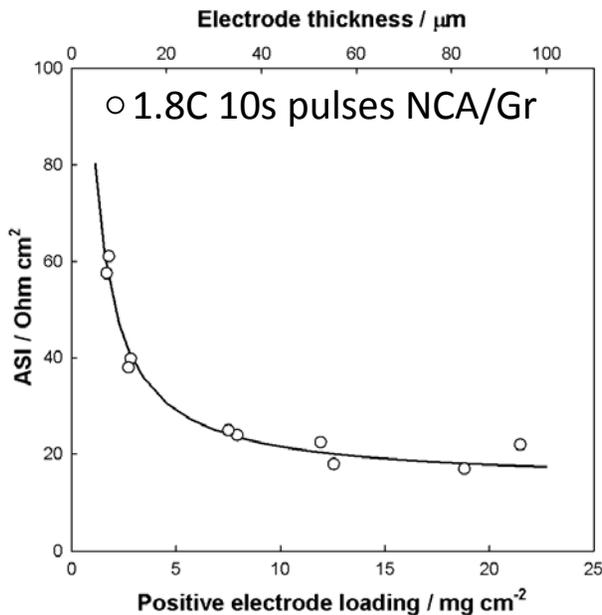
- Changes in electrode thickness
- Limiting currents

$$ASI_{\text{intf}}^{\text{pos}} = \frac{1}{L} \left[\frac{RT}{ai_o F} \left\{ \left(1 - \frac{I}{I_{\text{lim}}^{\text{ionic}}} \right) \left[1 - \left(\frac{r_c}{r_{c,\text{lim}}} \right)^2 \right] \right\}^{-0.5} \right] \frac{dU}{dy} \frac{t_{\text{pulse}}}{3600 Q \rho \epsilon_{\text{act}}}$$

Kinetic & concentration Thermo factor

- Improved treatment of ASI allows for calculation of battery design and cost for many different power to energy (P/E) ratios

$$ASI_{\text{echem}} = ASI_{\text{intf}}^{\text{pos}} + ASI_{\text{intf}}^{\text{neg}} + ASI_{\text{const}}$$



Validation of cost calculations

- Costs are obviously a bit more difficult to validate
- Public and private peer-reviews essential
- General approval of final assumptions
 - Input material costs and capital costs
 - Breakdown of projected “2020” costs
 - Reasonable financial overhead structure
 - Correct proportion of materials costs to depreciation, etc
- Design approach key to achieving correct battery costs
 - Electrode thickness limitations
 - Cell capacity limitations
 - Accounting for the details (e.g. polymer applied to terminals to enable good seal or high efficiency insulation around pack)

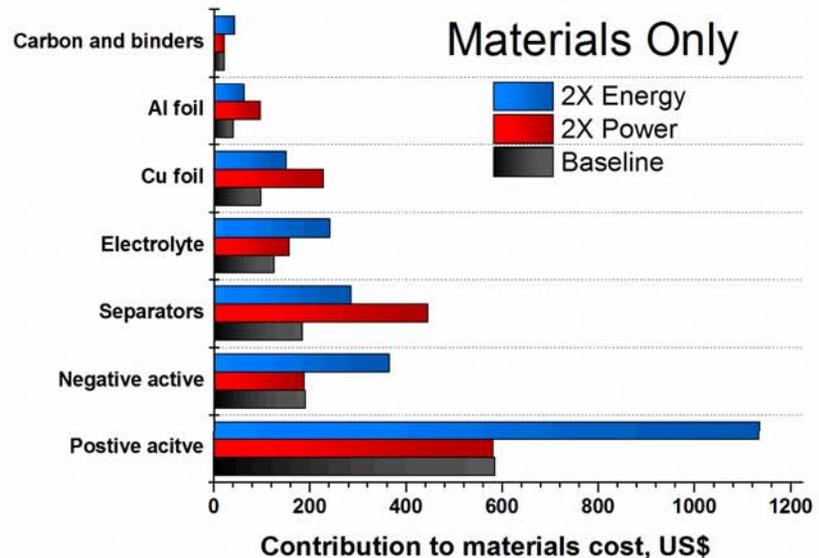
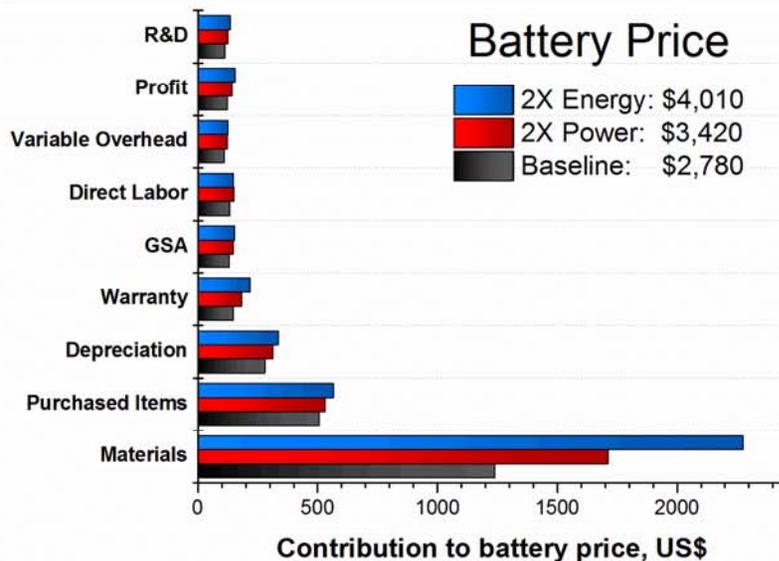
Pack integration components

- These estimates are derived from conversations with industry for predictions of high volume, year 2020 market
- Thermal management
 - Active liquid thermal management for all calculations
 - Cooling at the module level (not individual cells)
 - Adds ~ \$225-350 to PHEVs or EVs (not including electric compressor)
- Battery management system
 - State of charge control at cell level ~\$2.50/cell
 - Module control and pack current/voltage sensing ~\$200
- Disconnects
 - Automatic disconnects for grid-charging packs ~\$200
 - Contactors, fuses, and circuitry
 - Manual disconnects ~\$15

Illustrative results: power and energy

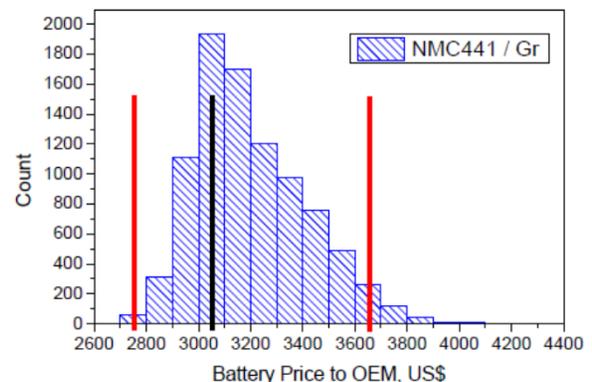
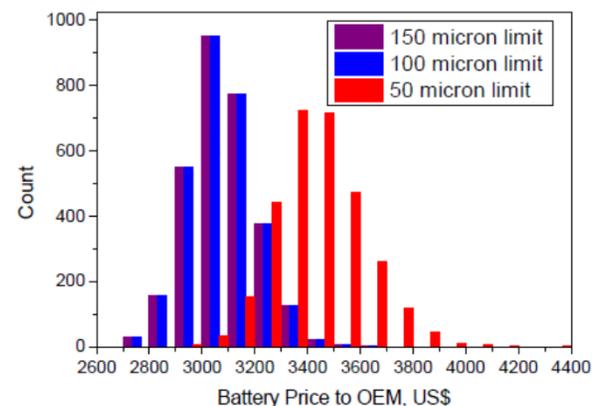
- Model accounts for changes in materials and processing costs
- Examine simple changes to baseline battery and plant
 - 2x energy (8 to 16 kWh) increases price 44%
 - 2x power (50 to 100 kW) increases price 23%

NCA/ Gr, PHEV20 360 V, 50 kW, 8 kWh_{tot}



Uncertainty study

PHEV25: 65 kW, 10.7 kWh 360V



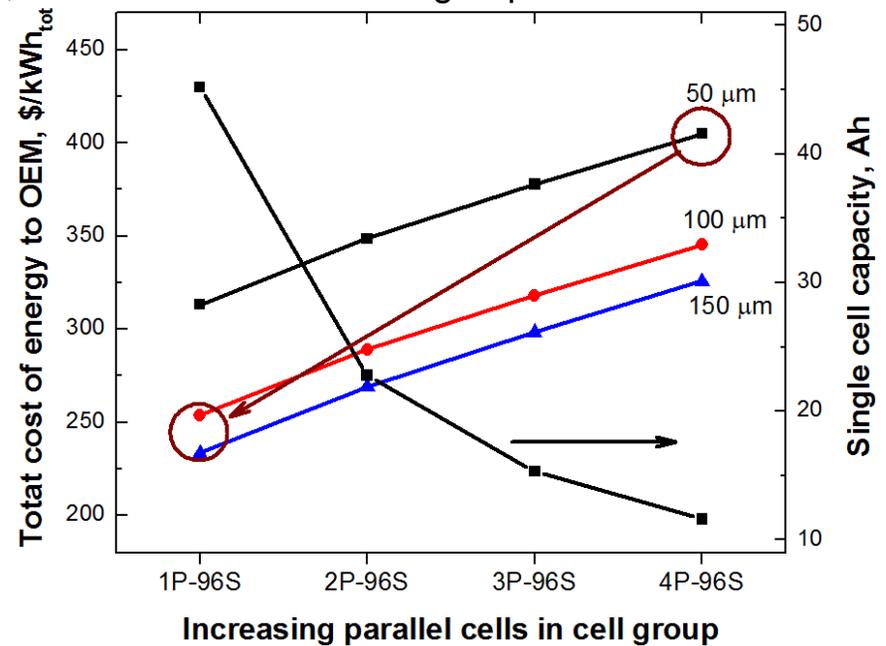
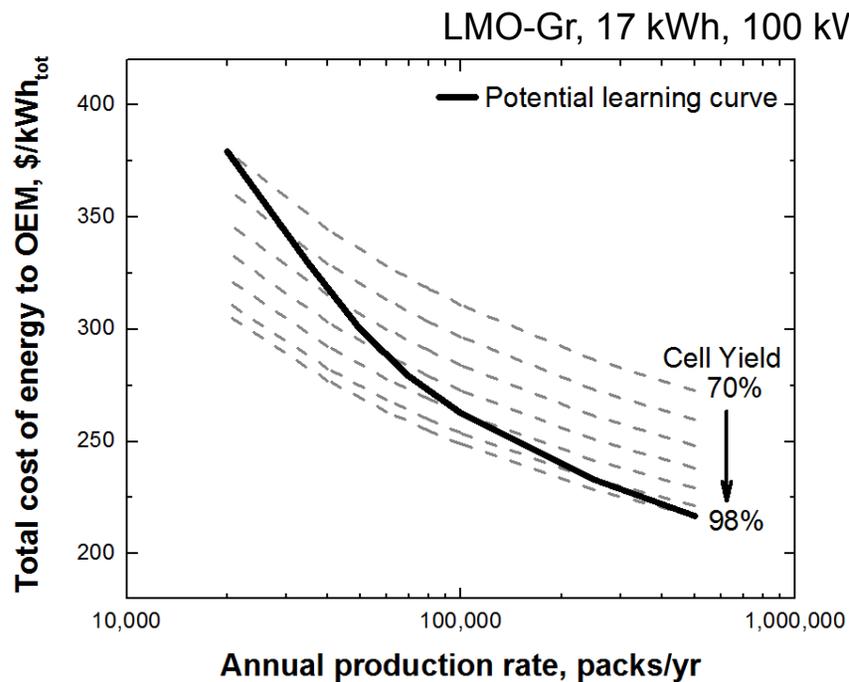
- Addressed top eight high-cost contributors
- Monte Carlo study on input costs
 - Active materials, separator, Cu foil
 - State-of-charge electronics
 - Capital cost of coating & formation
- Uncertainty in design limitations
 - Electrode thickness limitation
 - Cell capacity limitations (adds parallel cells)
- Conclusion
 - Materials cost error is $\sim\pm 10\%$ regardless of active materials
 - Electrode thickness limitation is often the next most significant
 - Use PHEV limits of 50/100/150 microns (min/med/max)
 - Electrode thickness still calculated \rightarrow thus not always controlled by limit!

Flexibility of the model

- Model designed to be flexible
 - We (Argonne) modify it for almost every study we do
 - Our unofficial slogan: If you don't like our assumptions or values, feel free to put your own in
- Assumed manufacturing facility
 - Less obvious how to change for line speed increases, etc
 - However, all inputs can be changed
- Many others outside of Argonne have used the model as a framework for their own
 - EPRI
 - McKinsey
 - The Committee on Climate Change

Learning / manufacturing scale capabilities

- Yield and manufacturing volume
- Design improvements
 - Moving to thicker electrodes
 - Moving to larger capacity cells



What is left to be done? - Chemistries

- Advanced Li-ion chemistries studied through DOE-EERE VTP ABR
 - Advanced anodes – silicon alloys, etc
 - Advanced cathodes – Li- and Mn-rich, 5V spinel, etc
- The beyond Li-ion chemistries and novel battery designs will be explored within the Joint Center for Energy Storage Research (DOE-SC Energy Innovation Hub)
 - Metal – Oxygen/Sulfur
 - Multivalent intercalation
 - Novel, unproven technologies



Kevin Gallagher, Steven Goebel, Thomas Greszler, Mark Mathias, Wolfgang Oelerich, Damla Eroglu and Venkat Srinivasan “Quantifying the Promise of Lithium–Air Batteries for Electric Vehicles” *Energy & Environmental Science*, **2014**, DOI:10.1039/C3EE43870H





Battery Performance and Cost (BatPaC)

Modeling the energy density and cost of Li-ion batteries for use in transportation applications

Kevin Gallagher, Paul Nelson, and Shabbir Ahmed

Chemical Sciences and Engineering Division