Impact of Materials Advances on Batteries for the Coming Electric Vehicle Revolution

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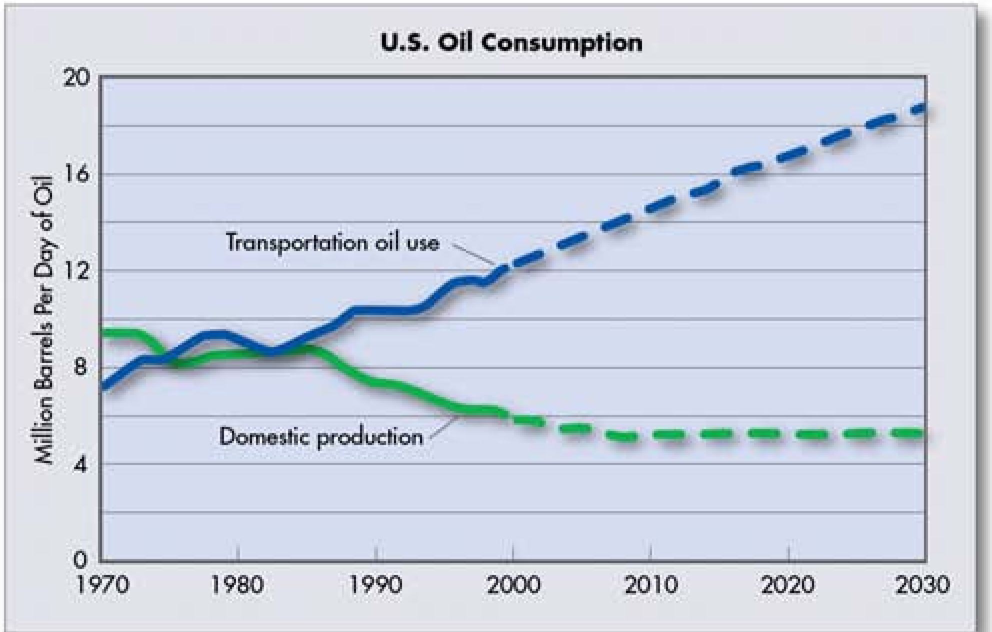
Acknowledgements: Nonglak Meethong, Hsiao-Ying Shadow Huang, Ming Tang, Yu-Hua Kao, W. Craig Carter, Scott A. Speakman, and the team at A123Systems






Energy Security and Climate Change are Driving the Electrification of Vehicles



While U.S. domestic production of oil has decreased 44% since the 1970s, the use of oil for transportation has increased 83%, and the gap is widening. Given a continuation of this pattern, U.S. oil consumption is expected to grow 60% over the next 25 years, with consequential increases in transportation fuel costs, carbon emissions, and security vulnerability. (Source: Energy Information Administration)

Bono and Al Gore ruminating at Davos, 2008

Roadmap (to the talk)

- **What has happened in the last 5 years to make (some of) us think that a revolution is imminent? (State of technology readiness.)**
- **What are the perceived benefits of the widespread electrification of vehicles (esp. the Plug-in Hybrid Electric Vehicle (PHEV)?**
- **What isn't yet possible, and how might we get there?**

2007
100+ mpg
PHEV
Conversion

2010
150 mpg
Chevy Volt
PHEV-40

Very Different Battery Requirements for Portable Devices vs. Transportation

Lithium-ion cells for portable devices

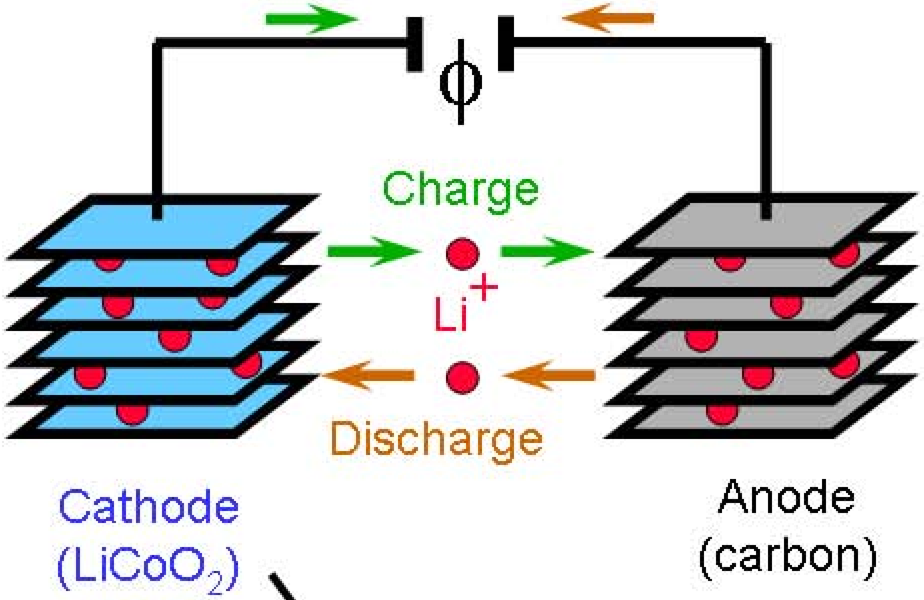
- Volumetric energy is the key metric
- 300 charge/discharge cycles (1 yr life)
- Slow charge/discharge, ~1C rate (1hr) or slower
- Small (<5 Wh) cell size
- In market place since early 1990's; billions produced
- Still, >50 million batteries recalled over the past 2 years for safety reasons

2010 Chevy Volt Plug-In Hybrid

Advanced batteries for transportation

- Gravimetric power and energy are key, and favor lithium chemistry
- 6000 deep cycles for PHEV
- 300,000 shallow cycles for HEV
- 3C to >50C pulse charge/discharge rates
- 15 year calendar life
- Extreme safety in large packs (>5 kWh)
- Affordable

Intrinisic Energy Density (Voltage x Capacity) is Determined by Properties of Cathode and Anode



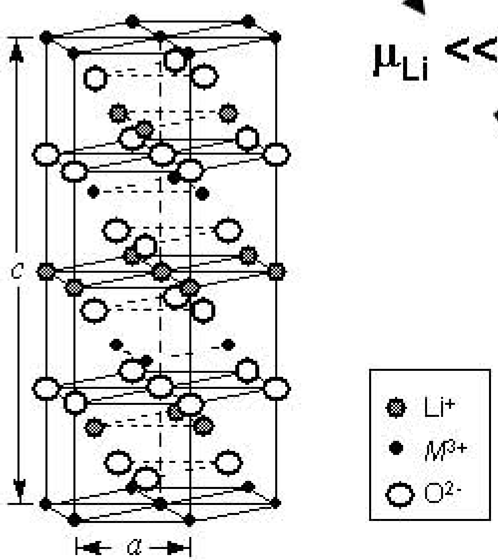
Lithium Chemical Potential At Anode

$\mu_{Li} \leq \mu_{Li,\,metal}$

- Li metal
- Carbon
- Metal alloys
- Nanoscale oxides

$$\Delta\phi = -\frac{1}{z_i F}\left(\mu^0_{i,cathode} - \mu^0_{i,anode}\right) = \frac{-\Delta G^0}{z_i F}$$

$\mu_{Li} << \mu_{Li,\,metal}$

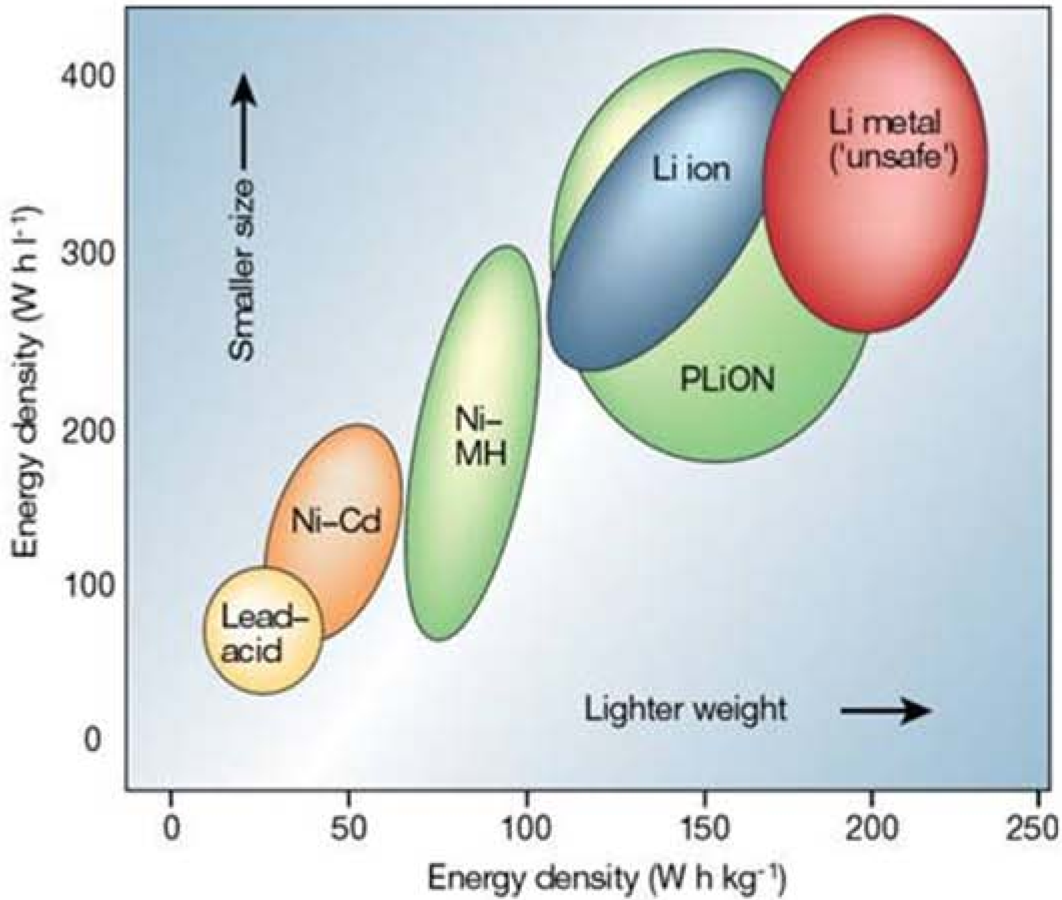


$\mathrm{Li}M\mathrm{O_2}$ ($R\bar{3}m$)

Material	Average Voltage vs. Li	Specific Capacity (mAh/g)	Energy Density of Electrode (Wh/kg)
$Li_{1-x}CoO_2$	3.9	137	534
$Li_{1-x}NiO_2$	3.8	220	836
$Li_{1-x}Mn_2O_4$	4.0	119	476
$Li_{1-x}FePO_4$	3.5	170	595

Comparison of Energy Densities: Lithium Chemistry is Still King

Volumetric and Gravimetric Energy Density



J.-M. Tarascon and M. Armand, *Nature* 414, 359 (2001)

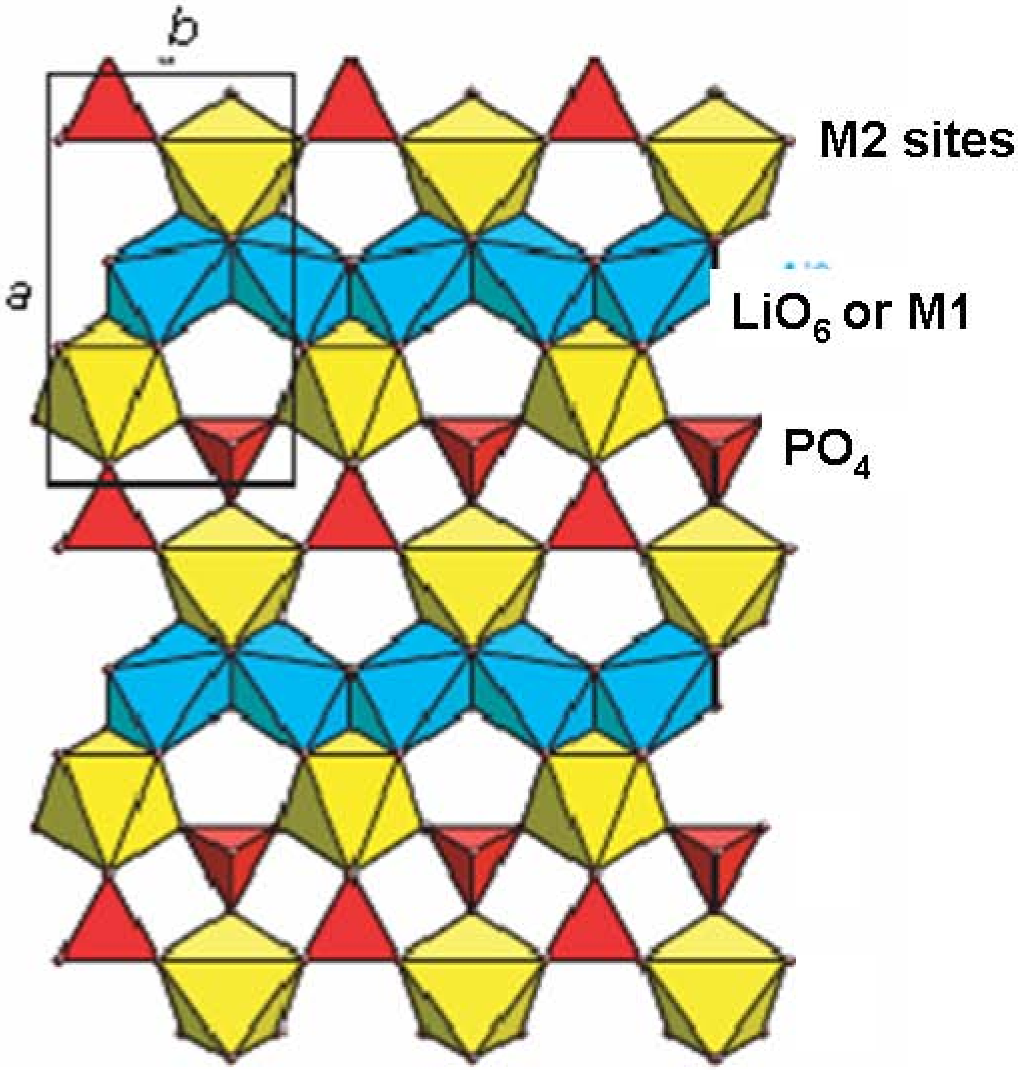
Currently Several Lithium Battery Chemistries are under Development for HEV and PHEV Batteries

- $Li(Ni,Co,Al)O_2$ – carbon
  - High power and energy (3.8V)
  - Safety?
  - Life?

- $LiMn_2O_4$ – nano $Li_4Ti_5O_{12}$
  - High power but lower energy due to lower specific capacity and voltage (2.5V)
  - Safest anode
  - HEV suitable; probably too low energy for PHEV

- Nano olivines ($Li_{1-x}M_{1+x}PO_4$) – carbon
  - High power and reasonably high energy (3.3-4V)
  - Safest cathode
  - HEV and PHEV suitable

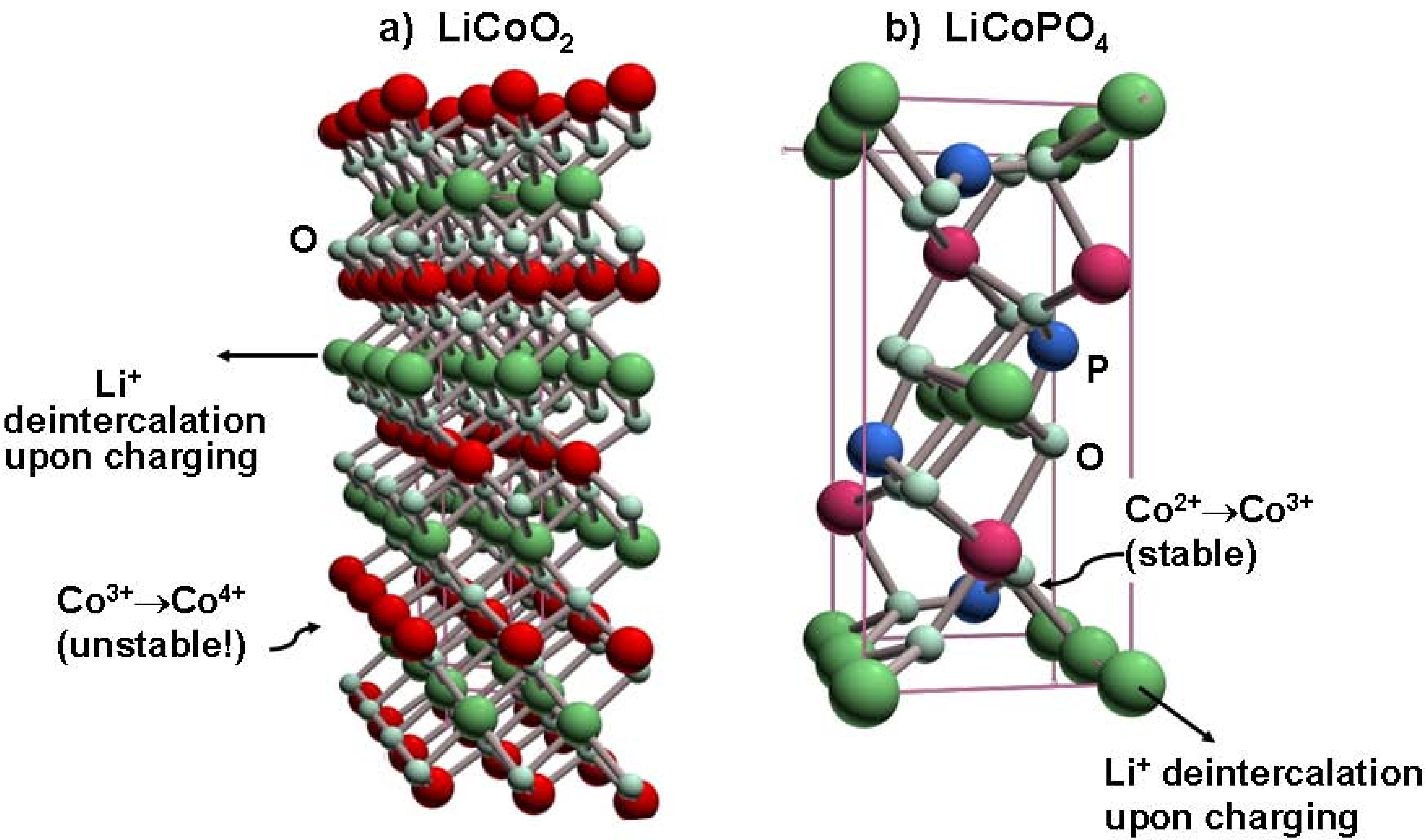
Lithium metal olivines LiMPO$_4$ (M = Mn,Fe,Co,Ni) as positive electrodes for rechargeable batteries



Characteristics of LiMPO$_4$:

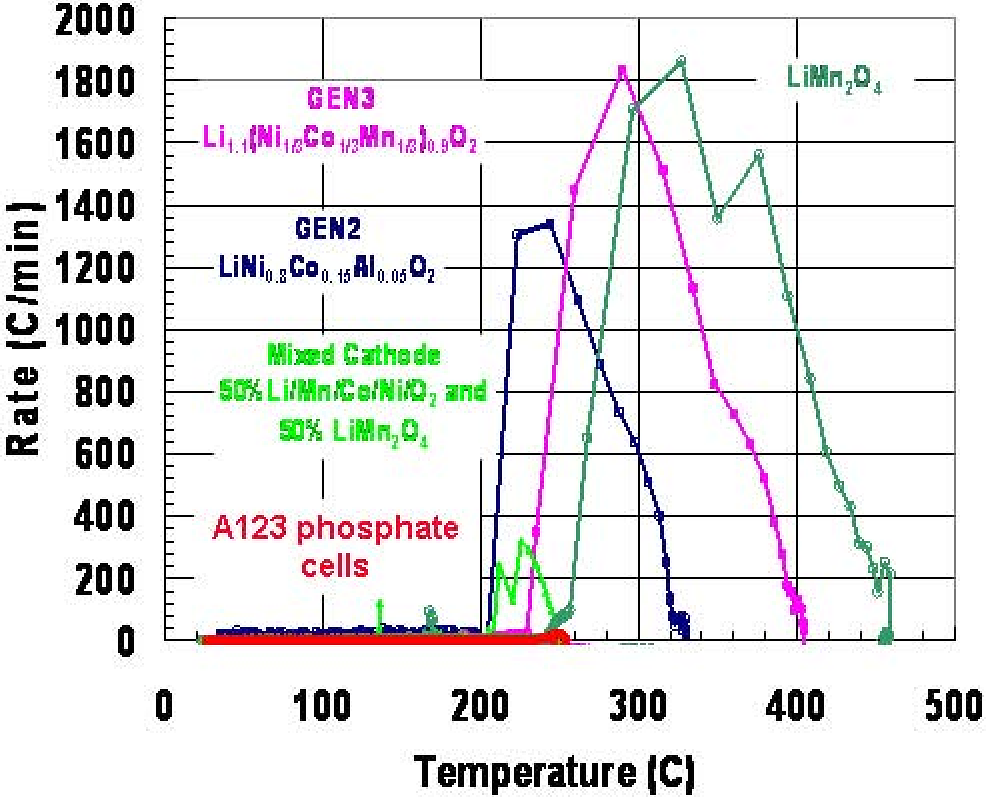
- \+ Low cost
- \+ High specific capacity
- \+ High thermal stability
- \+ Low toxicity
- \+ Flat discharge plateau
  - Fe @ 3.5 V
  - Mn @ 4.1 V
  - Co @ 4.8 V
  - Ni @ 5.1 V
- \- Poor Li-diffusion
- \- Poor electronic conductivity

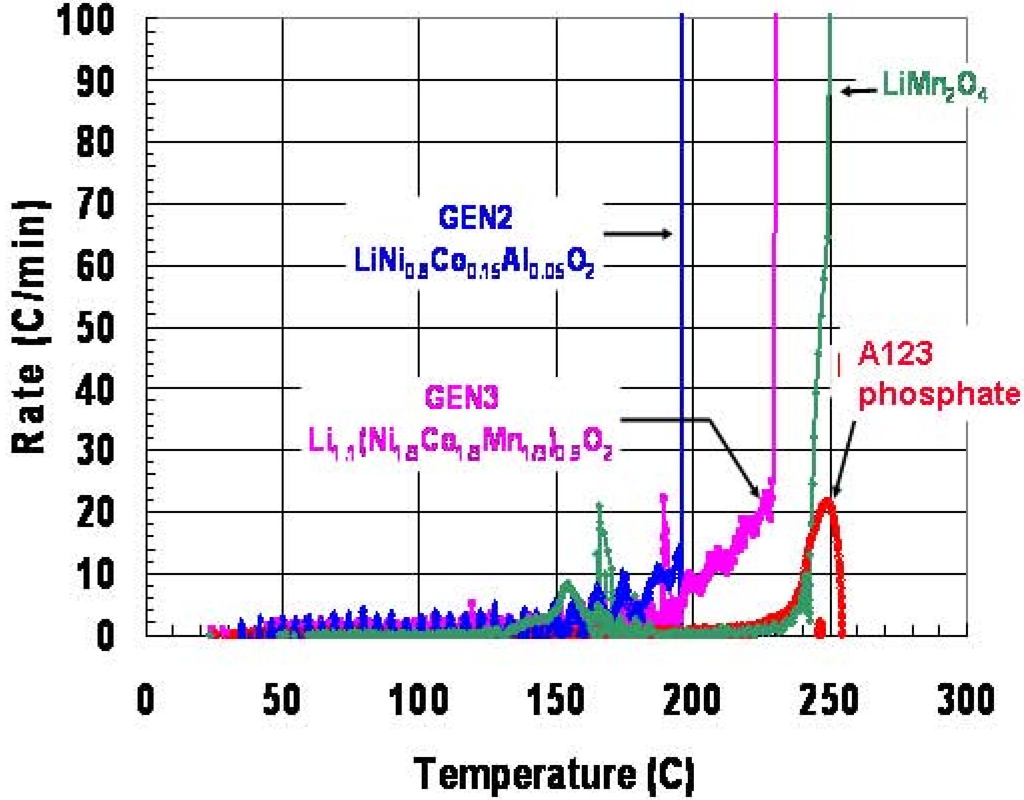
A key distinction is the transition metal oxidation state of a charged (delithiated) electrode



$LiCoO_2$ and its nickel-containing derivatives used as the positive electrode in lithium-ion batteries experience an oxidation of Co^{3+} to unstable Co^{4+} (or Ni^{3+} to unstable Ni^{4+}) as Li^+ ions are removed from the lattice upon charging. In contrast, a phosphate-based cathode such as $LiCoPO_4$ undergoes oxidation of Co^{2+} to a stable Co^{3+} state (or Mn^{3+}, or Fe^{3+}), resulting in a safer, fault-tolerant cell chemistry.

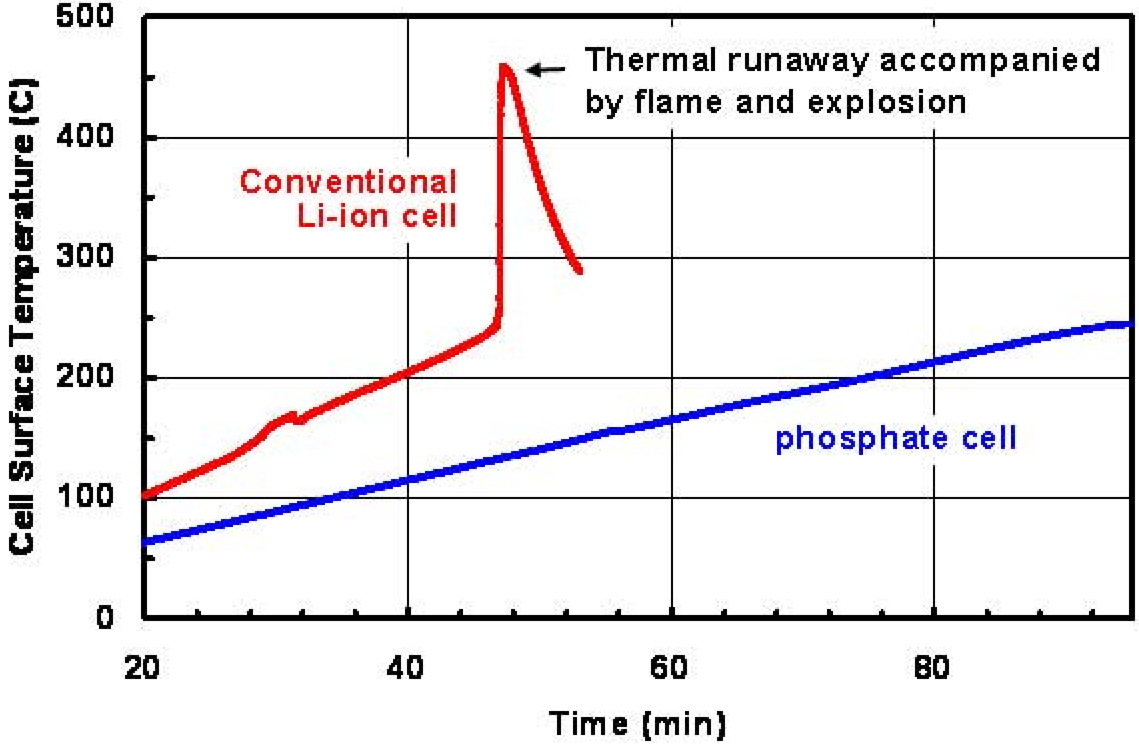
Comparison of Self-Heating Rate of Charged (delithiated) Cathodes





Peter Roth, Sandia National Laboratory

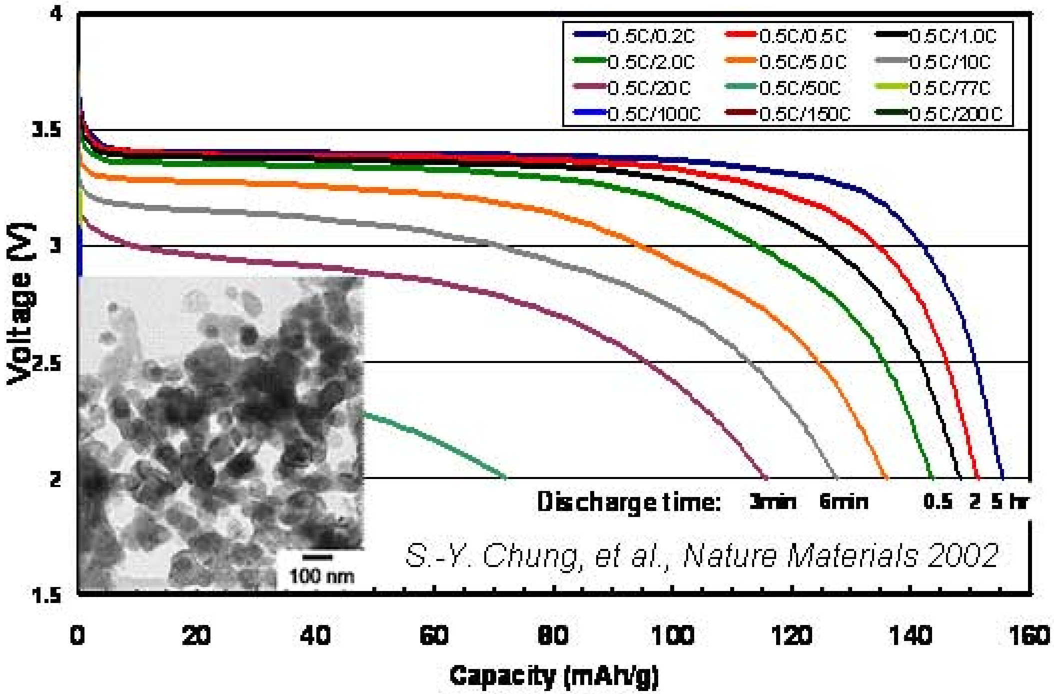
Comparison of cells with and without thermal runaway

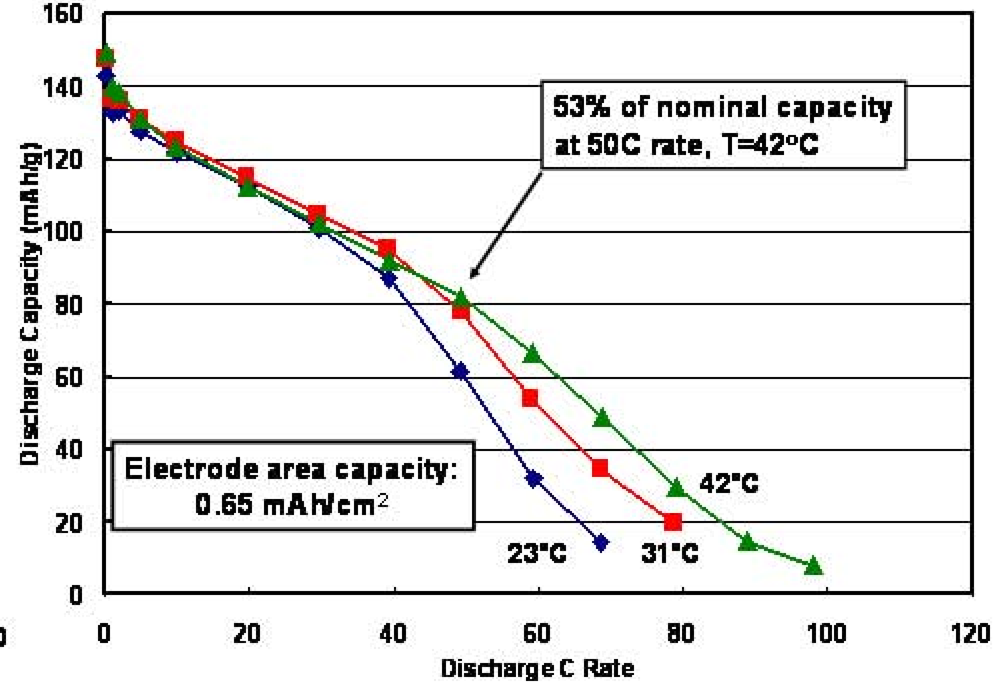


Sandia National Lab test chamber

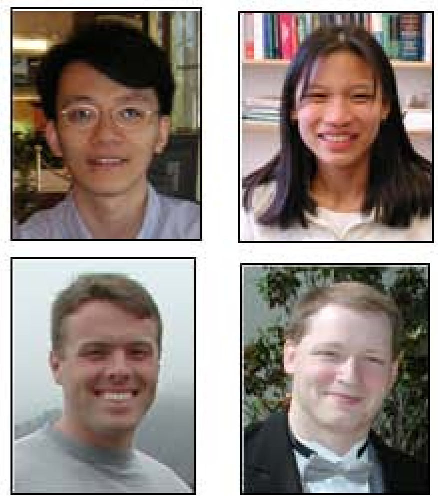
Comparison of conventional lithium-ion battery exhibiting thermal runaway followed by flaming and explosion, with intrinsically safer phosphate-based lithium ion cells. (Test data performed at Sandia National Laboratory on full-size cylindrical cells. Charged cells are instrumented with thermocouples and heated at constant rate to seek thermal events.)

But olivines initially had both lower energy density and lower power than incumbants ($LiCoO_2$, $LiMn_2O_4$)





NYTimes reporter: *So how long do you think it will be before real batteries will be made using these new materials?*

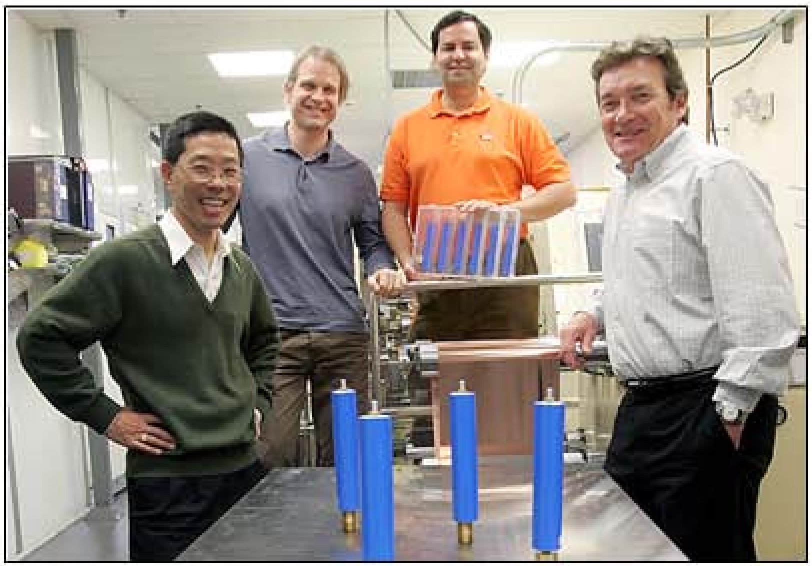


MIT Team
Circa 2002

MIT spins out A123Systems in late 2001

2002

- 5 employees
- $100,000 DOE SBIR grant
- 0.5g of material from MIT

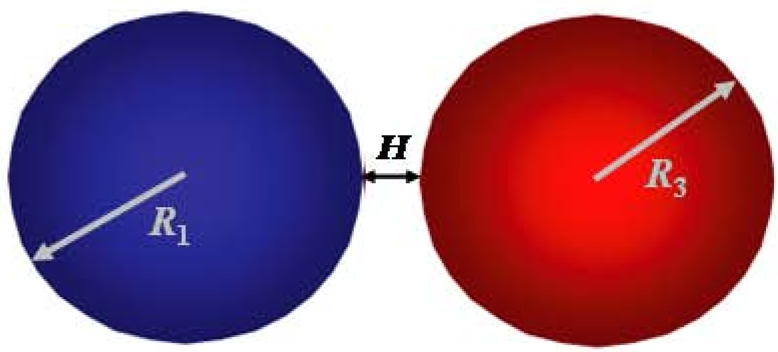


2007

- >850 employees
- Fortune 500 customers
- Producing millions of batteries and >200 metric tons of active materials annually
- First US lithium-ion company to reach this scale

A123Systems owes its name to the Hamaker force constant which is used to calculate the attractive and repulsive forces between particles at nano dimensions:

$$A_{123} \equiv \frac{3}{4} kT \left(\frac{E_1 - E_2}{E_1 + E_2}\right)\left(\frac{E_3 - E_2}{E_3 + E_2}\right) + \frac{3}{8}\frac{h\nu_e}{\sqrt{2}} \frac{(n_1^2 - n_2^2)(n_3^2 - n_2^2)}{(n_1^2 + n_2^2)^{1/2}(n_3^2 + n_2^2)^{1/2}\{(n_1^2 + n_2^2)^{1/2} + (n_3^2 + n_2^2)^{1/2}\}}$$



Interparticle Force Law:

$$F_{vdW} = -\frac{A_{123}\, R_1 R_3}{6 H^2 (R_1 + R_3)}$$

Early demonstration of high specific power

Power Tool Applications Beginning in 2005

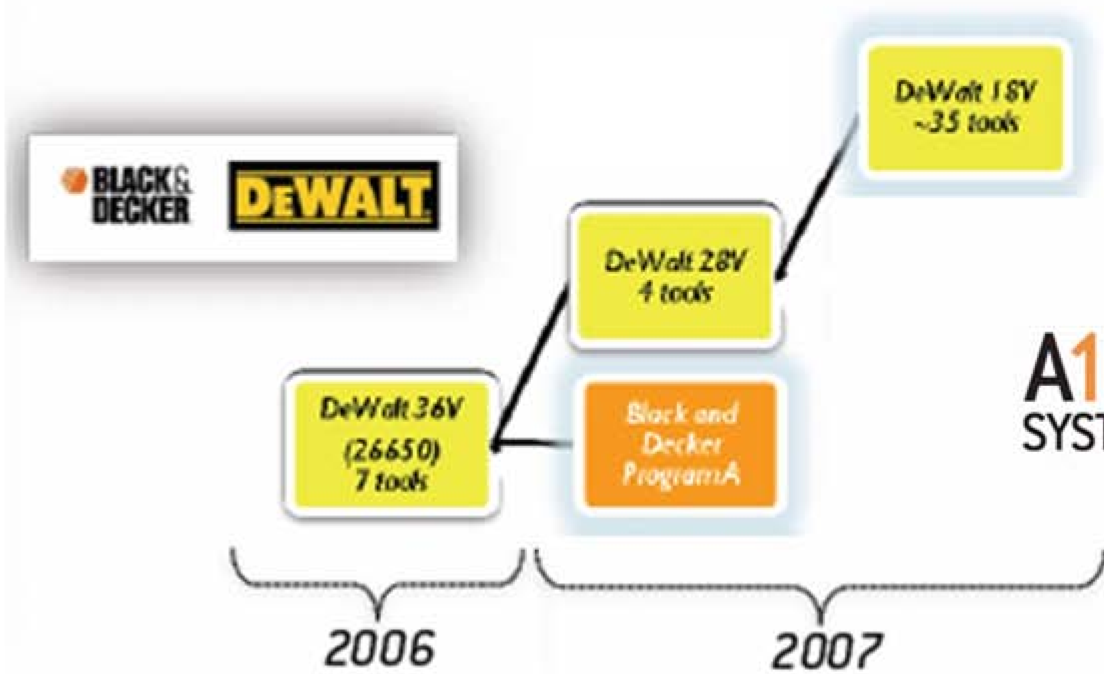
From 600-700W in 1.1kg
(18V NiCd battery pack)

to 3000W in 1.1 kg
(36V Li-ion battery pack)

→ 2x the peak power of corded power tools

- 3.3V, 2.3 Ah (7.2 Wh) cell of 26650 format
- >3000 W/kg peak power
- 110Wh/kg specific energy >150A pulse current
- 2000 cycles @100% depth of discharge
- >300,000 hybrid pulse power cycles
- Extremely low impedance growth

R&D 100



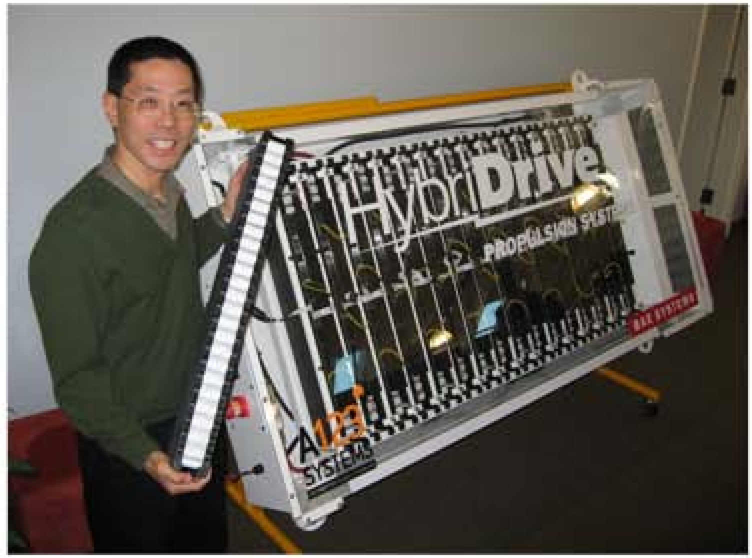
A123 SYSTEMS

www.A123Systems.com

From Power Tools to the Race Track

www.killacycle.com

Some New Applications Enabled by Safer High Power Batteries



Truck and bus Hybrid packs

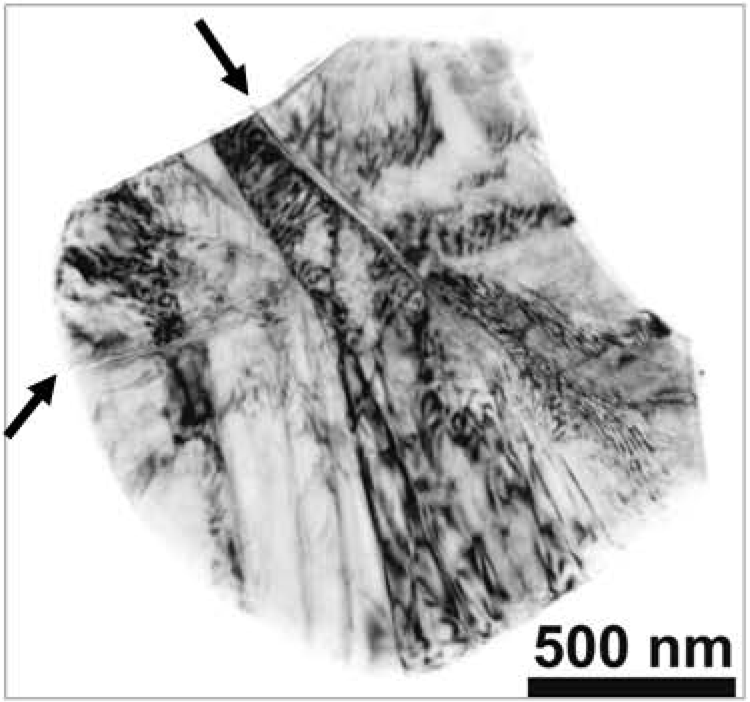
- 200 kW pack
- Saves 3400 lb

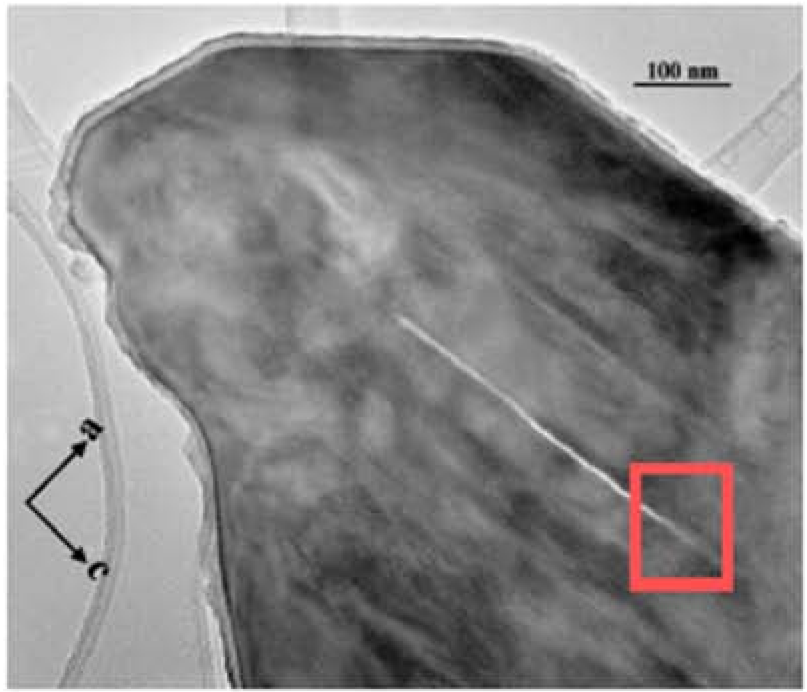
Aviation packs

2008 Daimler Chrysler Orion VII Bus

How Does One Design/Select Battery Materials for Power, Energy, and Life?

- First, must have adequate electronic and ionic conductivity (mixed conductor)
- In addition - many materials exhibit electrochemically-induced phase transformations – can this slow the rate of Li takeup and release?
- Most ion-storage materials exhibit fracture and fatigue in use - how to reach 300,000 shallow cycles for HEV, 6000 deep cycles for PHEV?





H. Wang et al., JECS 1999

$LiCoO_2$
50 charge/discharge cycles

$LiFePO_4$
1st chemical delithiation

G. Chen et al., ESL, 2006

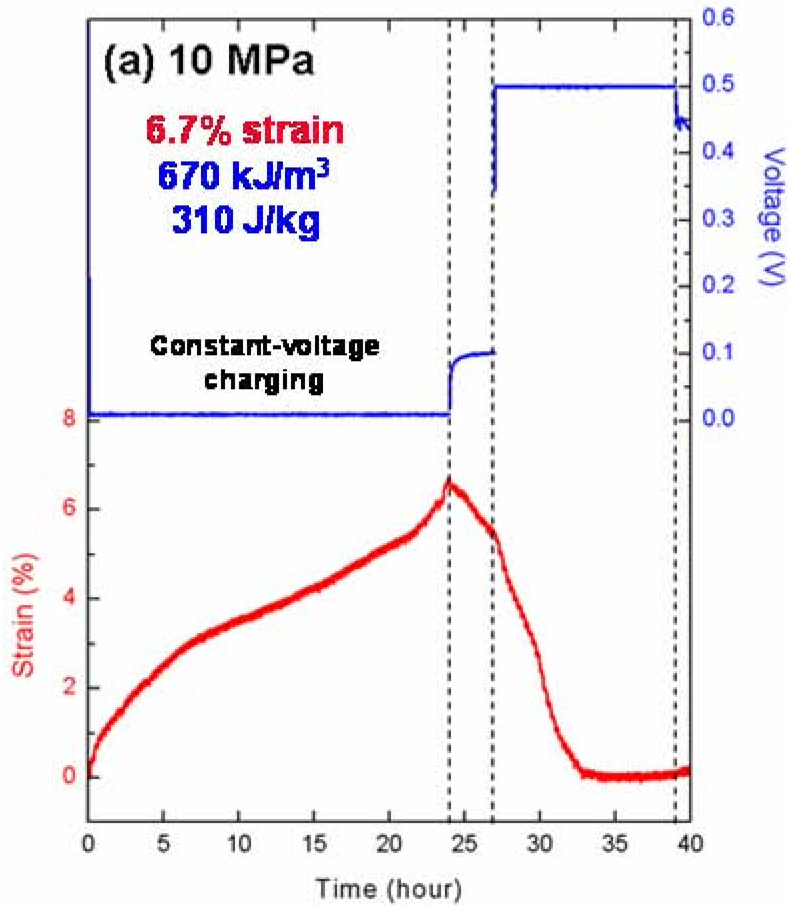
Most Lithium Storage Compounds Exhibit Significant Volume Changes upon Electrochemical Cycling

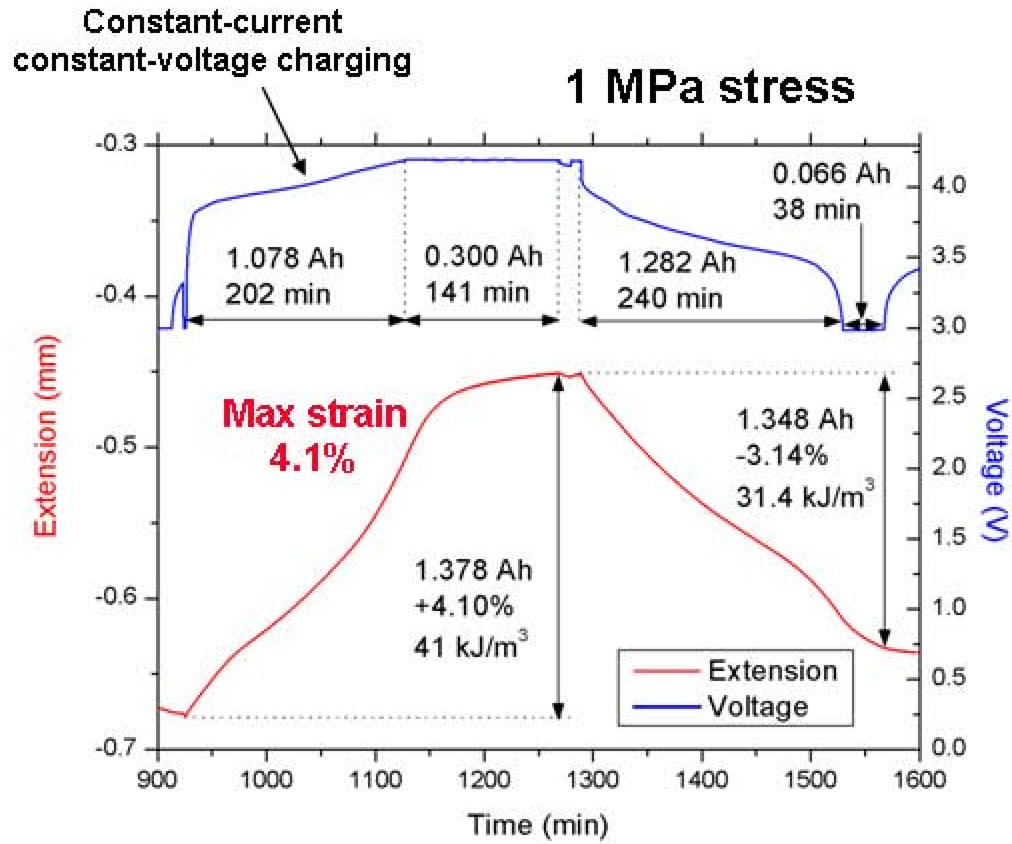
Lithium Storage Compound	Limiting Composition	Volume Strain $\Delta V/V_0$	Linear Strain* $\Delta L/L_0$	Potential vs. Li/Li^+
Li-extraction				
$LiCoO_2$	$Li_{0.5}CoO_2$	+1.9 %	+0.6 %	4.0 V
$LiFePO_4$	$FePO_4$	-6.5 %	-2.2 %	3.4 V
$LiMn_2O_4$	Mn_2O_4	-7.3 %	-2.5 %	4.0 V
$LiNiO_2$	$Li_{0.3}NiO_2$	-2.8 %	-0.9 %	3.8 V
Li-insertion				
C (graphite)	1/6 LiC_6	+13.1 %	+4.2 %	0.1 V
$Li_4Ti_5O_{12}$	$Li_7Ti_5O_{12}$	0.0 %	0.0 %	1.5 V
Si	$Li_{4.4}Si$	+311 %	+60 %	0.3 V
β-Sn	$Li_{4.4}Sn$	+260 %	+53 %	0.4 V

***Assuming isotropic expansion**

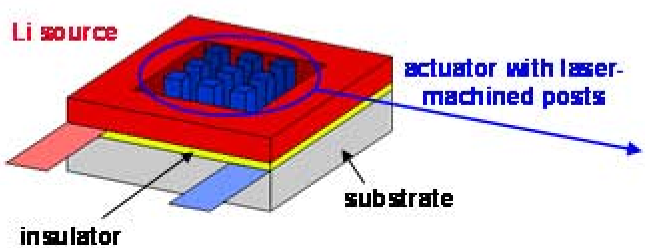
(Y. Koyama et al., Adv. Functional Mater., 2006)

Electrochemically-Induced Volume Changes Can Produce Useful Mechanical Work

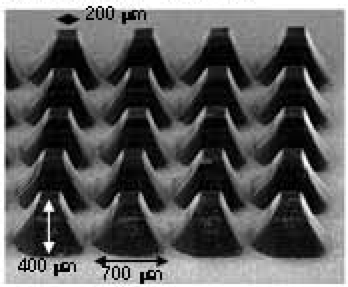


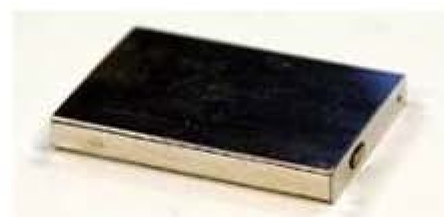


Laser micro-machining



Highly-Oriented Pyrolytic Graphite (HOPG): "single crystal" graphite



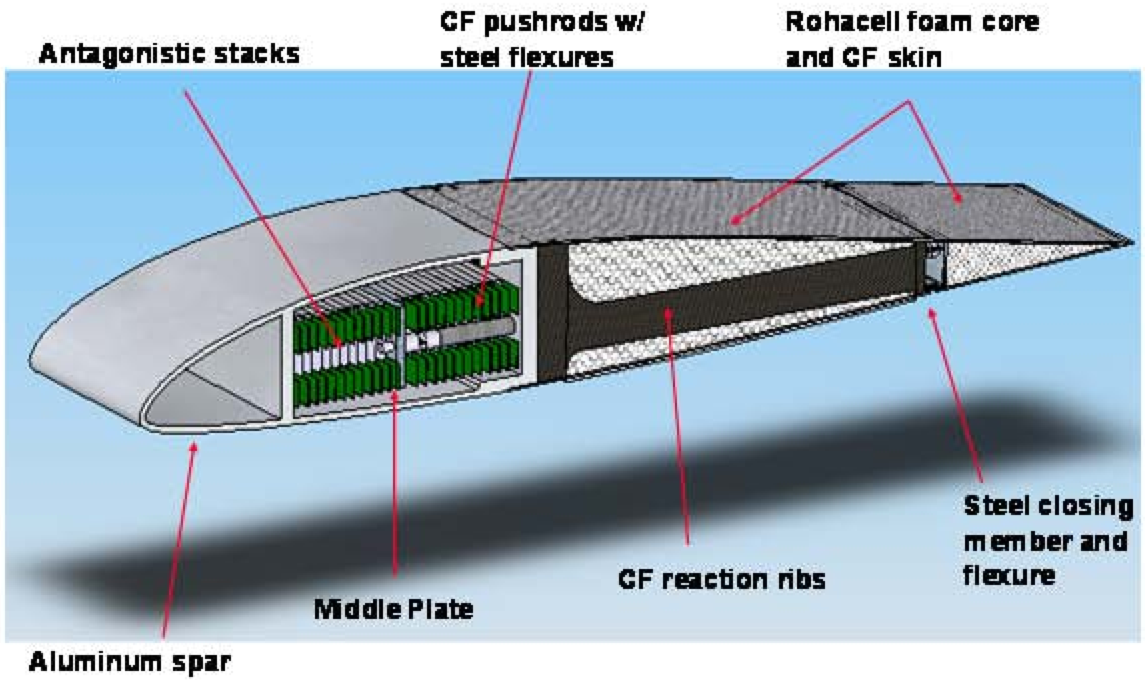


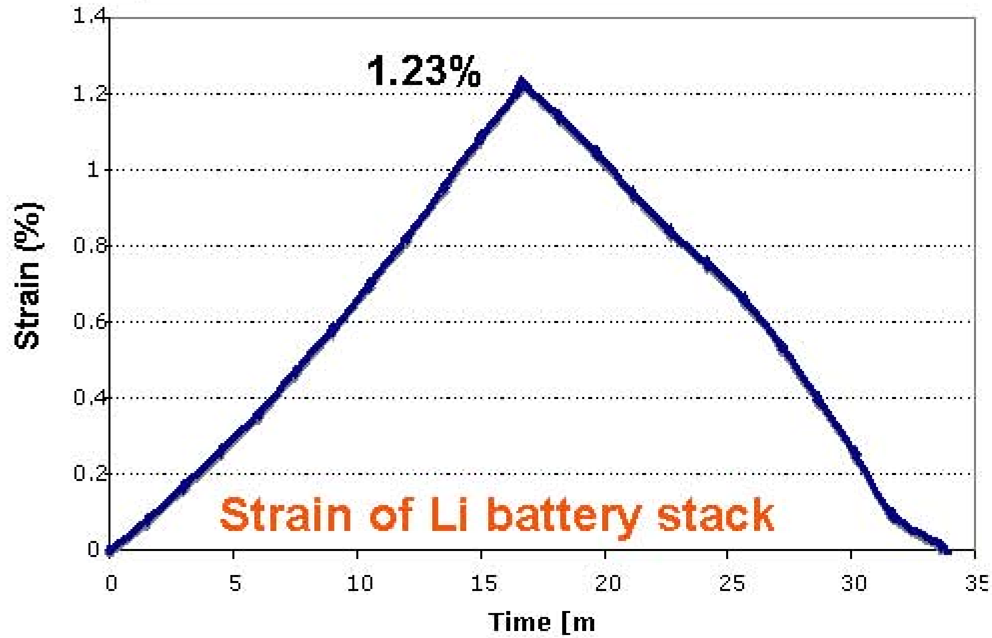
20 layer laminated cell, 6 x 34 x 50 mm

Electrochemically-Actuated Helicopter Rotor Blade

Full up-down cycle

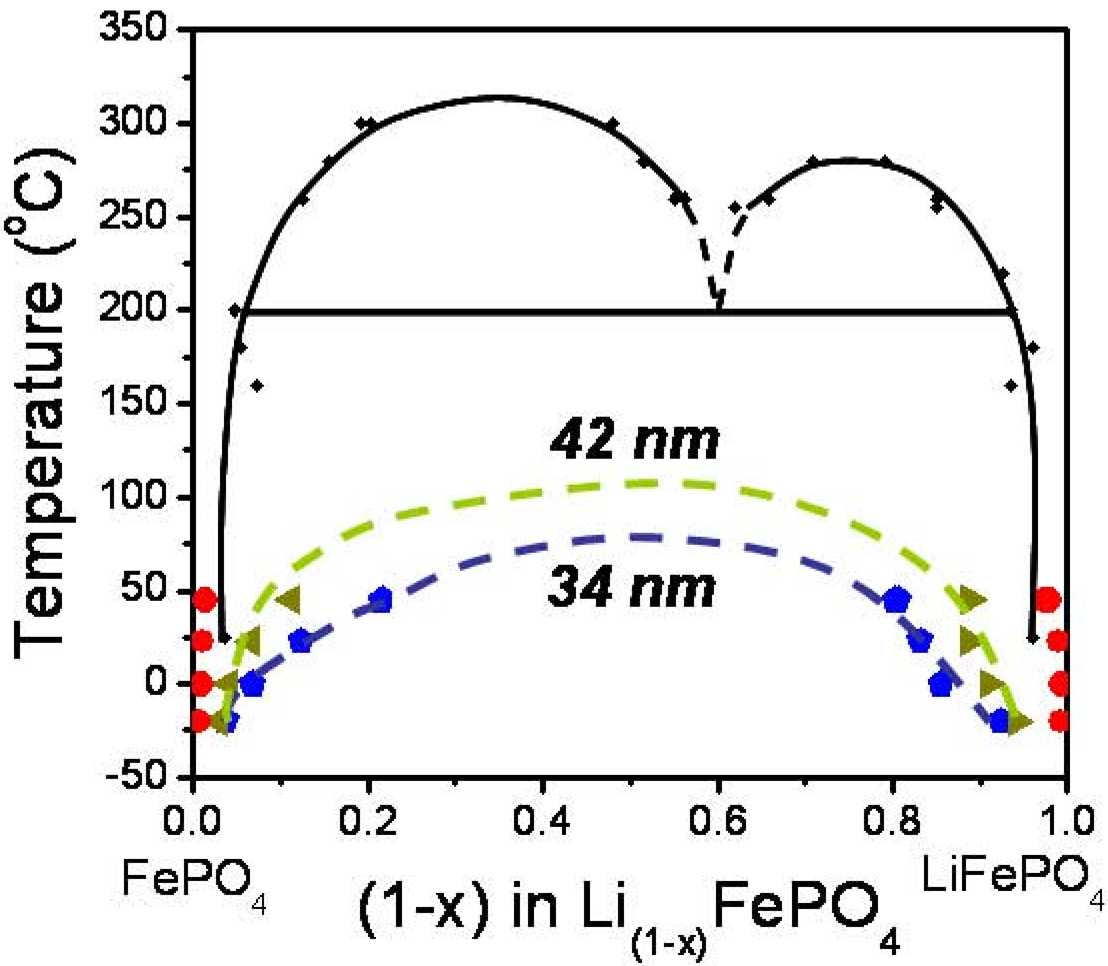
(with Steven R. Hall, Aero-Astro, MIT)

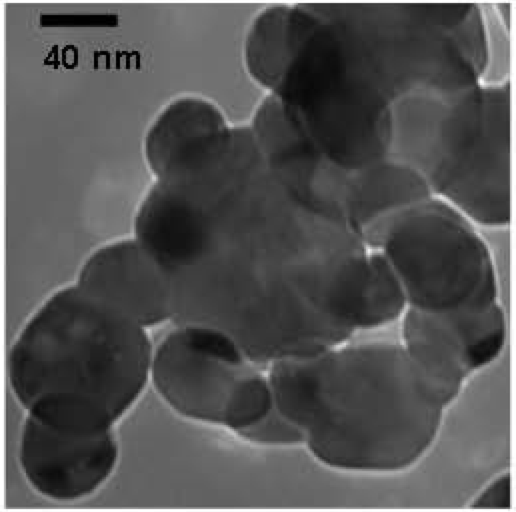


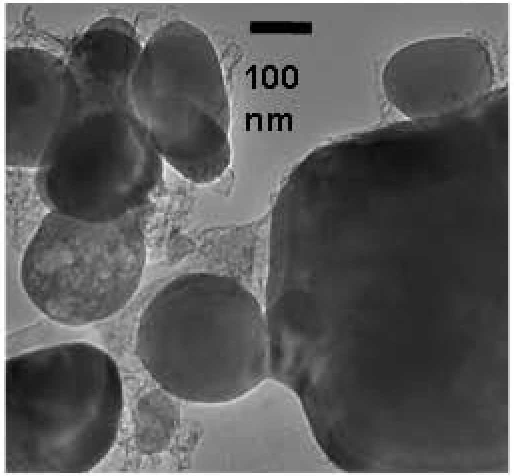


A Case Study: Electrochemically Induced Phase Transformations in Model Nanoscale Olivines $Li_{1-x}\mathit{M}PO_4$ (M = Fe, Mn)

Electrochemical, structural data show a sharp change in the width of the two-phase miscibility gap at crystallite size <100nm



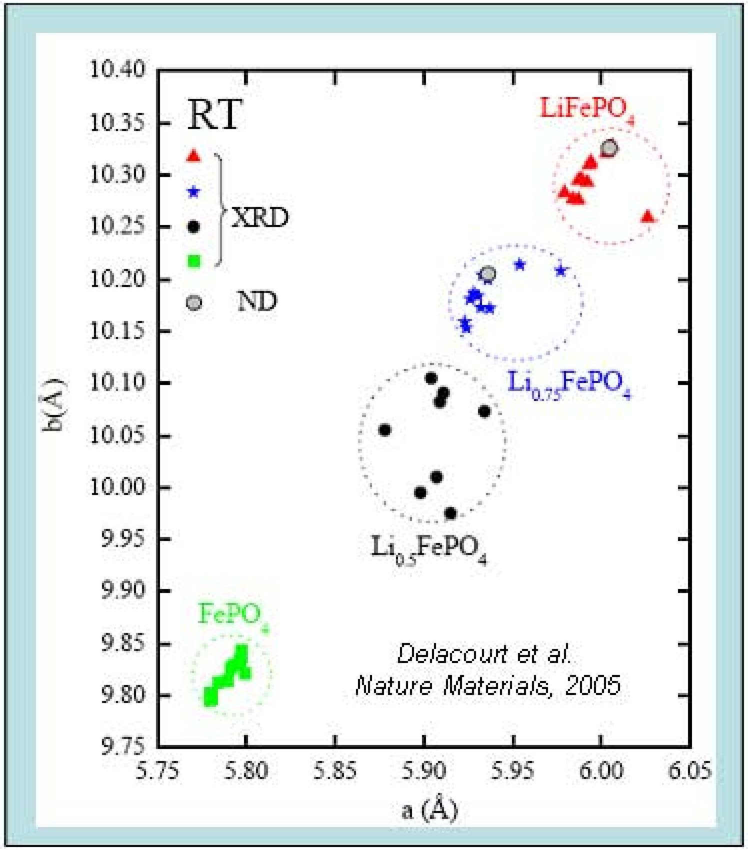




N. Meethong *et al.*, *Electrochem. Solid State Lett.*, 10[5] 134-138, 2007
(Undoped phase diagram from *Dodd et al., ESSL 2006)*

Miscibility Gap from Structure Measurements

Linear relation exists between crystal lattice constant and the concentrations of the constituent elements



Experimentally observed that lattice constants follow Vegard's law *(Delacourt et al. Nature Materials, 2005)*

Vegard's Law:

Nonstoichiometric parameters can be calculated

Solid solution Li_yFePO_4

$$y = (y_a + y_b + y_c)/3$$

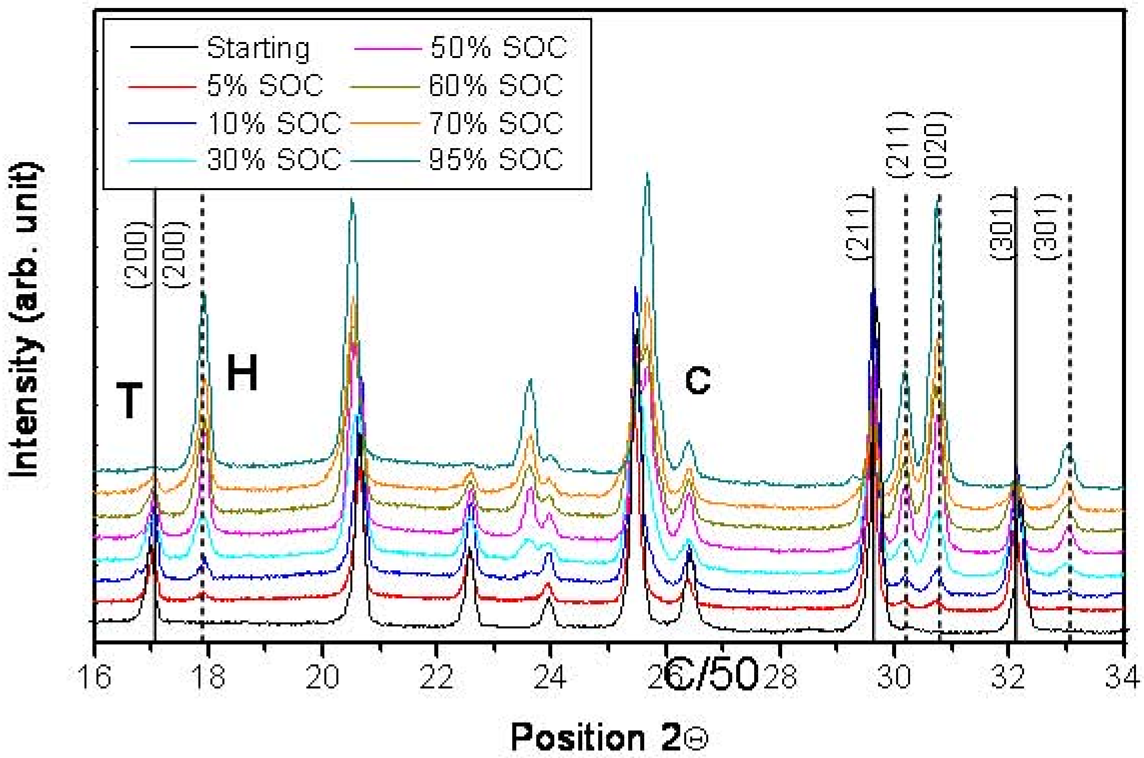
$$y_{a,b,c} = \frac{|a,b,c(Li_yFePO_4) - a,b,c(FePO_4)|}{|a,b,c(LiFePO_4) - a,b,c(FePO_4)|}$$

Solid solution $Li_{1-x}FePO_4$

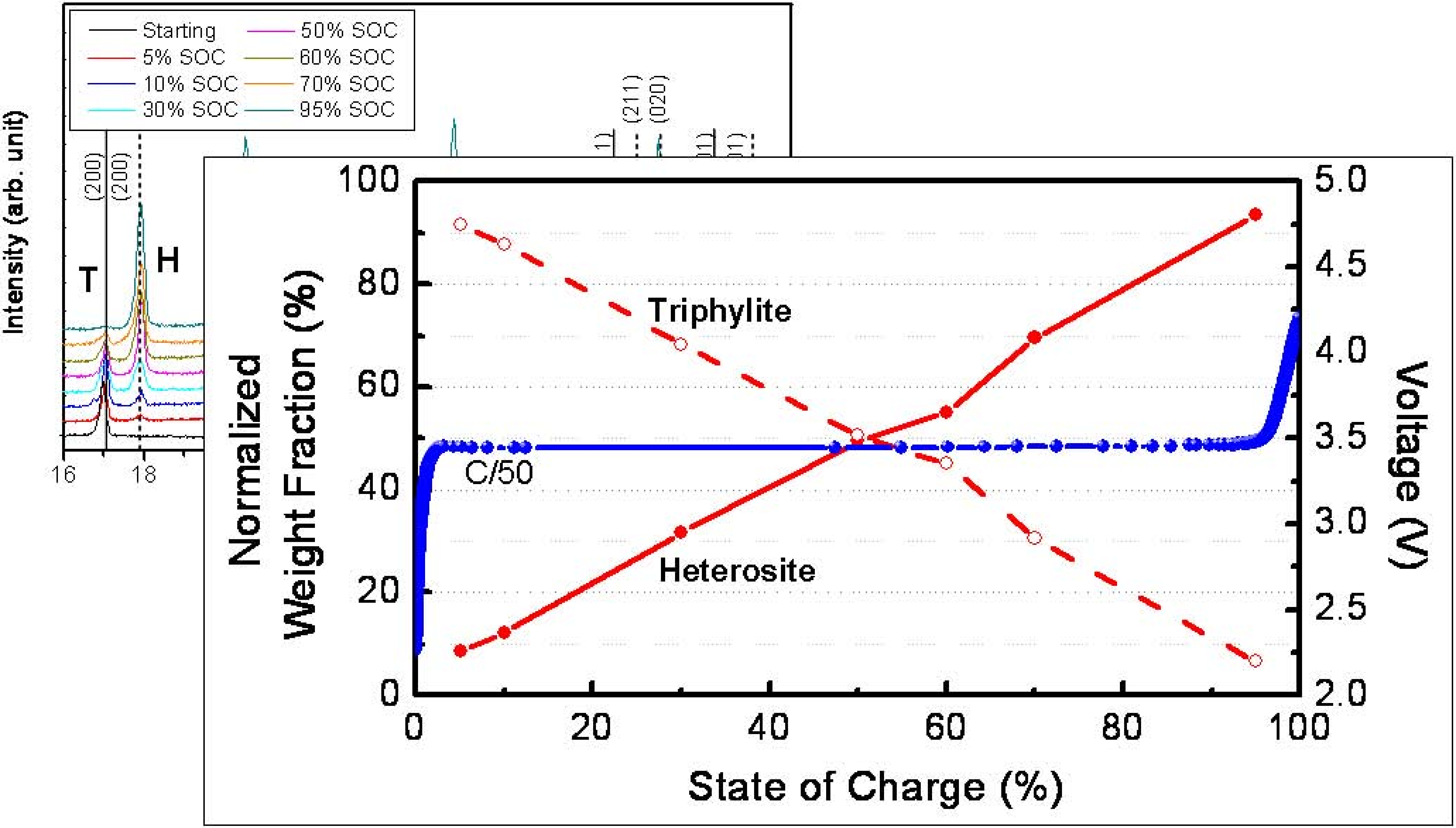
$$x = (x_a + x_b + x_c)/3$$

$$x_{a,b,c} = \frac{|a,b,c(LiFePO_4) - a,b,c(Li_{1-x}FePO_4)|}{|a,b,c(LiFePO_4) - a,b,c(FePO_4)|}$$

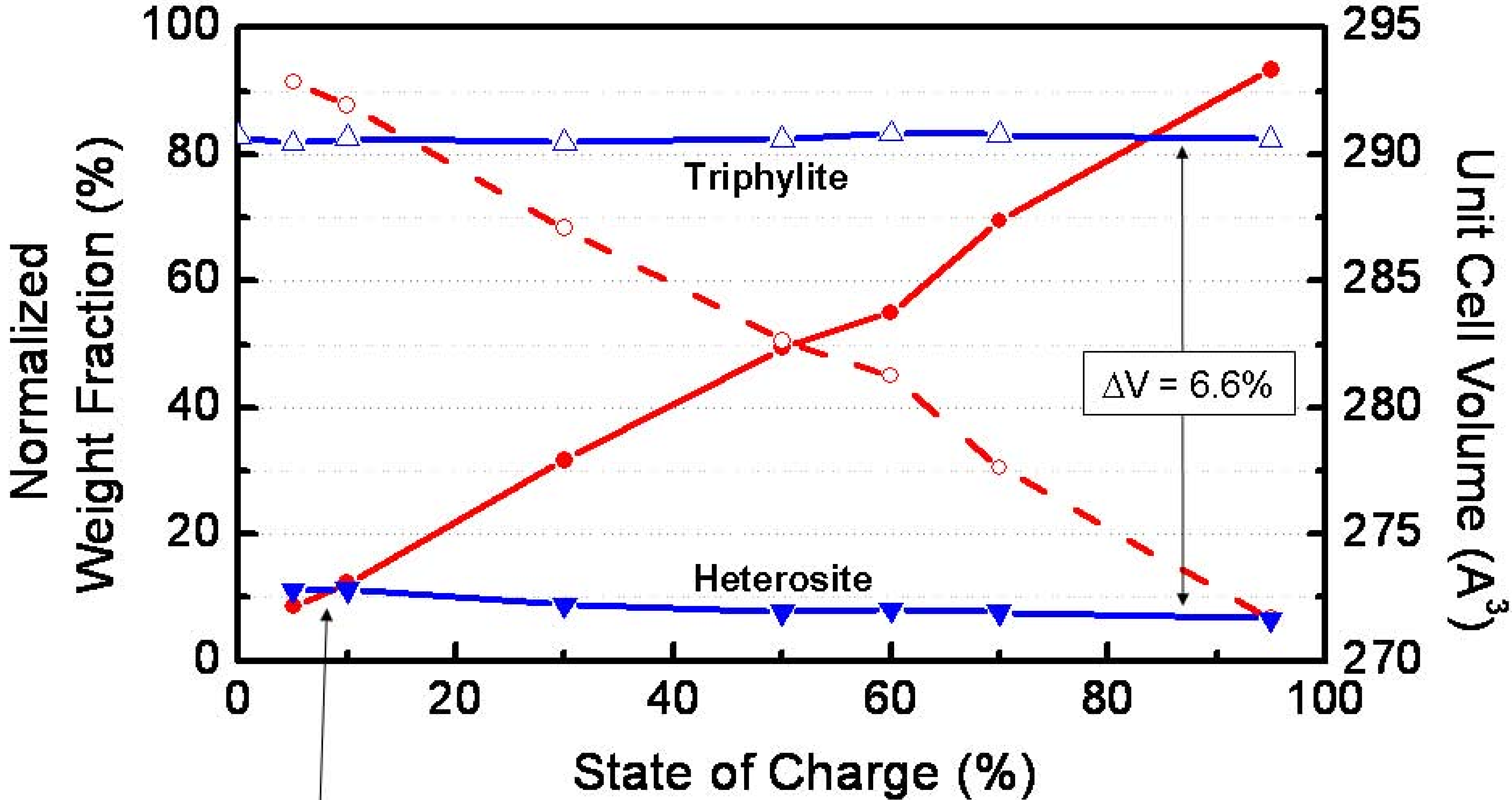
Nearly Ideal Phase Behavior in "Coarse" (113nm) $LiFePO_4$



Nearly Ideal Phase Behavior in "Coarse" (113nm) $LiFePO_4$

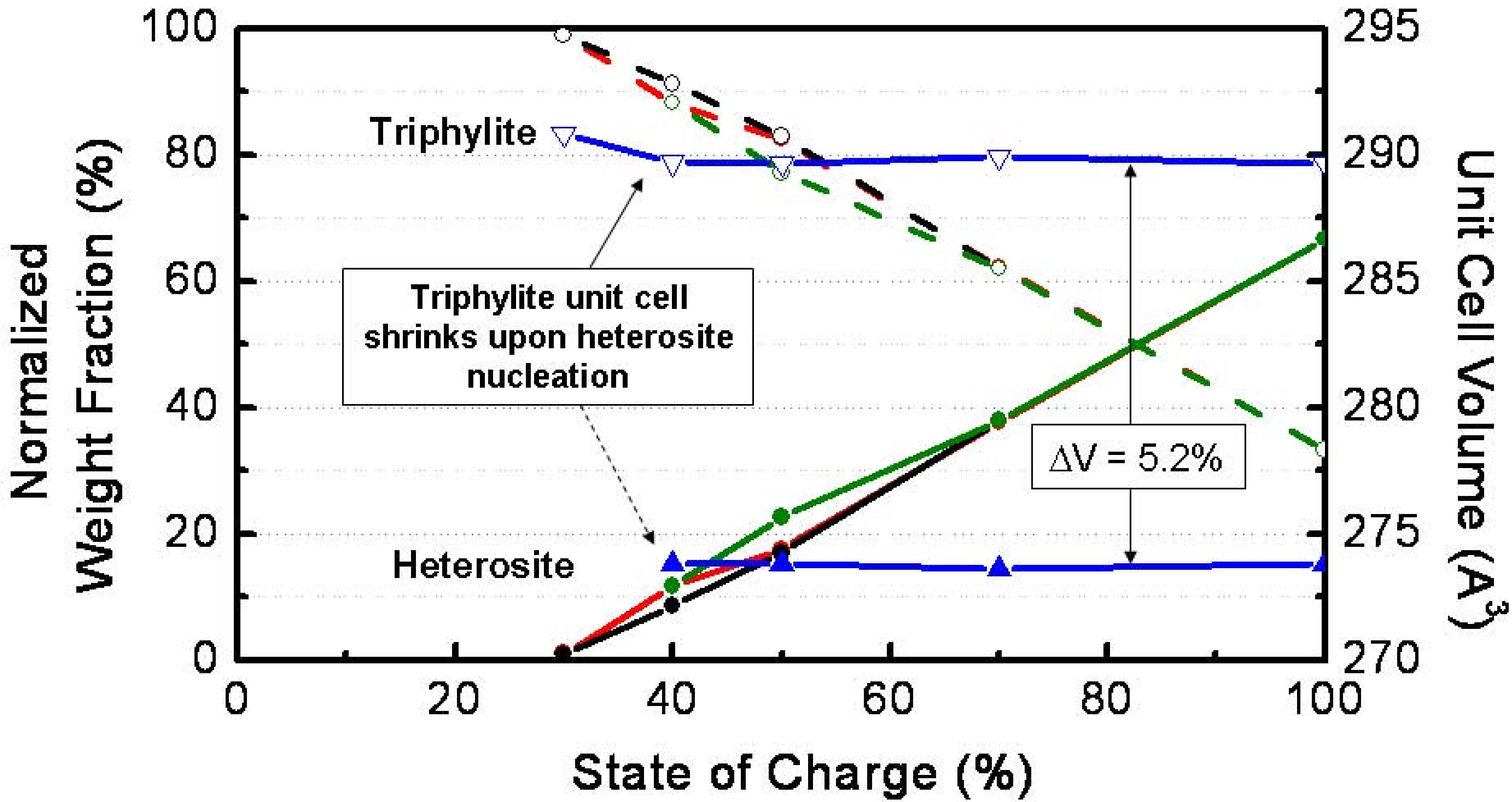


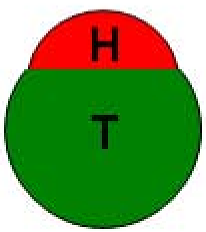
Crystal constants (from Rietveld) are nearly constant across two-phase domain in coarse (113nm) material



Slightly larger $FePO_4$ unit cell vol when first nucleated

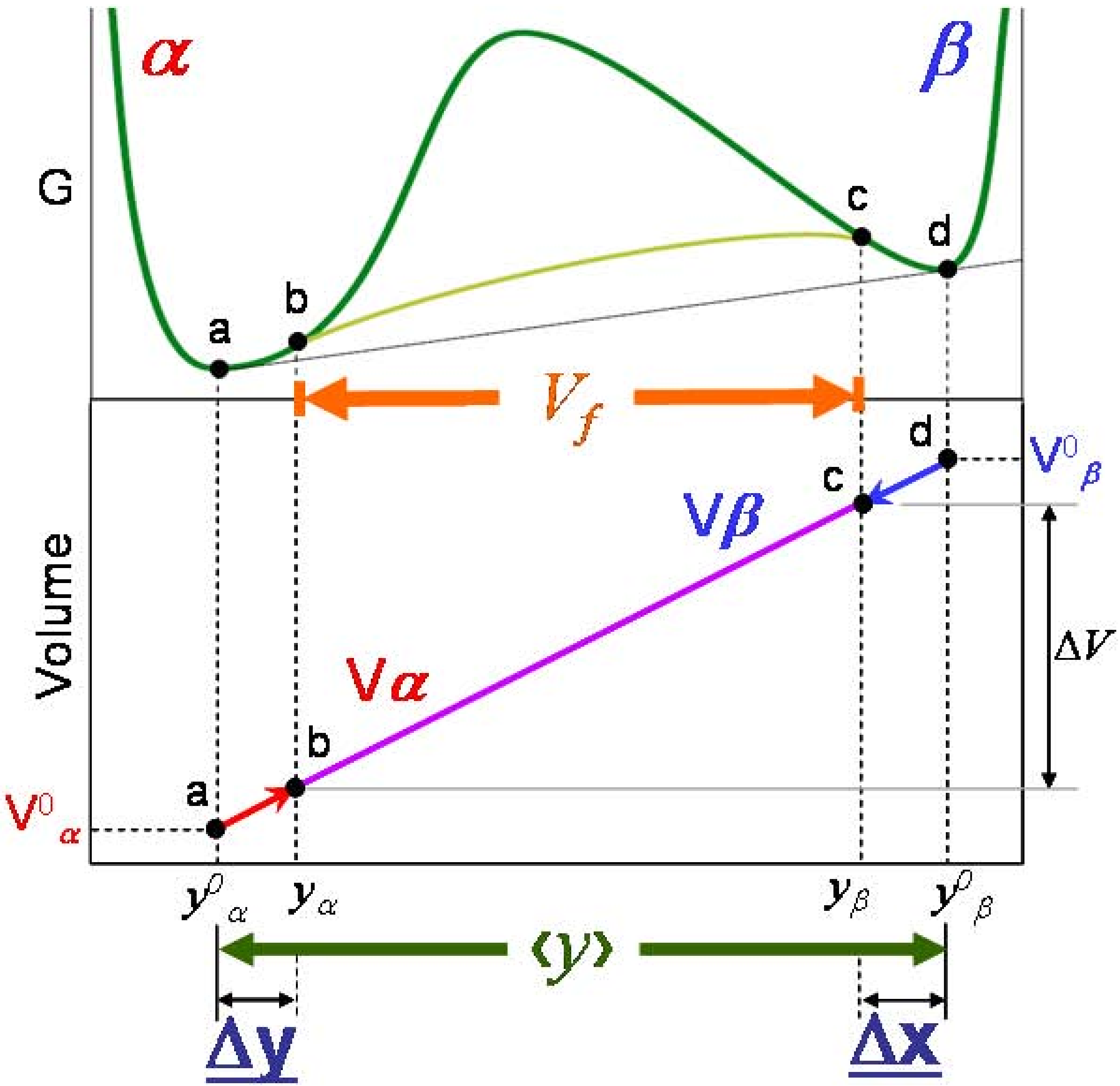
Nano (34nm) $Li_{1-x}FePO_4$: Lattice Constant Variation and Absolute Values Consistent with Retention of Coherency Stresses





Misfit between phases is reduced by coherency stress

Coherency Stresses Shrink the Miscibility Gap



New equilibrium compositions reduce elastic misfit energy

Result: Smaller miscibility gap, extended solid solutions of both phases

Rietveld Refinement of Structure Shows Reduced Lattice Misfit between Co-existing Phases in the Nanoscale Materials

Compositional state	Sample NC ~50% SOC	Sample AC ~50%SOC	Yamada (16) Stoichiometric	Yamada (16) Solid sol'n limits	Yamada (18) Stoichiometric	Padhi (1) Stoichiometric	Andersson (31) Stoichiometric	Yamada (30) Stoichiometric
Specific Surface Area (	39.2	14.8	7-13	7-14	unknown	unknown	unknown	unknown
Carbon Content (wt%)	2.4	1-3*	8	8	unknown	25	15	9.8
LiFePO4 phase								LiMnPO4
a (angstroms)	10							
b (angstroms)	5.							
c (angstroms)	4							
V (angstroms^3)	287							
Strain (%)	0							
Crystallite size (A)	2							
FePO4 phase								
a (angstroms)	9.							
b (angstroms)	5.							
c (angstroms)	4.7							
V (angstroms^3)	275							
Strain (%)	0.							
Crystallite size (A)	27							
Misfit (%)								
Linear Strain								
a axis	3.430	4.983	5.025	4.767	5.047	5.091	5.111	8.159
b axis	1.749	3.601	3.671	3.415	3.667	3.661	3.683	3.159
c axis	-1.022	-1.957	-1.883	-1.716	-1.903	-2.004	-1.926	-0.483
Volume strain	4.146	6.626	6.445	6.464	6.811	6.753	6.867	10.830
Planar Strain								
a-b plane {001}	5.178	8.581	8.691	8.179	8.711	8.747	8.790	11.311
a-c plane {010}	2.408	3.027	3.143	3.052	3.145	3.087	3.187	7.677
b-c plane {100}	0.727	1.645	1.788	1.700	1.765	1.657	1.757	2.676

**Quoated by manufacturer*
*** Taken as the difference/mean value*

Reduced crystallographic mismatch between co-existing phases

Volume mismatch: 4.15% (doped nano) vs. 6.5 – 6.6% (conventional)

Strain in {100} ***plane of least misfit*** between coexisting phases:

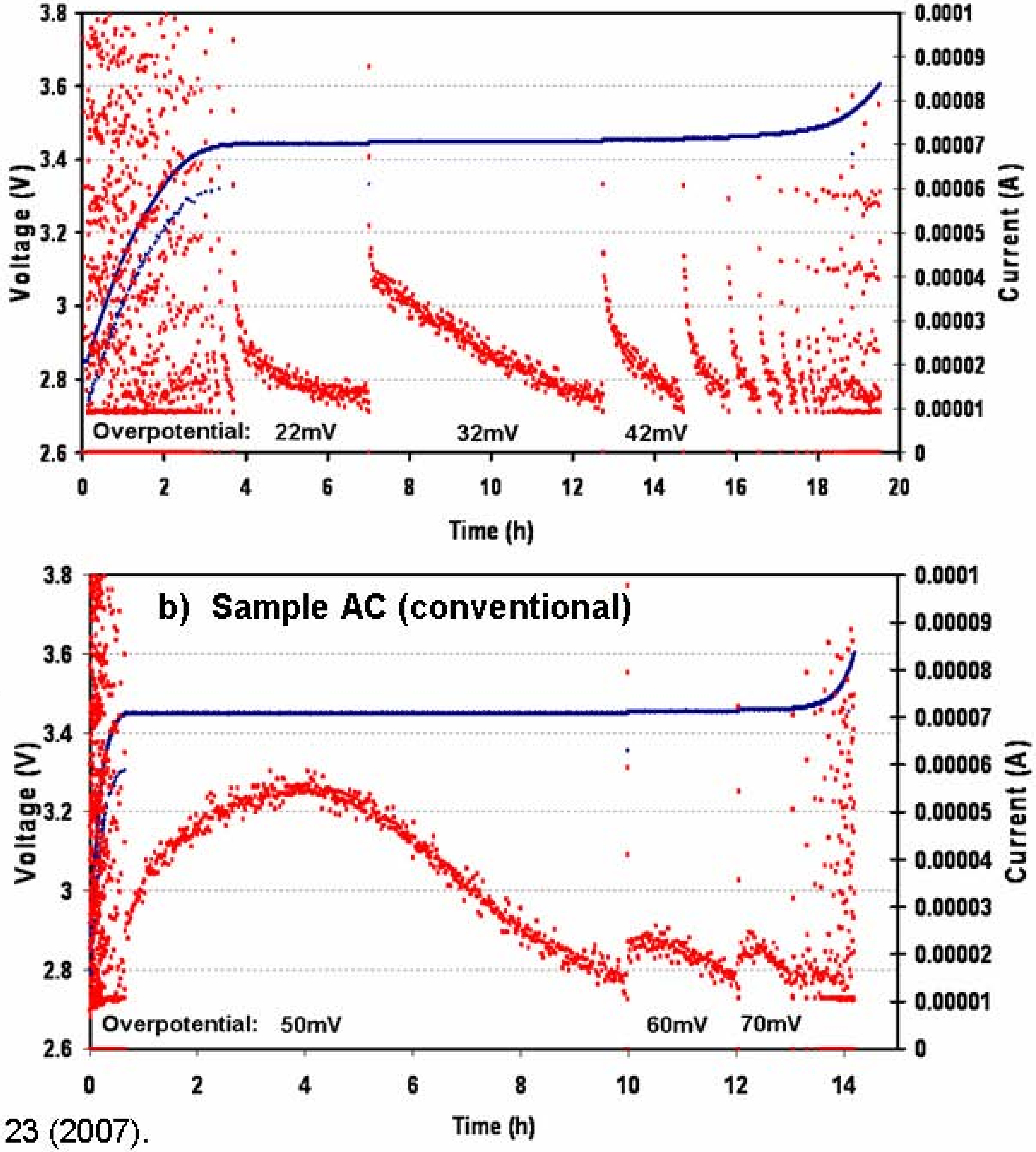
0.73% (doped nano)
1.65 – 1.79% (conventional)

→ Reduced misfit should permit ***coherent phase boundary between lithiated and delithiated phase***

Coherency Enables Faster Phase Transformation Kinetics → High Power

Kinetic Information from Potentiostatic tests:

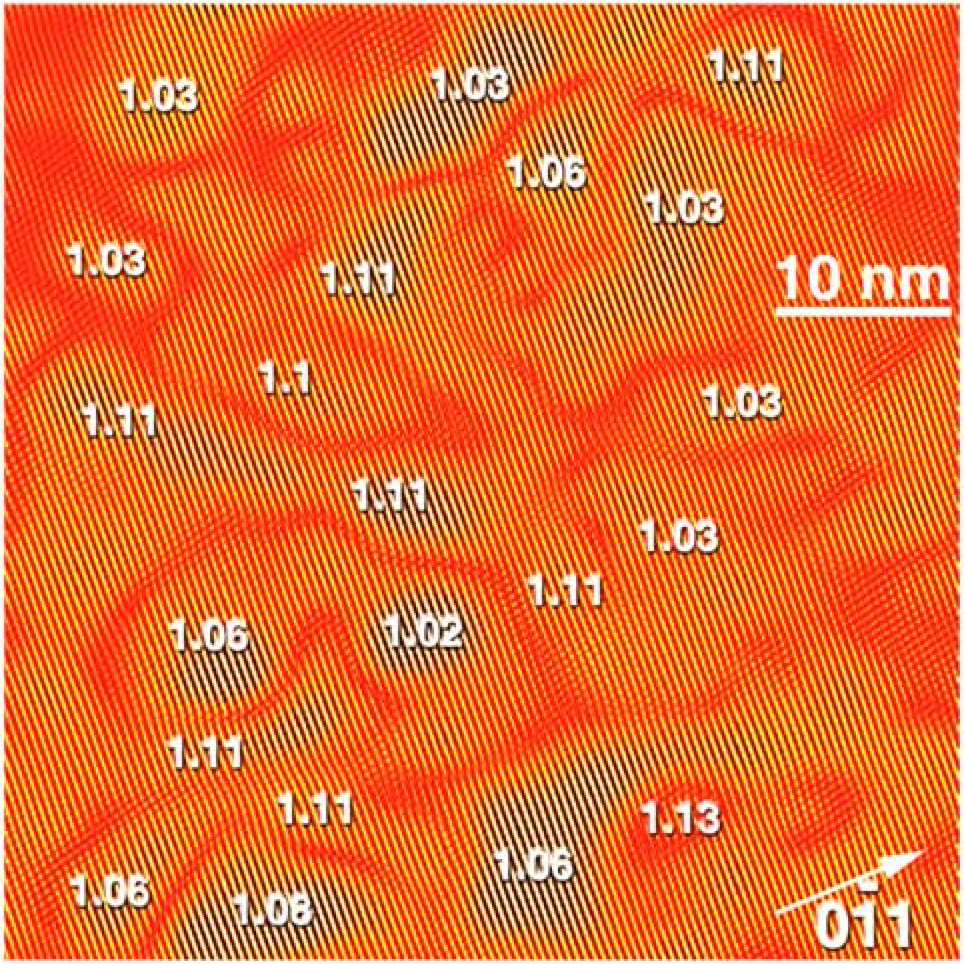
- Current flow (red) upon stepwise change in voltage is ***proportional to phase transformation rate***
- Completely different kinetics in the two types of materials
- Low-rate sample cannot be modeled with Fickian diffusion – nucleation barrier to phase transformation



N. Meethong *et al.*, *Adv. Funct. Mater.*, **17**, 1115-1123 (2007).

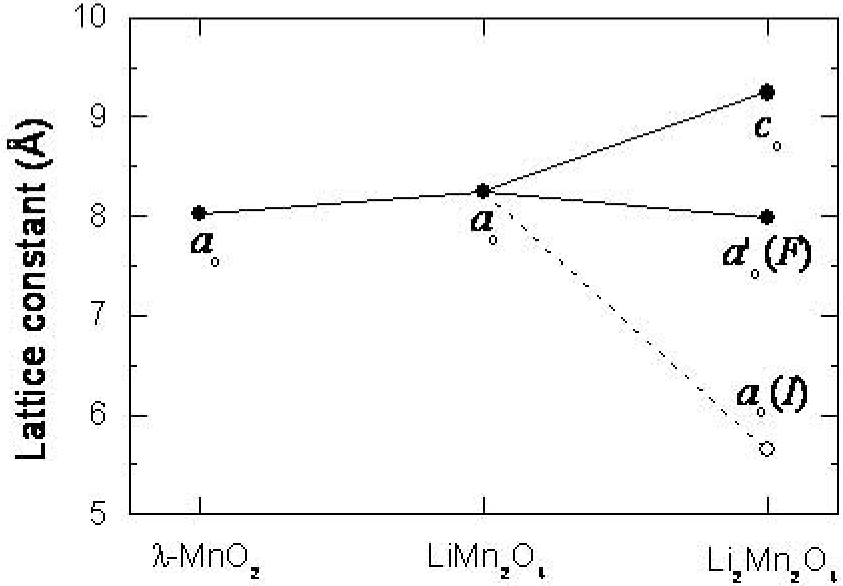
Another Example: Strain Accommodation in $Li_xMn_2O_4$ upon Electrochemical Cycling (cyclic variation in composition *x*)

Numbers: c/a ratio of tetragonal $Li_2Mn_2O_4$



Nanoscale ferroelastic domains accommodate reversible cycling

Y.-M. Chiang, H. Wang, Y.-I. Jang, *Chem. Mater.*, **13**, 53-63, 2001

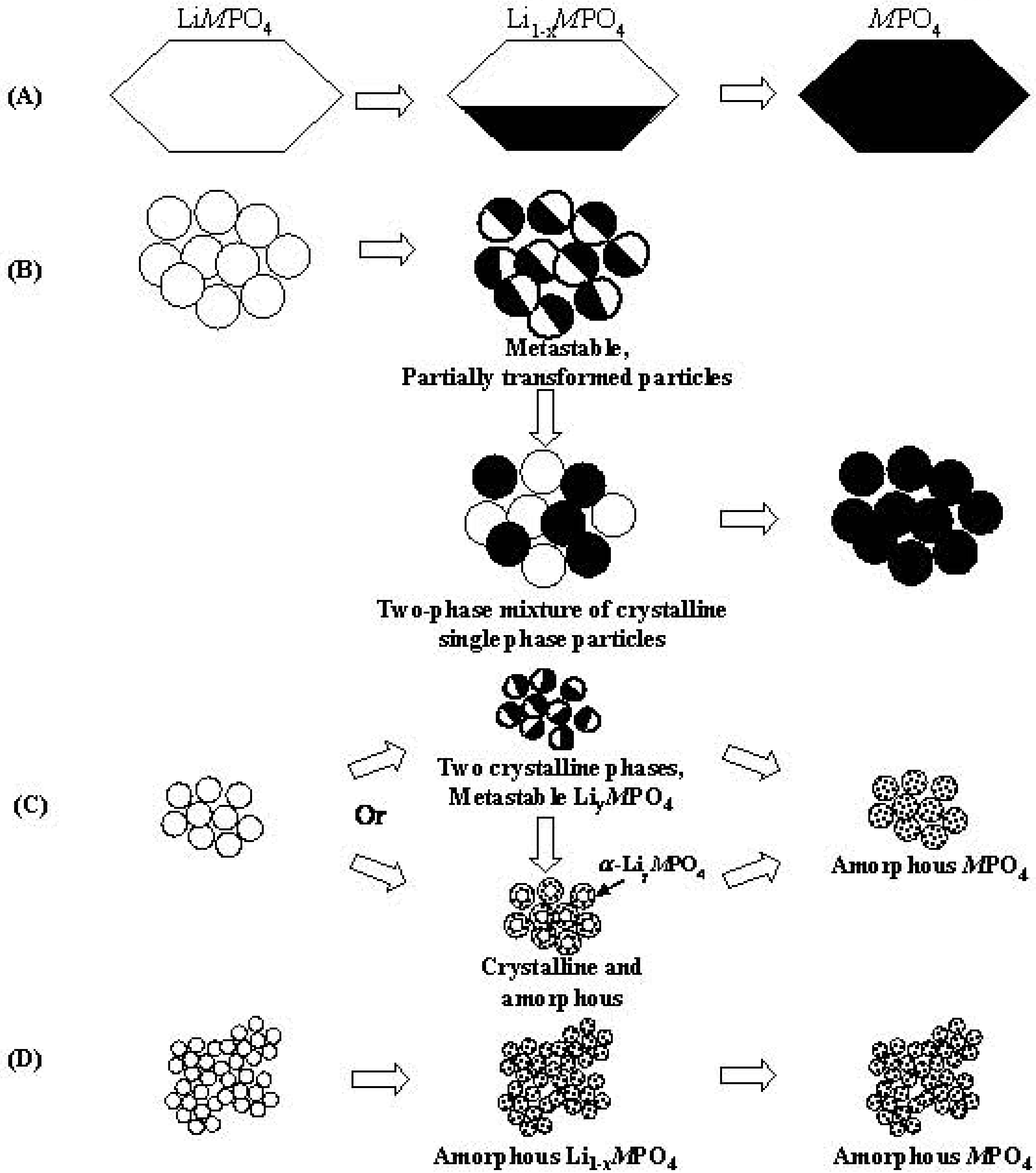


16% change in c/a ratio upon cubic to tetragonal transformation if unconstrained bulk phase

M.M. Thackeray, *Prog. Solid St. Chem.*, **25**, 1-71 (1997)

Gives high charge capacity (~250 mAh/g) but only at very low rates since overall particle size is large.

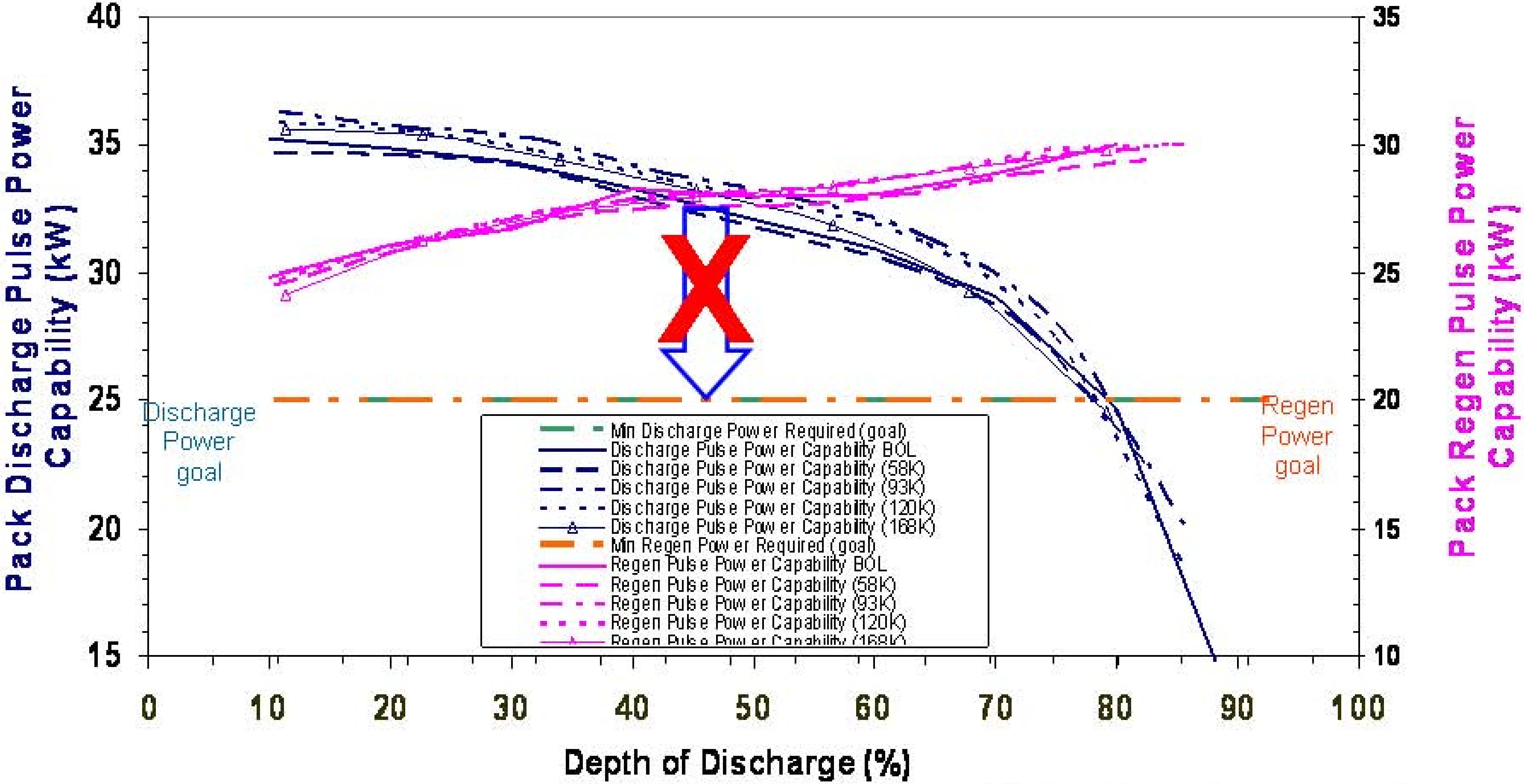
In reality, a variety of phase transformation paths are possible during cycling



Detailed path depends on composition, size scale, and affects electrochemical performance

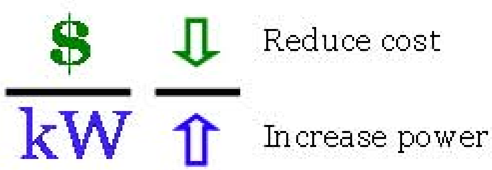
N. Meethong et al., MIT, 2007

High power coupled with long cycle life enables HEV applications: smaller packs, less "oversizing," lower cost



In typical systems, curves shift down due to impedance growth

Minimal impedance growth: no substantial loss of power with cycling



Improving power *reduces* system cost.

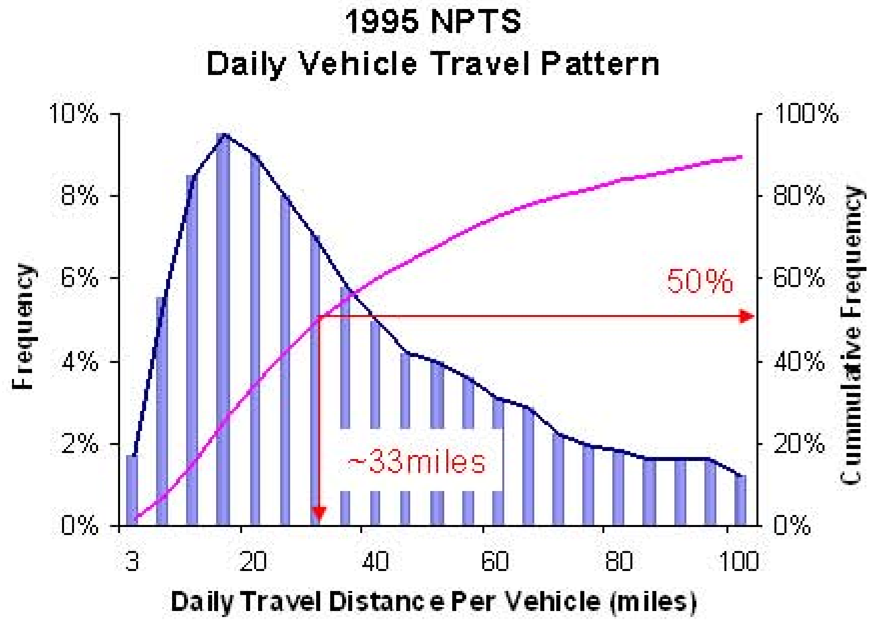
A123 SYSTEMS

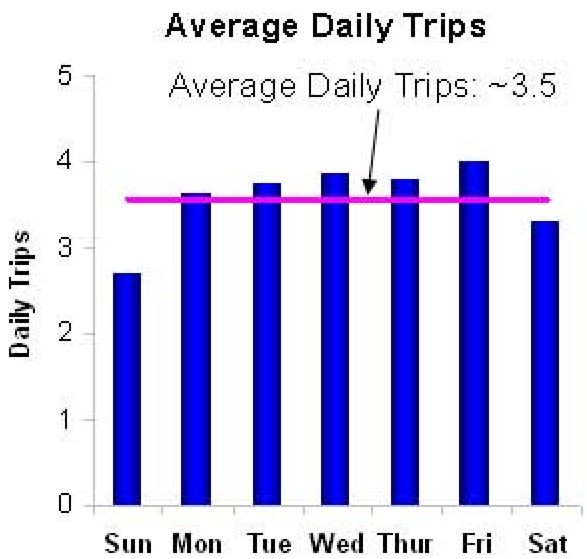
The Case for Plug-in Hybrids

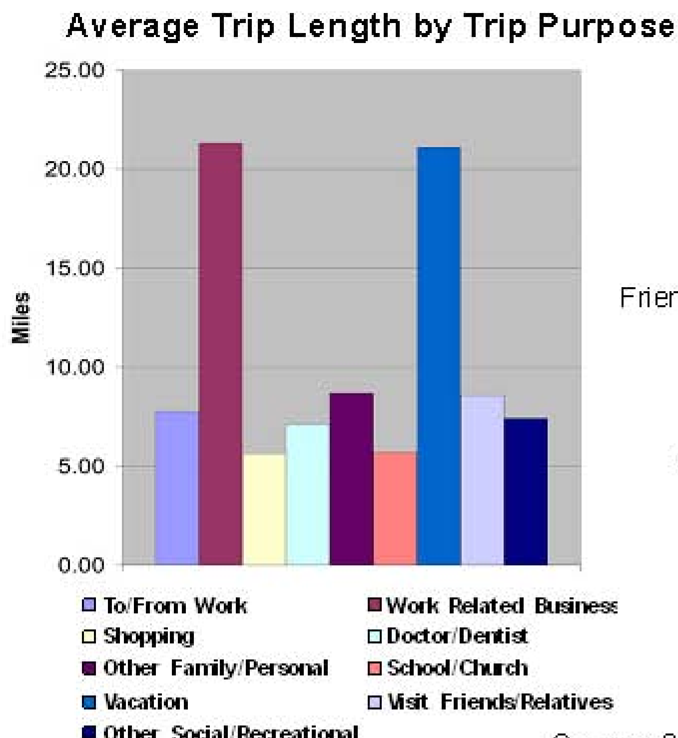
Lucy Sanna, EPRI

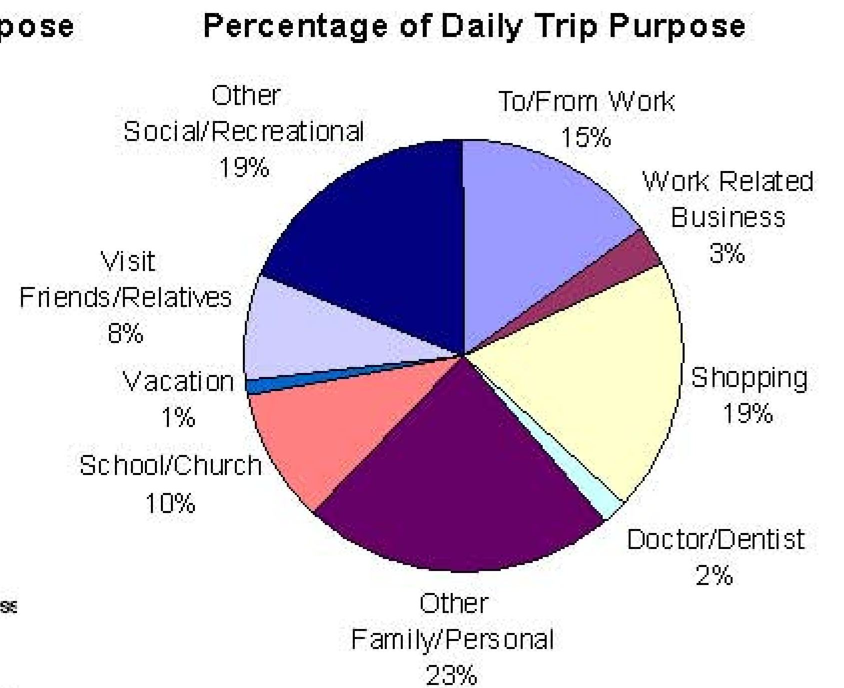
American Driving Habits Favor PHEVs over Pure EVs

- Half the cars are driven less than 40 miles
  - Median daily travel distance is ~33 miles
- Average vehicle travel ~3.5 trips per day
- Most of the daily trips are less than 10 miles
- 10% of vehicles travel >100 miles daily









Source: 2001 National Household Travel Survey

1st-Generation Plug-In Hybrids (PHEV)

- 80% lower gas consumption
- 50% lower greenhouse gas emission

Compared to 25 mpg gasoline powered car

Commuting Distance	Measured City MPG	Measured Highway MPG
20 miles	174	117
40 miles	153	103
60 miles	124	90

Hymotion Prius PHEV

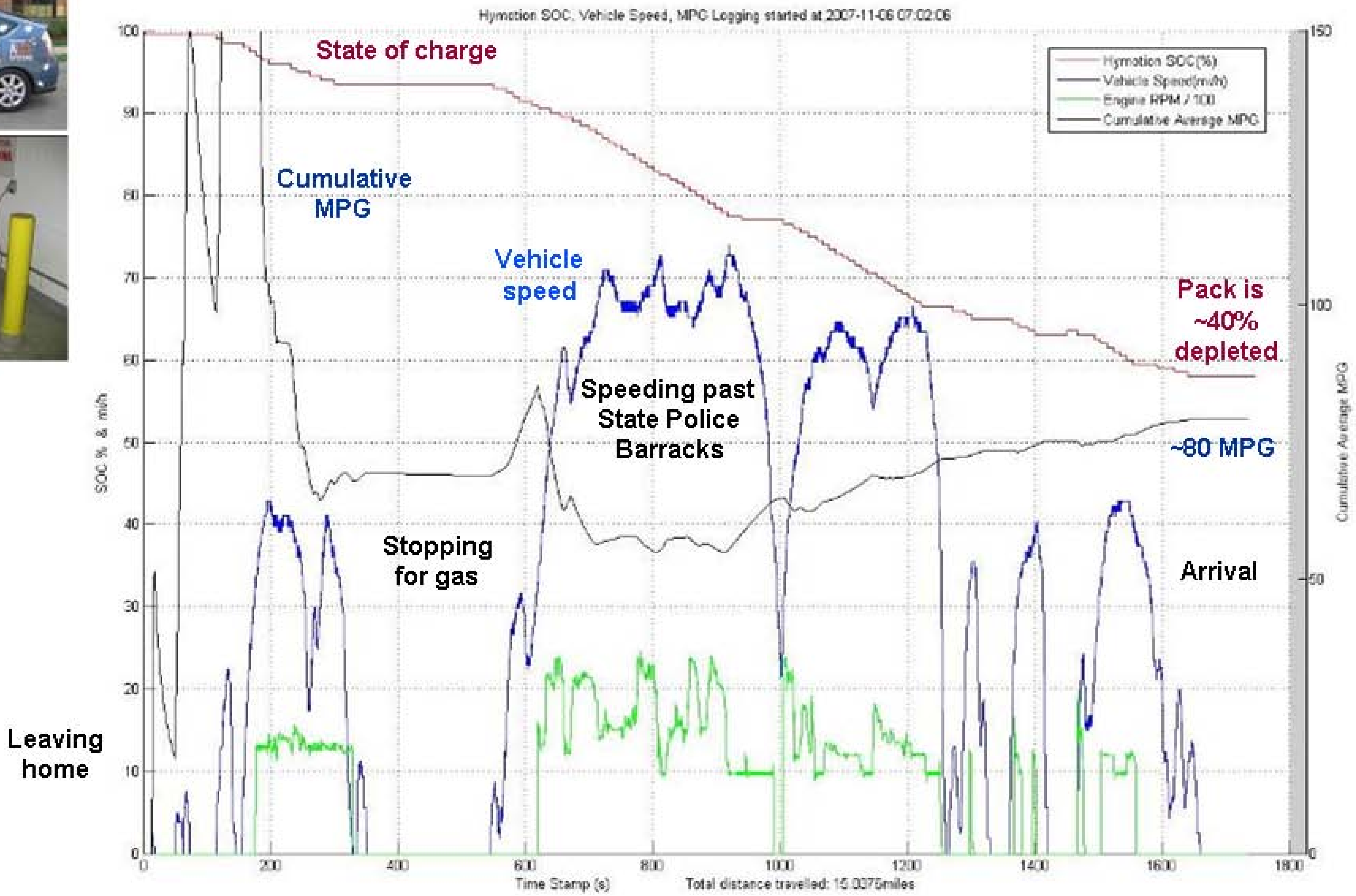
- Blended Mode PHEV(5kWh)
- Li-Ion battery pack added to stock NiMH pack
- Installed in ANL's highly instrumented Prius





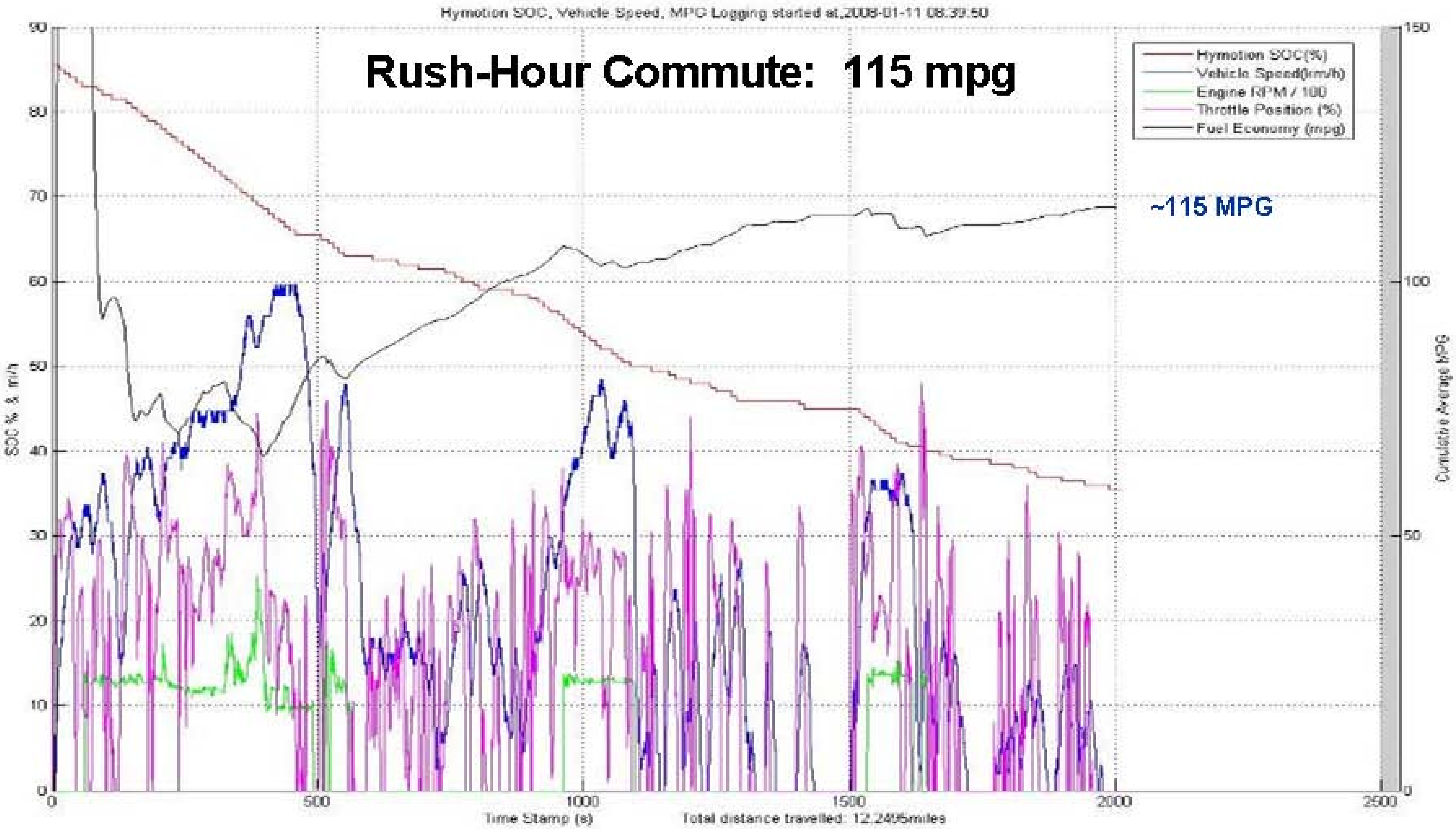
Hymotion

Data logging: Framingham MA to Cambridge in the A123 PHEV-converted Prius (5 kWh Li-ion pack)




Energy Monitor
ENGINE
BATTERY
ELEC MOTOR
Consumption
Current 99.9 MPG


Consumption
41°F
Energy
Average
96.8 MPG
9 miles
Reset
Current


Hymotion SOC, Vehicle Speed, MPG Logging started at,2008-01-11 08:39:50
Rush-Hour Commute: 115 mpg
Hymotion SOC(%)
Vehicle Speed(km/h)
Engine RPM / 100
Throttle Position (%)
Fuel Economy (mpg)
~115 MPG
SOC % & m/h
Cumulative Average MPG
Time Stamp (s)
Total distance travelled: 12.2495miles

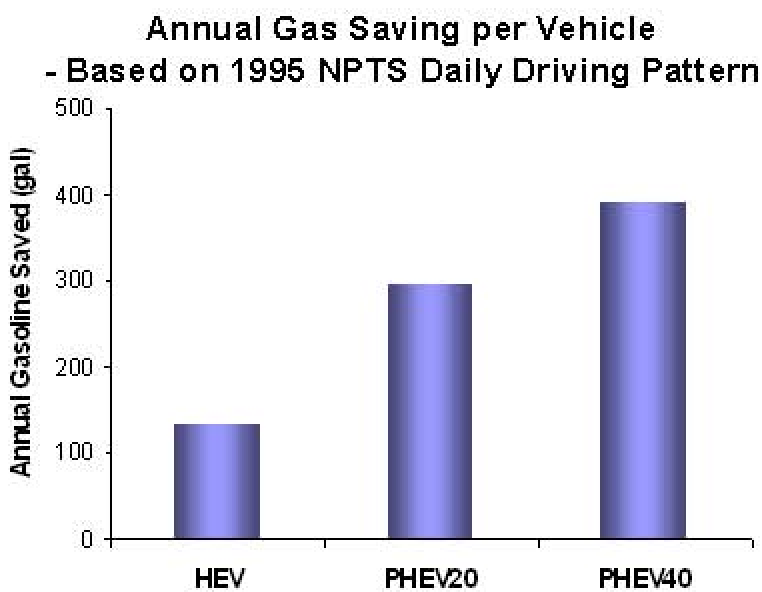
Impact of PHEVs on Annual Gasoline Saving Nationwide

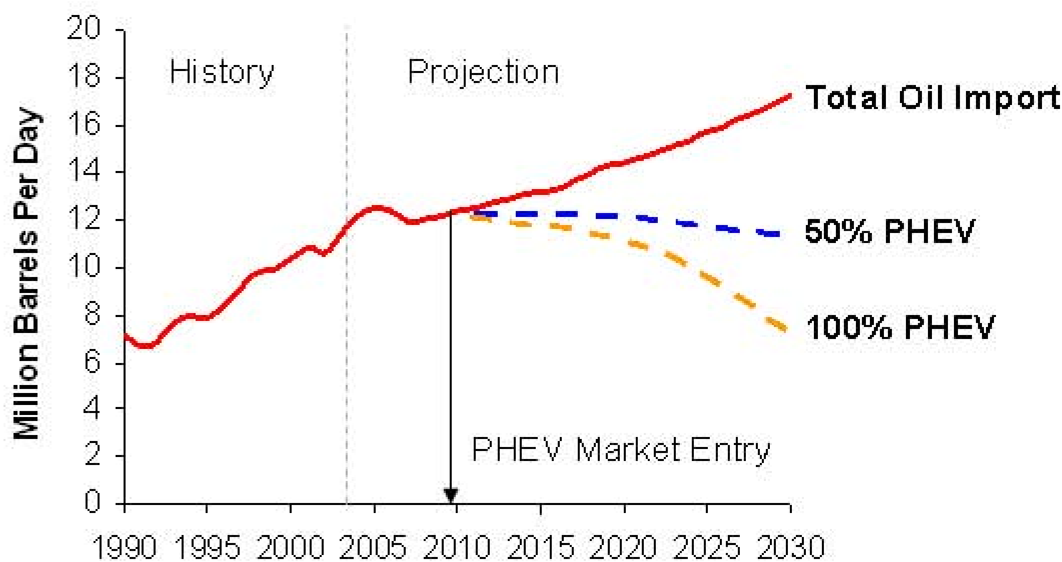
"Transportation accounts for 87% of the increase in petroleum consumption, dominated by growth in fuel use for light-duty vehicles."
- Annual Energy Outlook 2006 with Projections to 2030

By End of 2004 there are 243 Million passenger vehicle on the road.

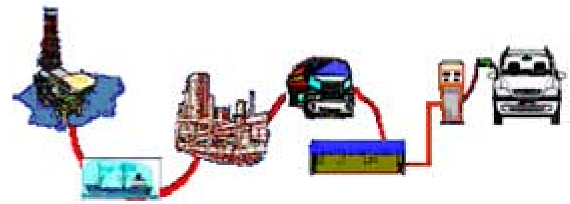
This number is projected to be double by 2030 ~500 million passenger vehicle

- If half of that are PHEV40 oil consumption in US will drop 6 million barrel per day
- If all of that are PHEV40, oil consumption in US will drop 10 million barrel per day





Impact of Plug-In Hybrids on Well-to-Wheel GHG Emission

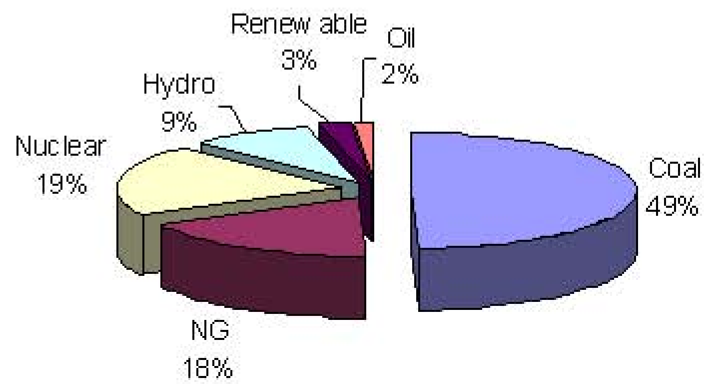


- Well-to-Wheel Paths:
  - Oil - Gasoline - CV
  - Coal - Electricity - EV
  - NG (CCGT) - Electricity - EV
- Well-to-Wheel CO_2 Emission:

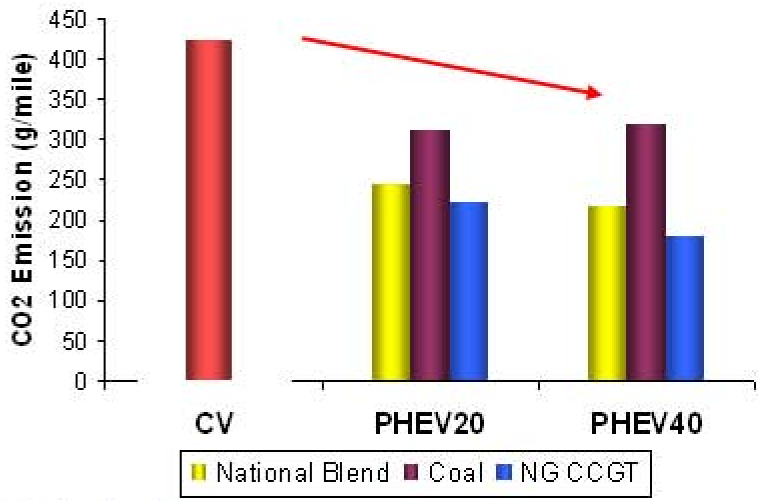
Oil - Gasoline	166 lb/MMBtu	181 miles/MMBtu	416 g/mile
Coal -Electric	224 lb/MMBtu	312 miles/MMBtu*	327 g/mile
NG - Electric	138 lb/MMBtu	447 miles/MMBtu*	141 g/mile

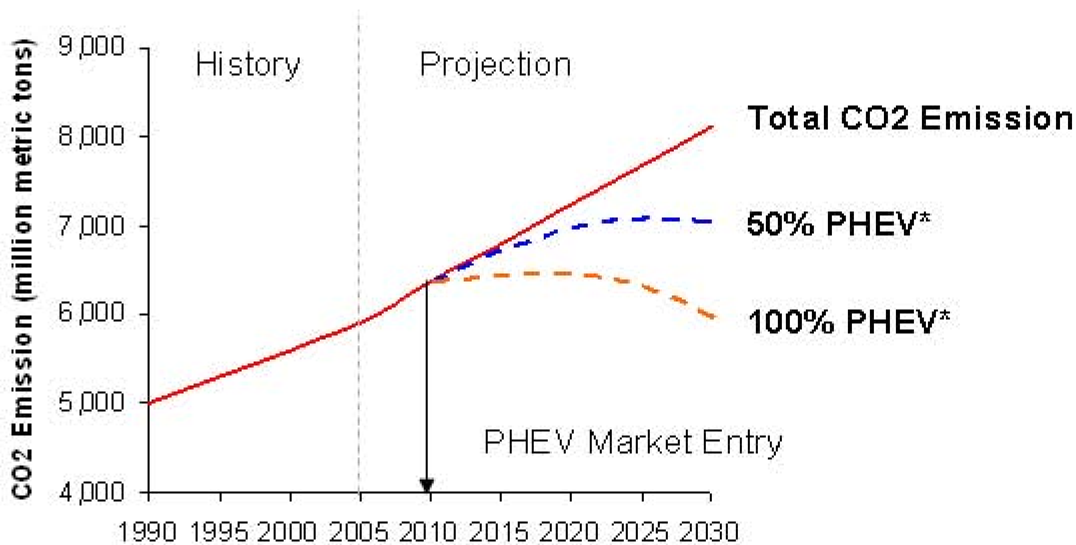
* Pure EV miles

US Power Generation (National Blend)



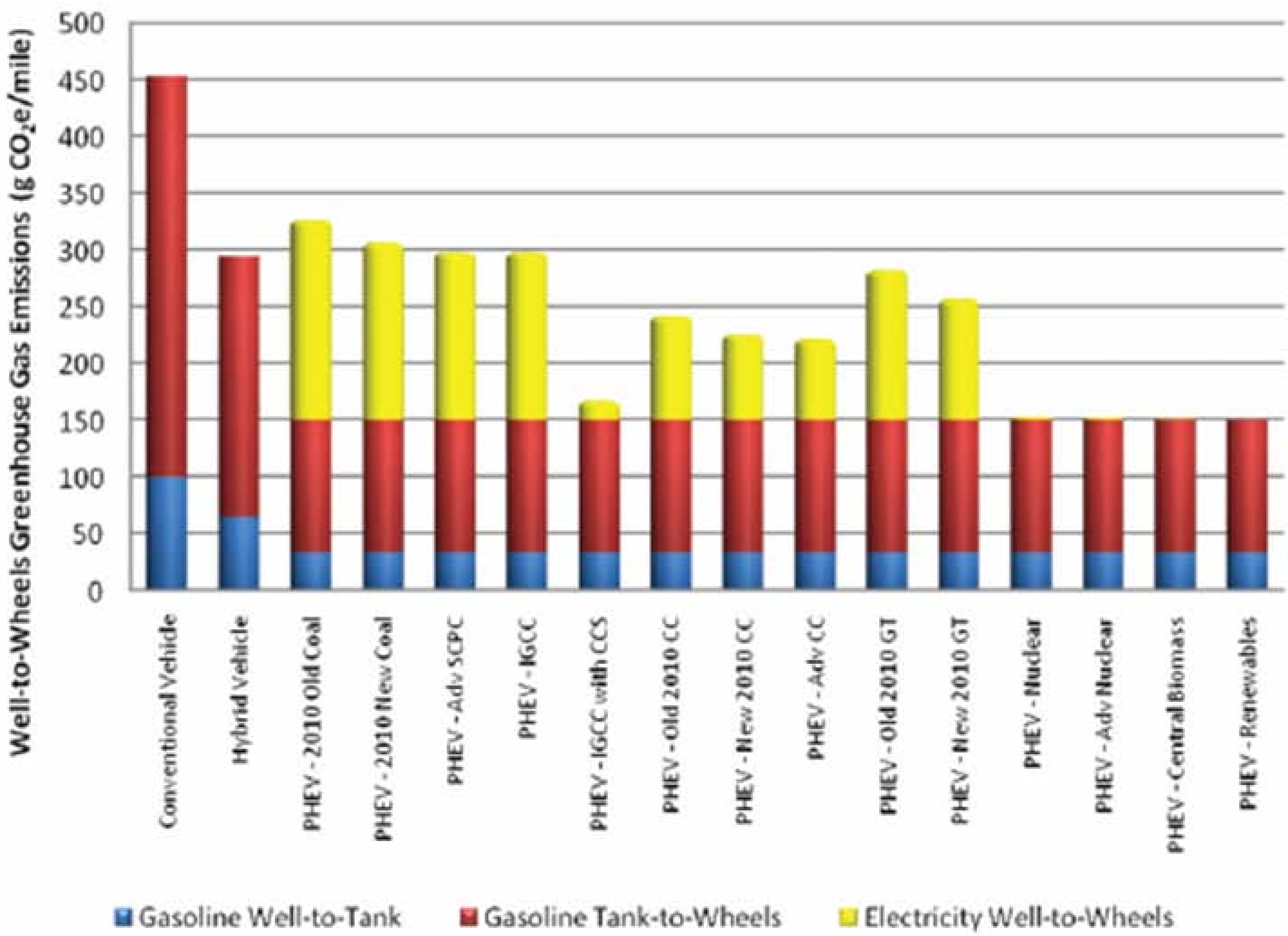
CO2 Emission (g/mile)





* Assuming 500million passenger vehicle in 2030

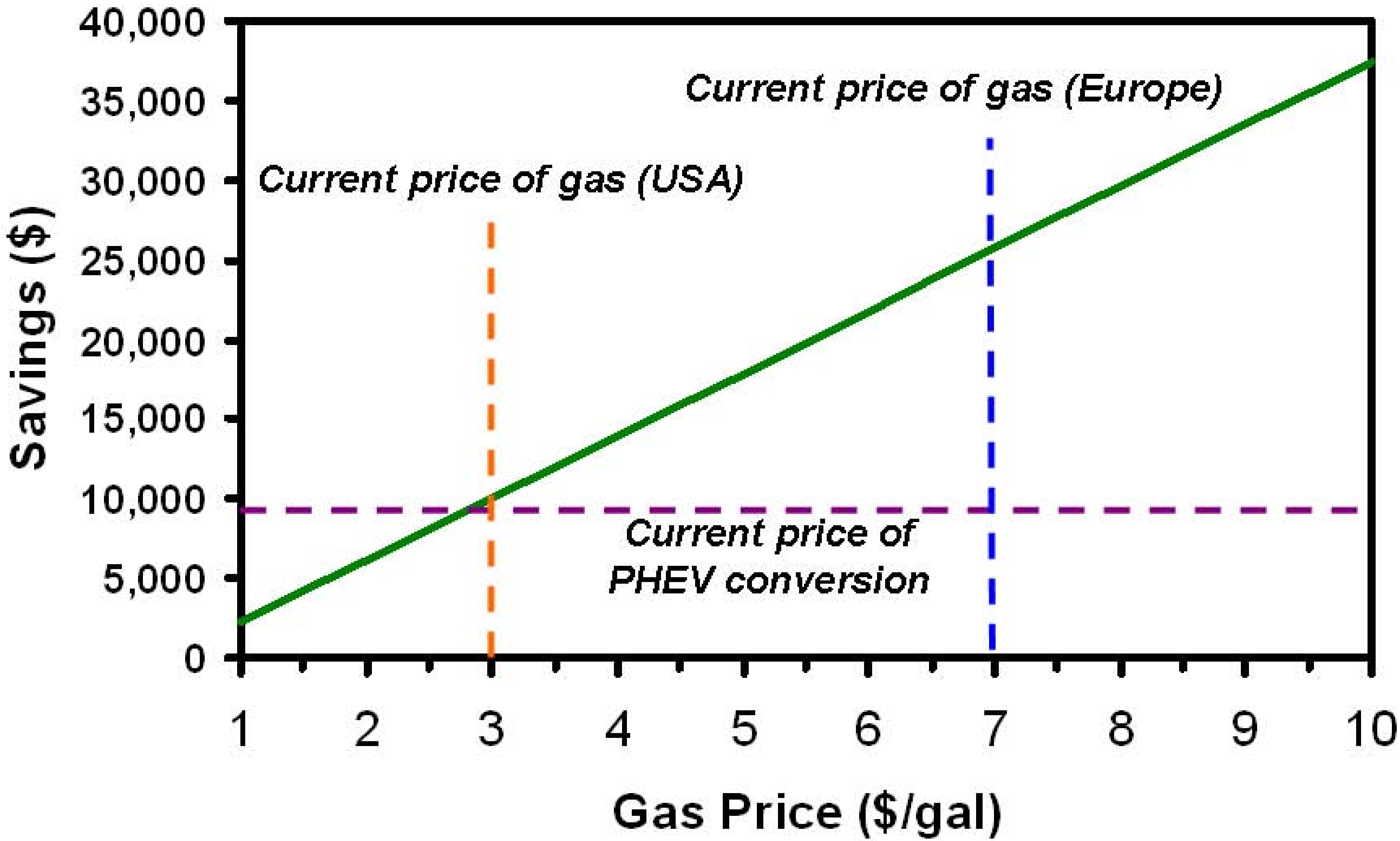
2010 Scenario: CO_2 reduction vs. power plant technology



Year 2010 comparison of PHEV 20 GHG emissions when charged entirely with electricity from specific power plant technologies (12,000 miles driven per year).

Payback Scenario

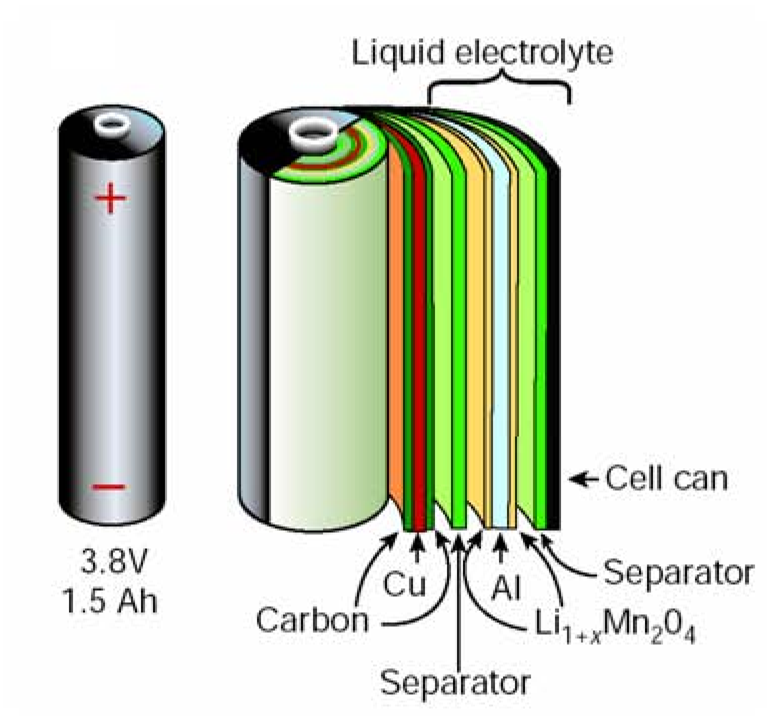
- Dollar savings of 100mpg PHEV40 over 25mpg conventional vehicle
- Driven 13,000 miles/yr for 10 yrs
- Electricity cost $0.10/kWh, ~150 Wh/mile



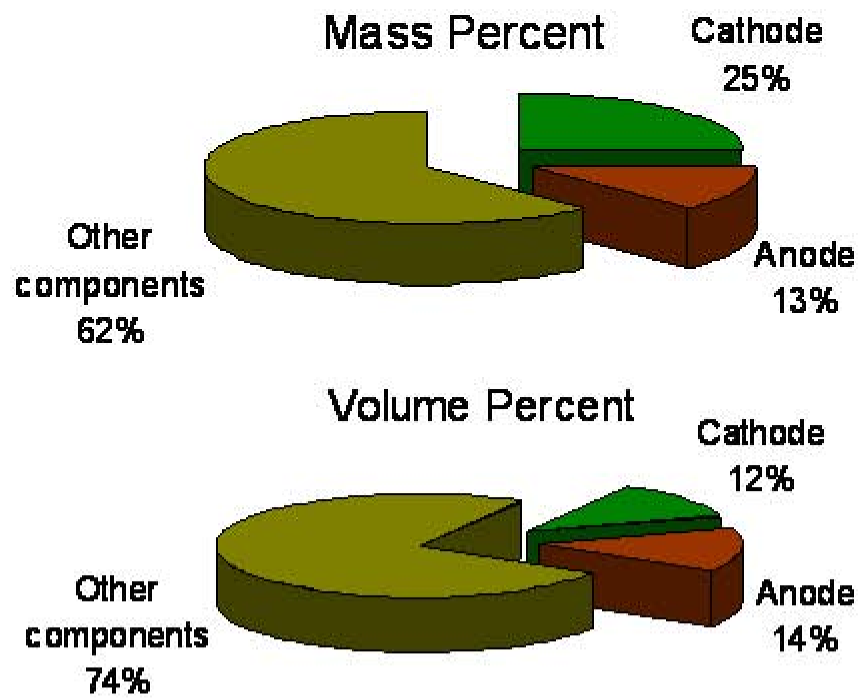
Continuing Challenges (The Wish List)

- The ultimate safe system
  - No thermal events at cathode or anode at any state of charge
    - For example, a 0.6-0.8V anode to replace carbon
  - Nonflammable electrolytes (ionic liquids?)
- Enough specific energy to enable a 200 mile EV
  - ~3 miles per kWh for a 3000 lb car
  - Need ~70 kWh pack, at 100 Wh/kg, 200 Wh/L → 700 lb, 350 L pack
  - Tesla Roadster weighs 2700lb, is 1/3 battery (900lb)!
- Low enough cost to enable a 200 mile EV (aside from the Tesla Roadster)
  - 70 kWh per car at projected costs of $0.50 - $1.00/Wh – $35K to $60K packs!
  - Need lower cost *everything*: cathode, anode, separator, electrolyte, manufacturing methods

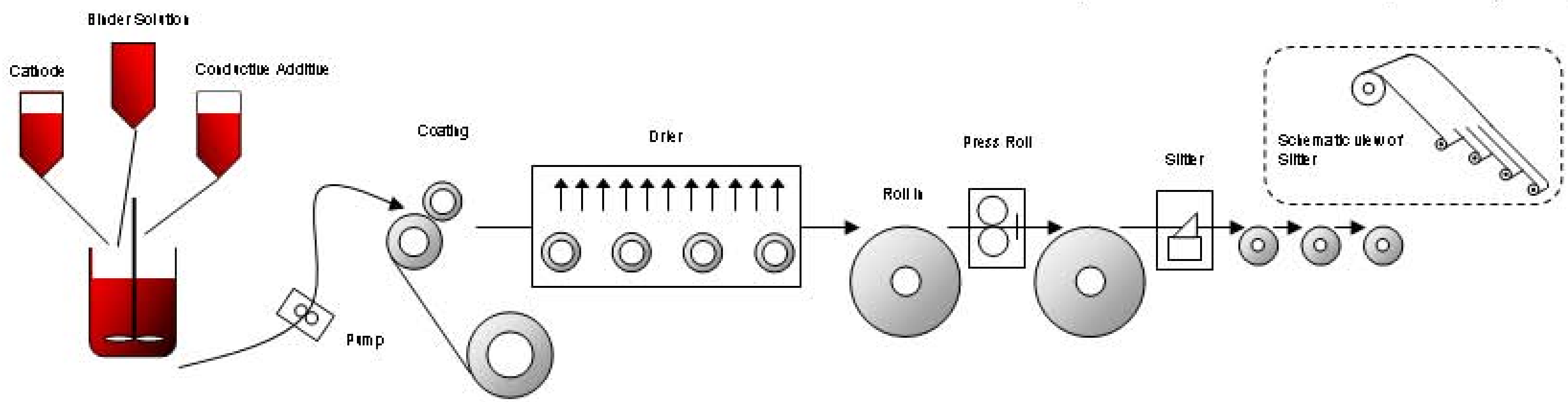
Design is an overlooked area: Conventional battery designs are highly mass and volume inefficient



J.-M. Tarascon, *Nature* 414, 359 - 367 (2001)

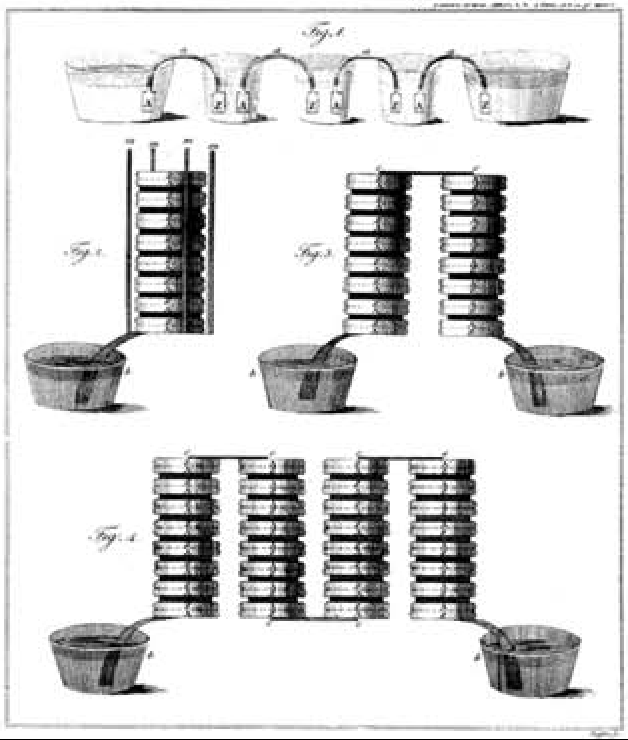


R. Moshtev, *J. Power Sources* 91, 86-91 (2000)

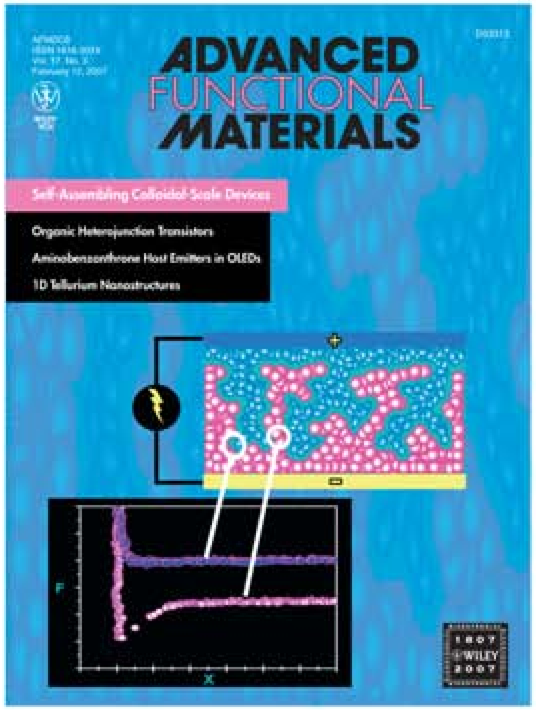


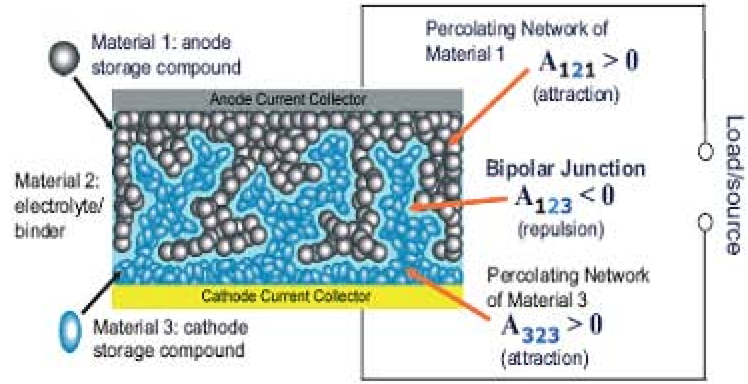
Can we break the 200 yr Old Paradigm in Device Design?

Alessandro Volta, 1800



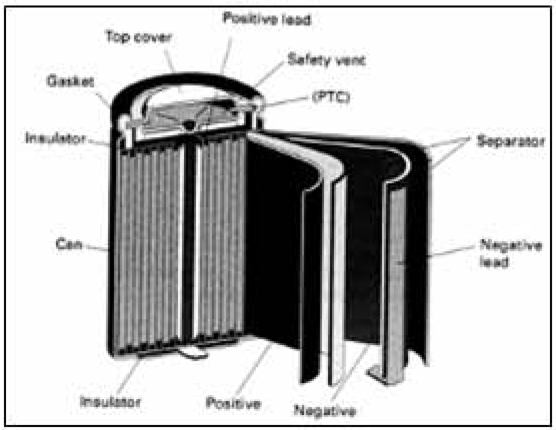
Some alternative concepts



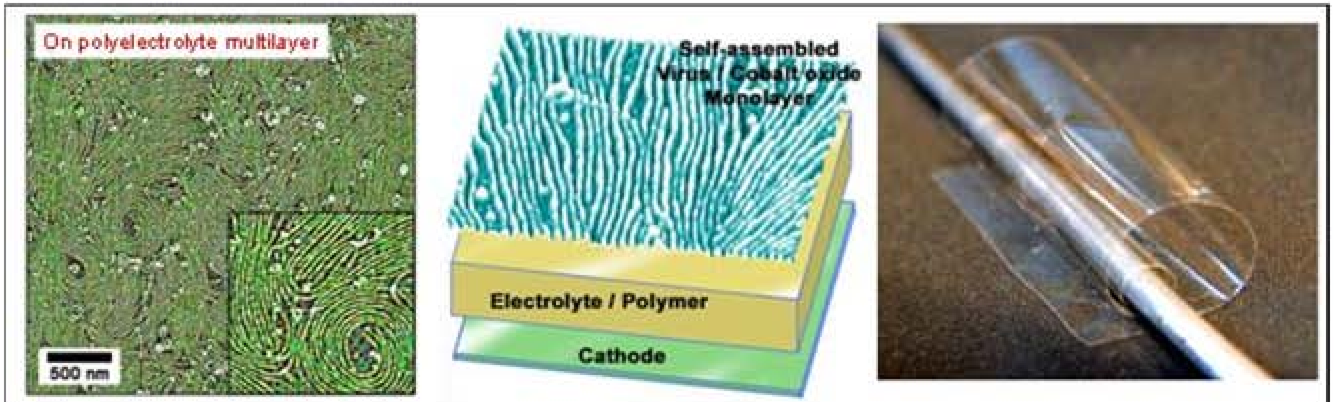


Batteries that make themselves

Y.-K. Cho et al., 2007



Not so different



Virus based assembly (Belcher et al., MIT)

Questions?