Electrochemical Energy Storage for Transportation and the Power Grid

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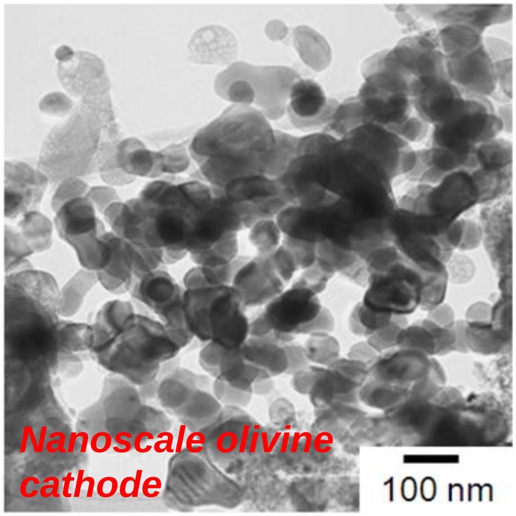
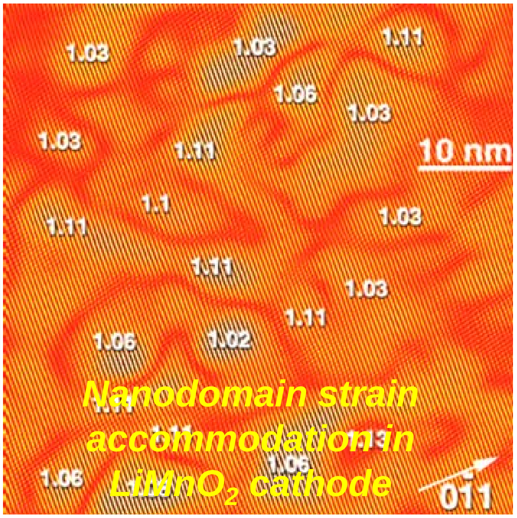
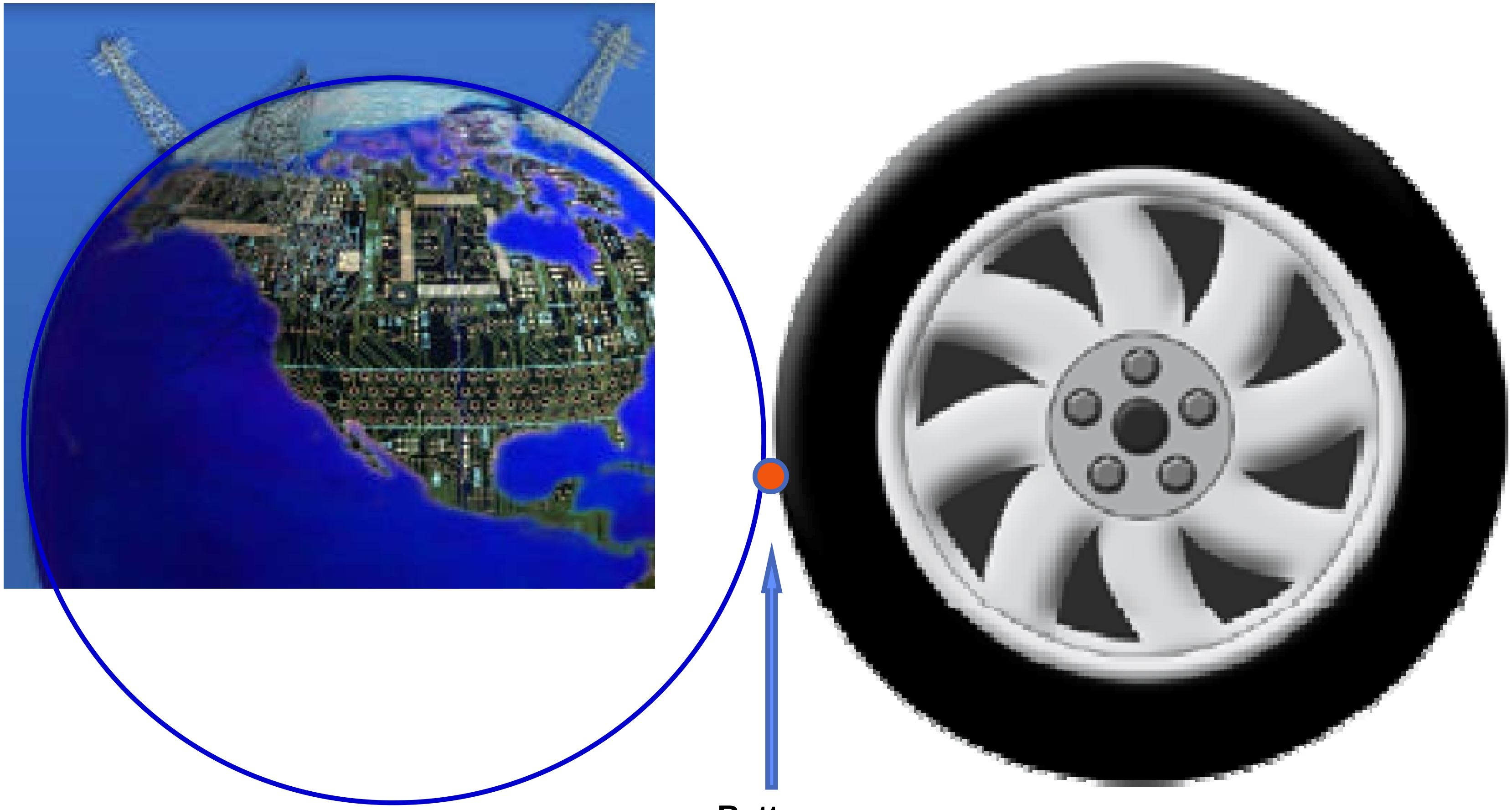

Nanoscale olivine cathode


Nanodomain strain accommodation in $LiMnO_2$ cathode

Two huge industries are transforming and a new one is emerging...



Batteries, Ten Years Ago…..

- Li-ion batteries had become the preferred power source for cellphones and laptops
- Safety issues in early 2000's: laptop battery fires in the news, millions of units recalled
- The Toyota Prius hybrid electric vehicle (HEV) had just launched, to much skepticism
- Unclear whether lithium ion batteries could ever have the power, safety, lifetime, to be used in automotive applications
- Performance metrics not suitable for automotive: 100 Wh/kg, 200 W/kg, 300 cycles

Batteries, Today…..

- Toyota Prius is (was?) best-selling car in U.S., Chevy Volt PHEV and Nissan Leaf BEV ready to launch in 2010
- Multiple Li-ion battery makers scaling up to mass production
- Debate has shifted to battery cost and how fast it will decrease
- Performance of automotive Li-ion cells: 150 Wh/kg, 3000 W/kg, >1000 cycles, ~10 year projected calendar life, \$1000-\$1700/kWh at system level
- Highest power Li-ion: 20,000 W/kg, 65 Wh/kg
- Li-ion making inroads into large scale grid storage (2MW, 0.5 MWh units)

Batteries, In 10 Years….

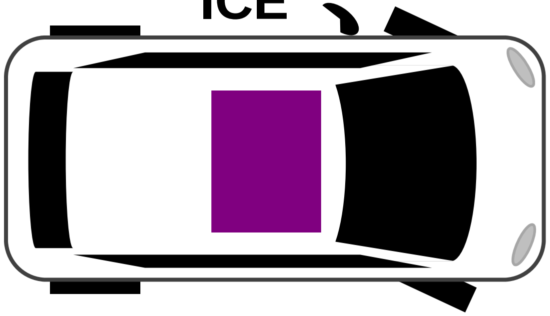
- HEV option for all vehicles; a million PHEVs on the road
- Cell level performance of 400 Wh/kg, 800 Wh/L, <$100/kWh will enable 200 mile battery electric vehicles
- Next-gen, “beyond-lithium” chemistry?
- Widespread adoption of batteries for high power, short-term storage in the electric grid
- Renewable (PV, wind) have integrated storage options



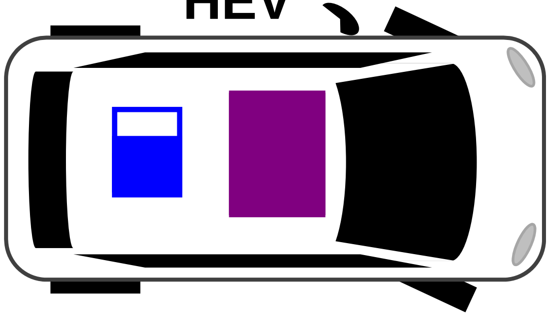

Electrification of Transportation

XEVs: Multiple Levels of Electrification

ICE

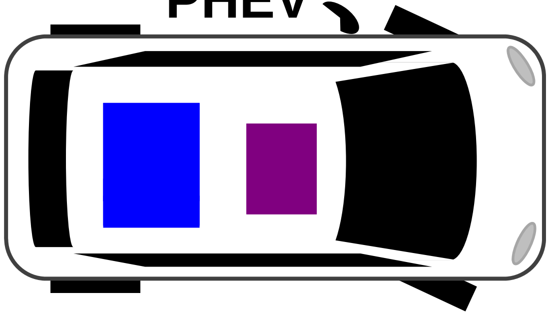


HEV



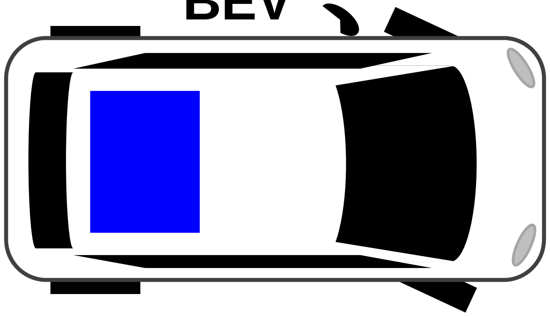
Toyota Prius
Honda Insight
Ford Escape

PHEV



A123/Hymotion conversion
GM Volt
Fisker Karma

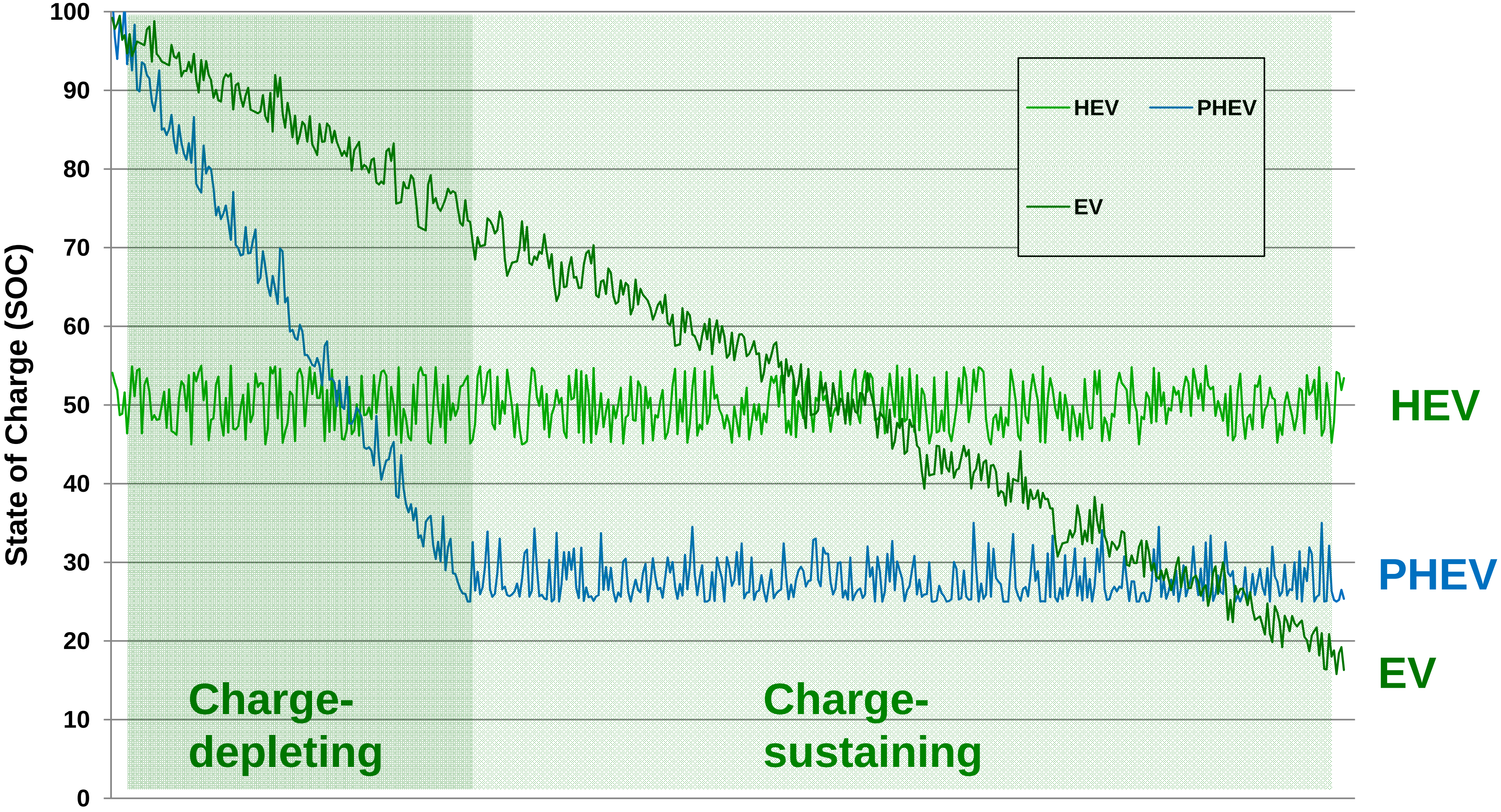
BEV



Tesla Roadster
Nissan Leaf

🟦 **battery**
🟪 **engine**

Charge-depleting vs. charge-sustaining



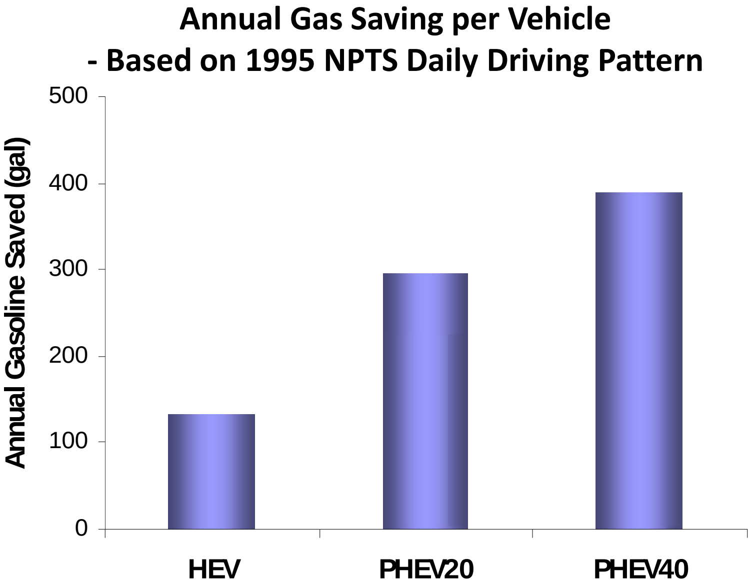
Impact of PHEVs on Annual Gasoline Saving Nationwide

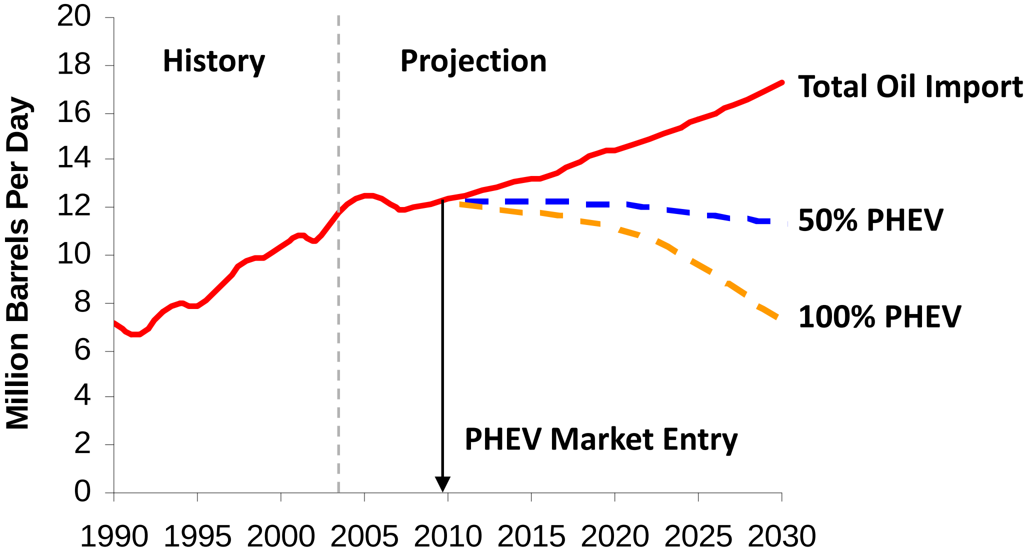
> "Transportation accounts for 87% of the increase in petroleum consumption, dominated by growth in fuel use for light-duty vehicles."
>
> - Annual Energy Outlook 2006 with Projections to 2030

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

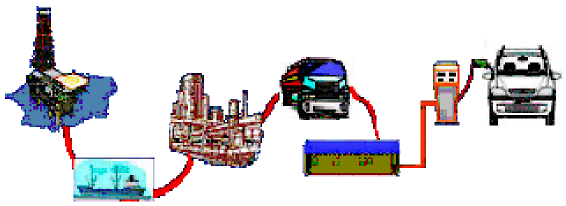
This number is projected to be double by 2030 ~500 million passenger vehicle

- **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

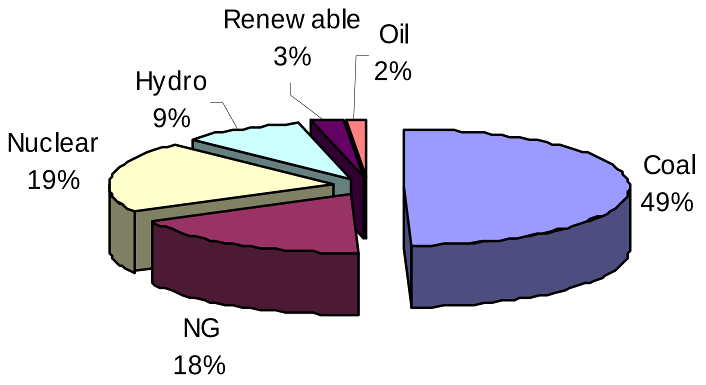


- **Well-to-Wheel Paths:**
  - **Oil - Gasoline - CV**
  - **Coal - Electricity - EV**
  - **NG (CCGT) - Electricity - EV**
- **Well-to-Wheel CO_2 Emission:**

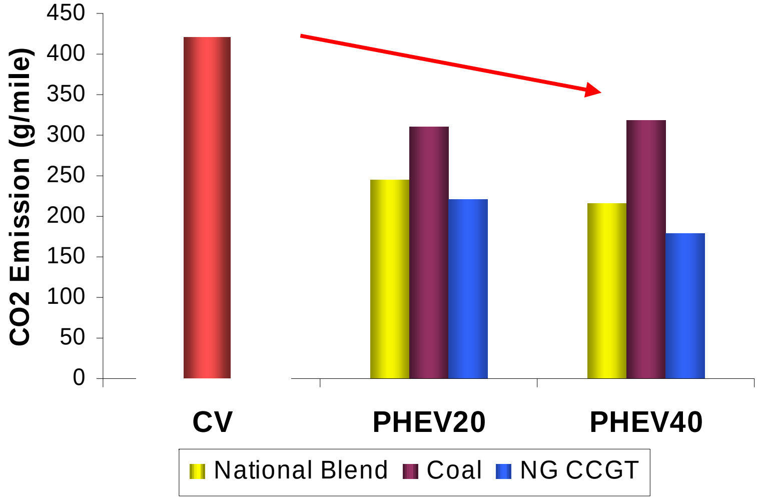
Oil - Gasoline	166 lb/MMBtu	181 miles/MMBtu	416 g/mile
Coal -Electric	224 lb/MMBtu	312 miles/MMBtu*	327 g/mile
NG - Electric	138 lb/MMBtu	447 miles/MMBtu*	141 g/mile

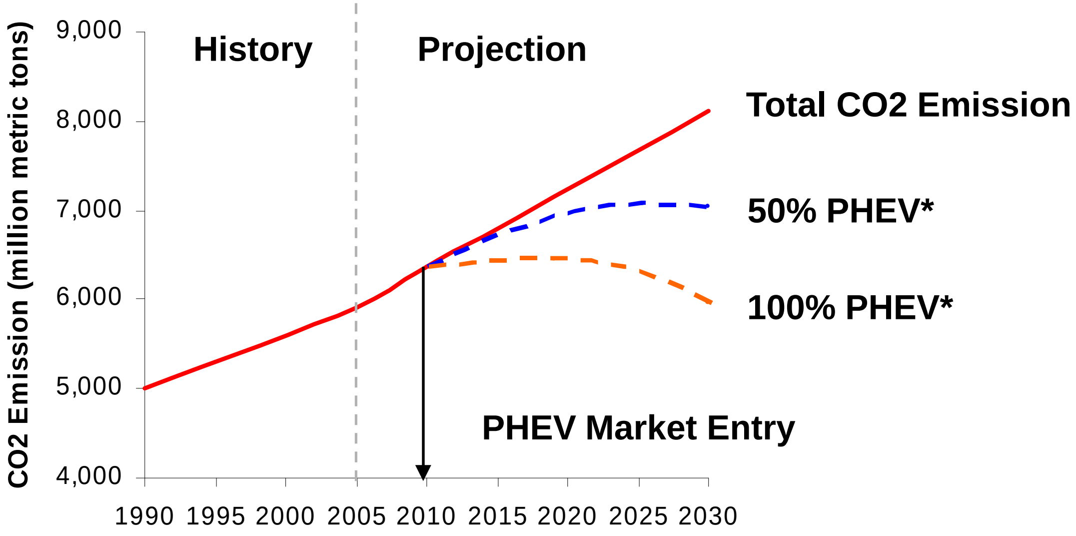
*** Pure EV miles**

US Power Generation (National Blend)



CO2 Emission (g/mile)

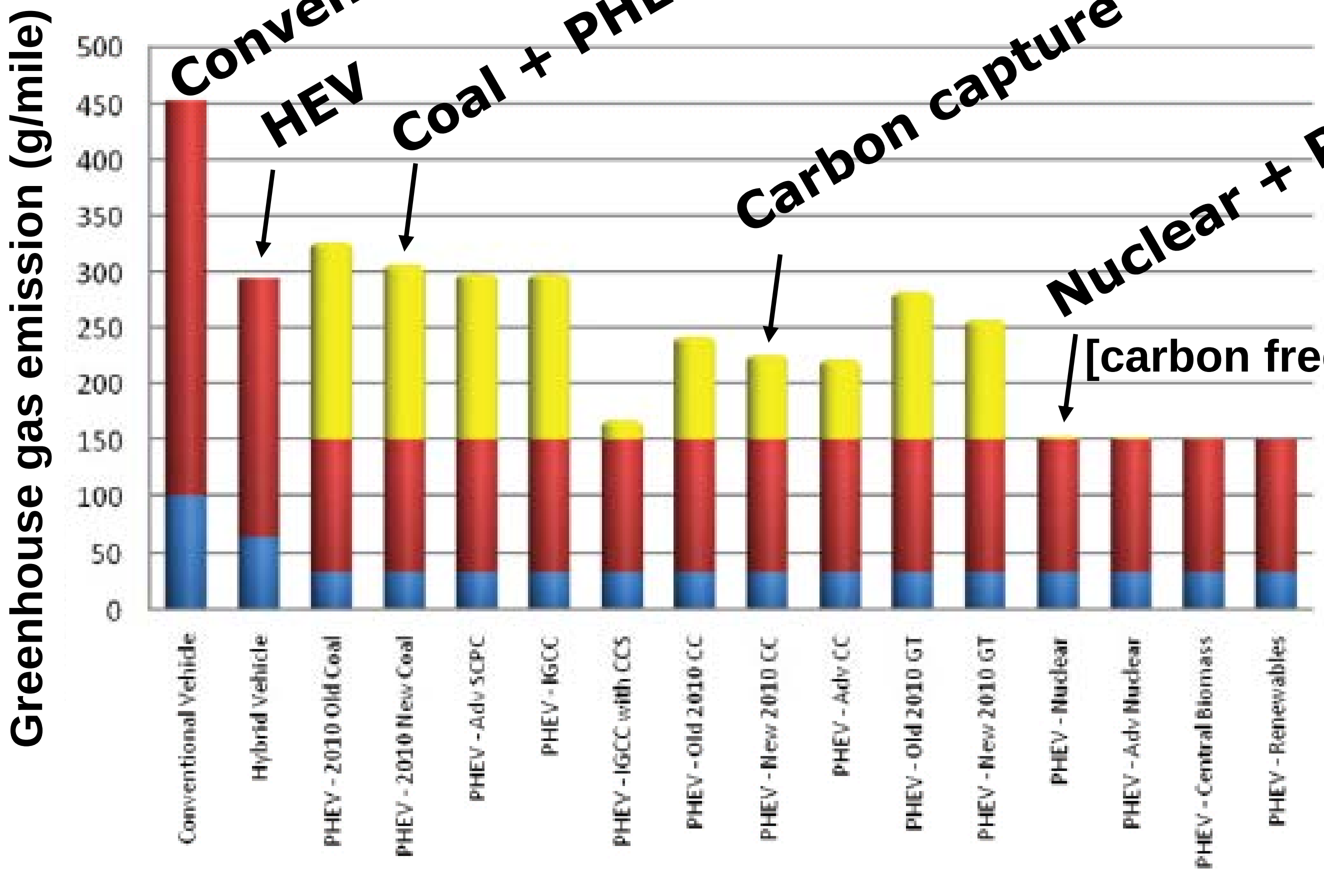




*** Assuming 500million passenger vehicle in 2030**

Also need new power generation technology

GHG for PHEV20



Conventional vehicles

HEV

Coal + PHEV

Carbon capture + PHEV

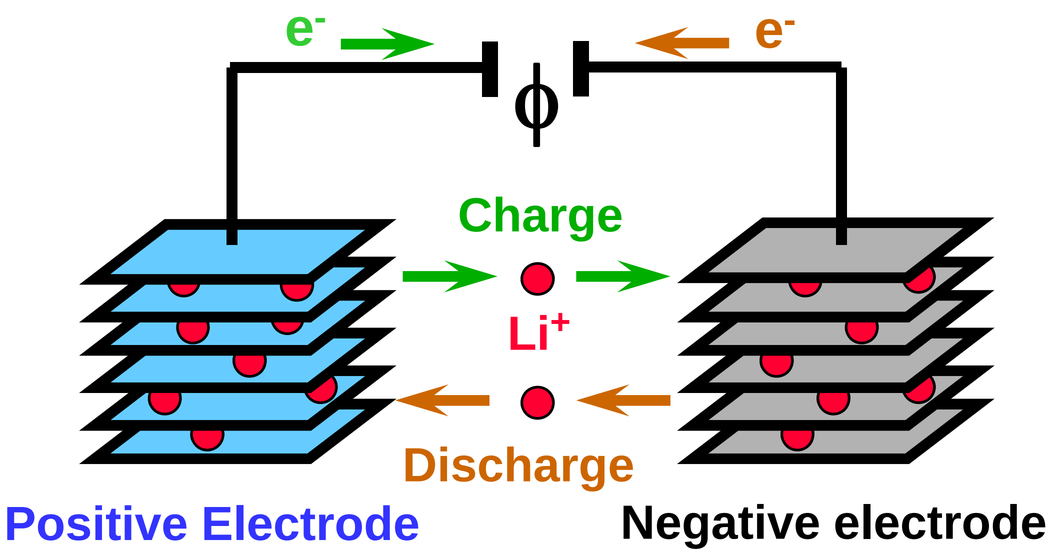
Nuclear + PHEV

[carbon free electricity]

Type of power plants

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

Electrochemical Reaction in a Lithium-Ion Battery



During Discharge:

$\mathrm{Li^+ + e^- + Co^{4+} = Li^+ + Co^{3+}}$

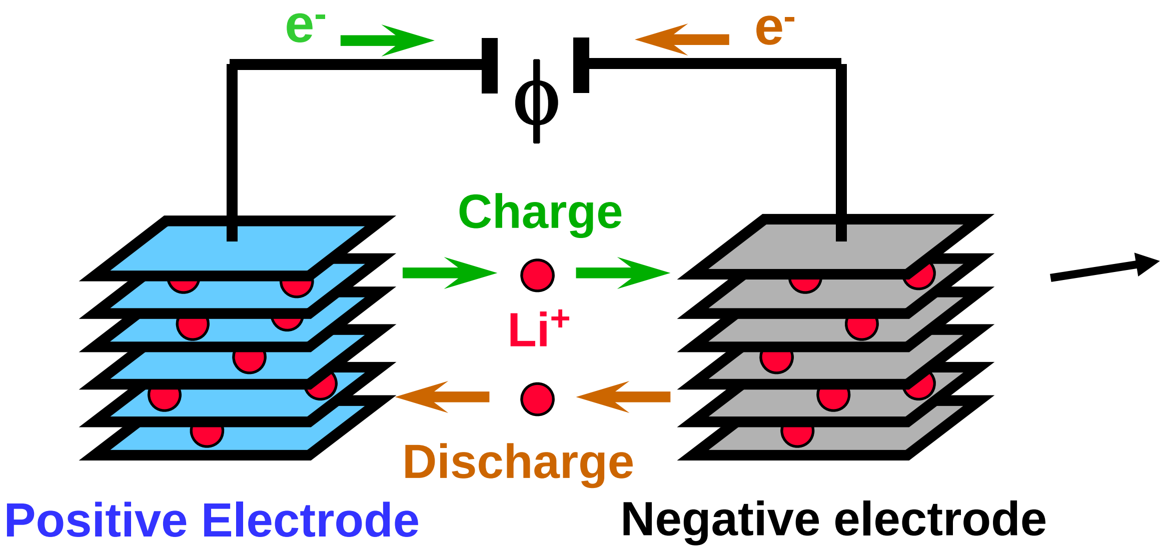
$\mathrm{Li_{1-x}CoO_2 \rightarrow LiCoO_2}$

$\mathrm{Li = Li^+ + e^-}$

$\mathrm{LiC_6 \rightarrow C}$

(Charging is the reverse of this)

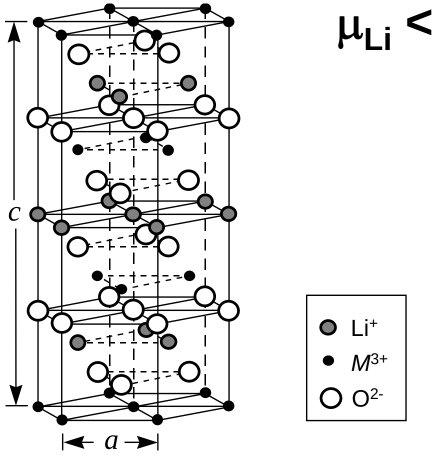
Energy of a Battery (Wh) = Voltage (V) x Capacity (Ah) Determined by Properties of Cathode and Anode



Lithium Chemical Potential At Anode

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

- Li metal
- Carbon
- Metal alloys
- Nanoscale oxides



$LiMO_2$ ($R\bar{3}m$)

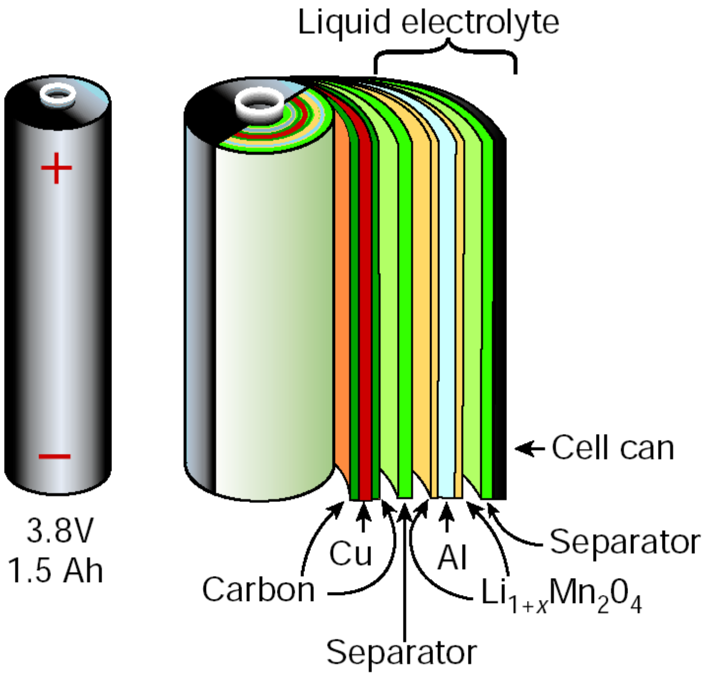
$\mu_{Li} << \mu_{Li,\,metal}$

Nernst Eq.

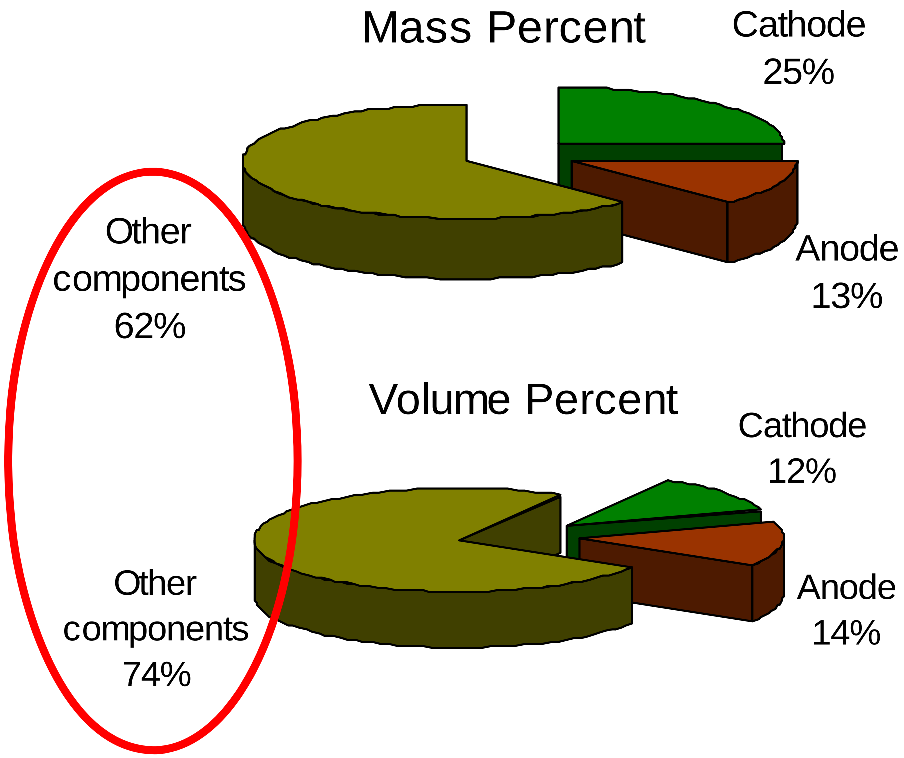
$$\Delta\phi = -\frac{1}{z_i F}\left(\mu^0_{i,cathode} - \mu^0_{i,anode}\right) = \frac{-\Delta G^0}{z_i F}$$

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

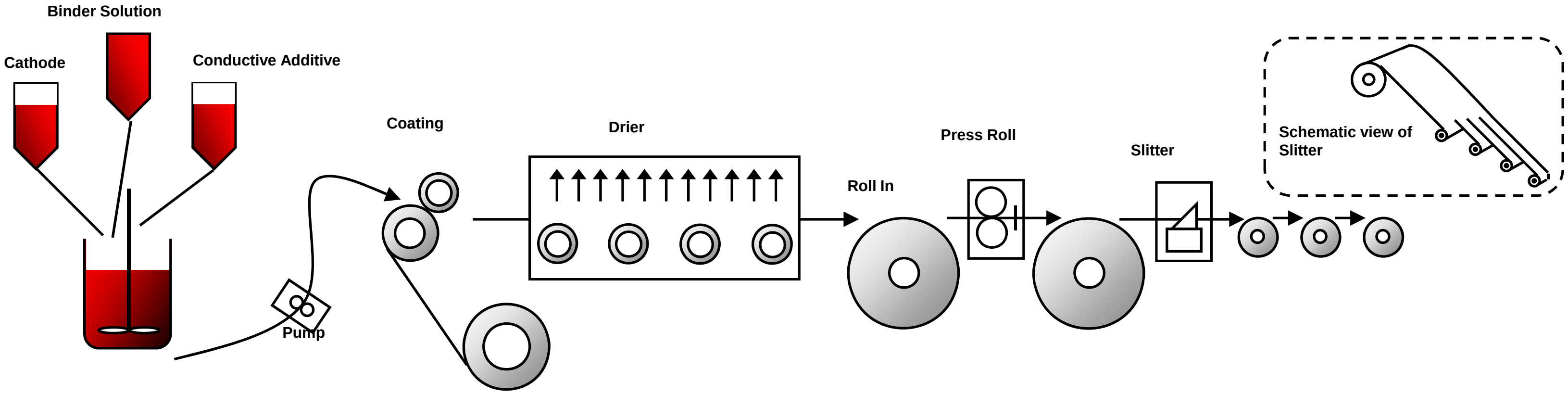
Existing Battery Designs are Highly Mass and Volume Inefficient



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



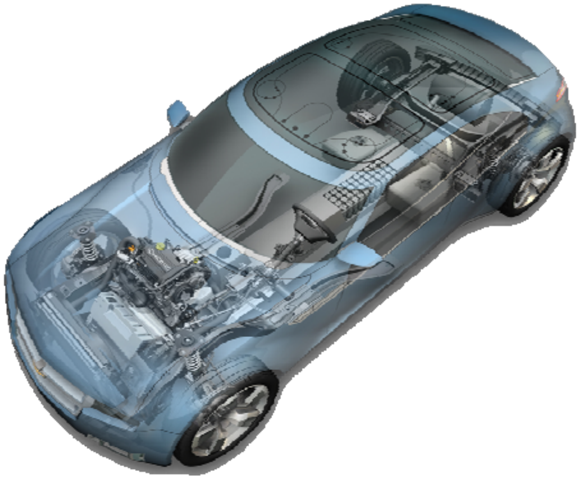
R. Moshtev, *J. Power Sources* 91, 86-91 (2000)



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
- Billions produced since early 1990's; billions produced
- >50 million batteries recalled for safety reasons – despite failure rate <1 ppm



2010 Chevy Volt Plug-In Hybrid

Advanced batteries for transportation

- Gravimetric and volumetric power and energy – currently favors Li chemistry
- 6000 deep cycles for PHEV
- 300,000 shallow cycles for HEV
- 3C to >50C pulse charge/discharge rates
- 10 - 15 year calendar life
- Extreme safety in large packs (>5 kWh)
- Affordable: $1000/kWh now, <$100/kWh needed

Summary: Power, energy, safety, life, cost

Approaches to Automotive Batteries

Engineering solution — *Improve 1st Gen Chemistry* — *New Chemistry*

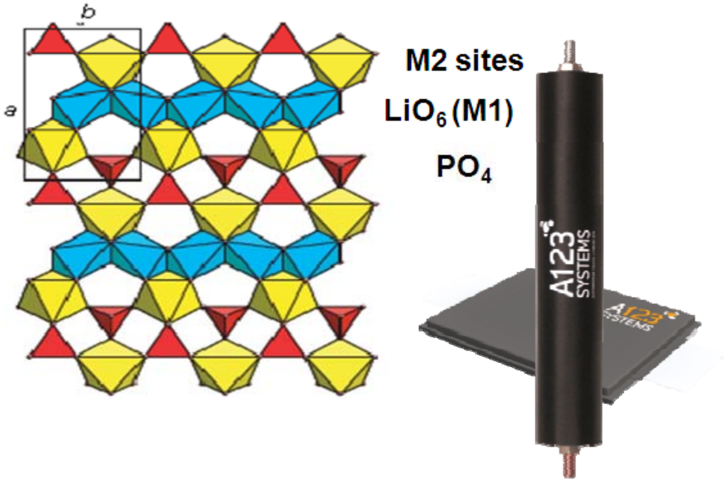
Pack engineering approach using individually cooled and monitored high energy laptop cells (18650s)

Example: Tesla Roadster

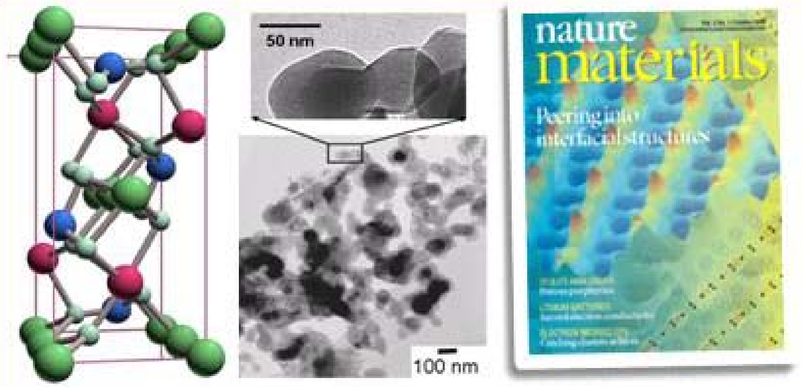
Derivatives of oxide chemistry from previous generation Li-ion (with improved safety, life)

Examples:
- **Lithium Nickel Cobalt Aluminum (SAFT, PEVE)**
- **Lithium Manganese Spinel (LG, NEC, Hitachi)**
- **Lithium Manganese Nickel Cobalt (Sanyo)**
- **Mixtures of various oxides**

New chemistries:
- **Olivine cathodes**
- **High voltage oxides (some with >250 mAh/g)**
- **Silicon-based anodes**
- **Metal-air**
- **Lithium-air**
- **Lithium-sulfur**



Case Study: From Basic Research to Energy Impact



BES Research in Nanoscale Olivines 2000 -2002

SBIR Grant, 2002
Commercialization, 2005

- 3.3V, 2.3 Ah (~2 Wh) cell of 26650 format
- ~3000 W/kg peak power
- 110 Wh/kg specific energy – 150A pulse current
- 2000 cycles @100% depth of discharge
- ~300,000 hybrid pulse power cycles
- Extremely low impedance growth

BUSINESS

Drilling for nanotech gold

Research funded by U.S. Dept. of Energy


Ultra Lightweight Aviation packs

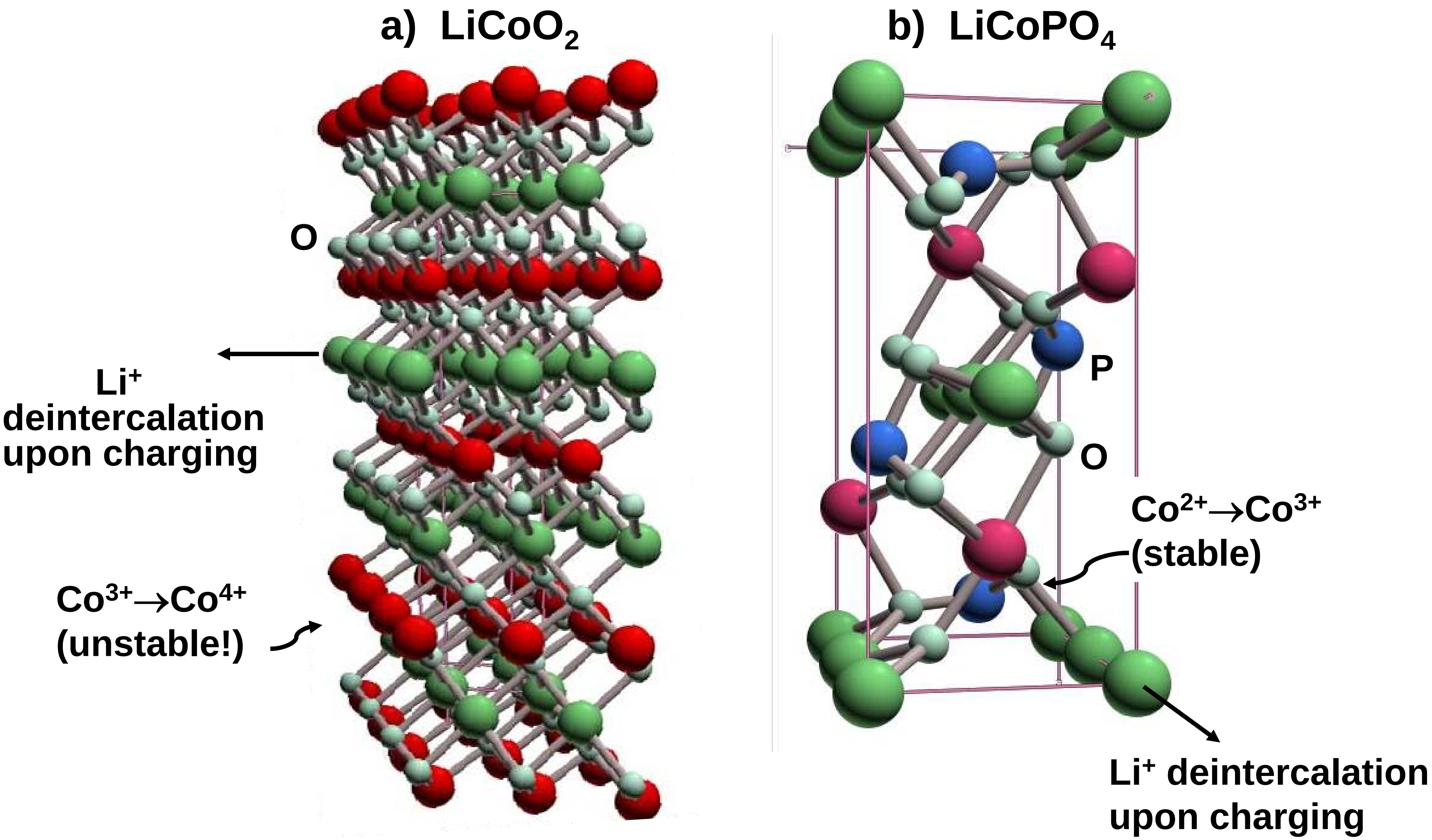

BAE HybriDrive System for 2008 Daimler Chrysler Orion VII Bus

USABC Program, 2006
Multiple Vehicles, 2007


Hymotion Prius Conversion

Electric Vehicles to Utility Scale Storage for the Smart Grid

Battery safety (slightly over)simplified: Cathode transition metal *oxidation state* is a key consideration



a) $LiCoO_2$

b) $LiCoPO_4$

Li^+ deintercalation upon charging

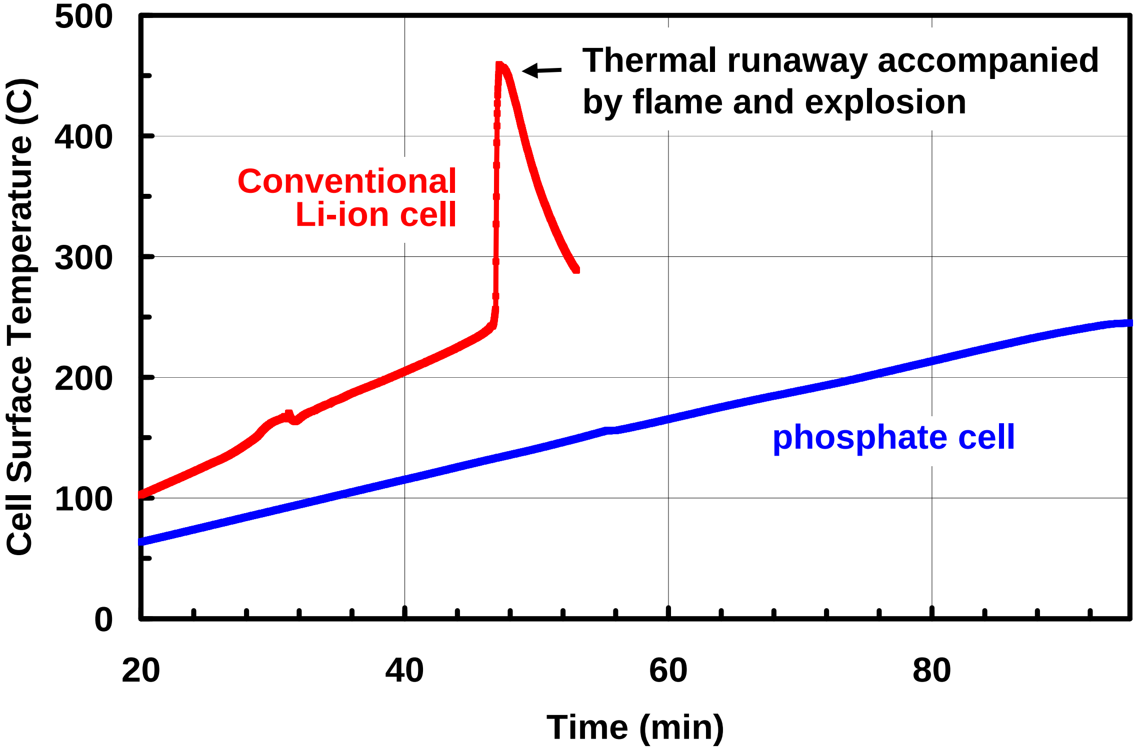
$Co^{3+} \rightarrow Co^{4+}$ (unstable!)

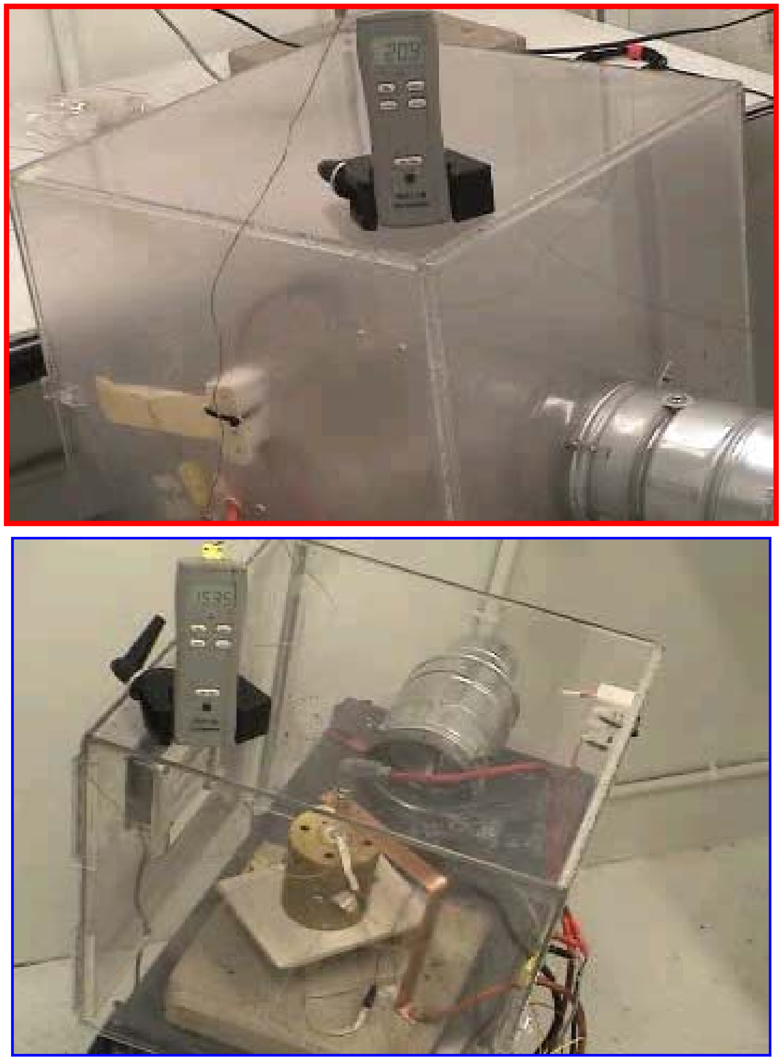
$Co^{2+} \rightarrow Co^{3+}$ (stable)

Li^+ deintercalation upon charging

$LiCoO_2$ 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 cells with and without thermal runaway

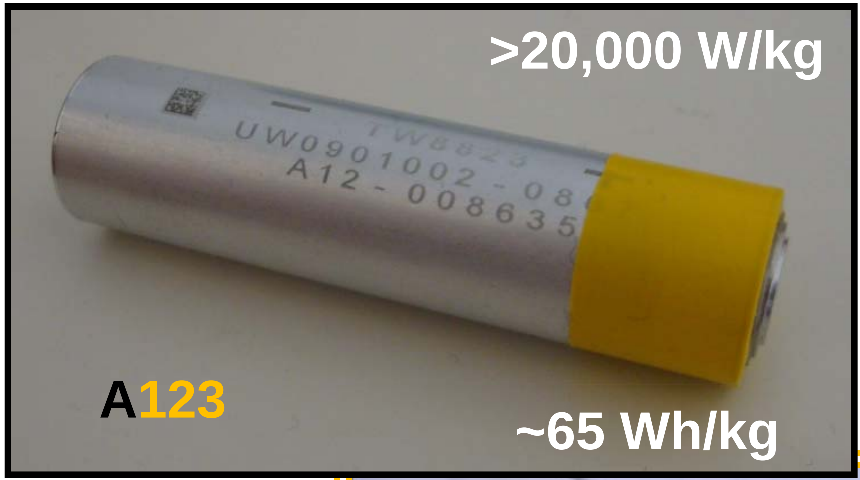


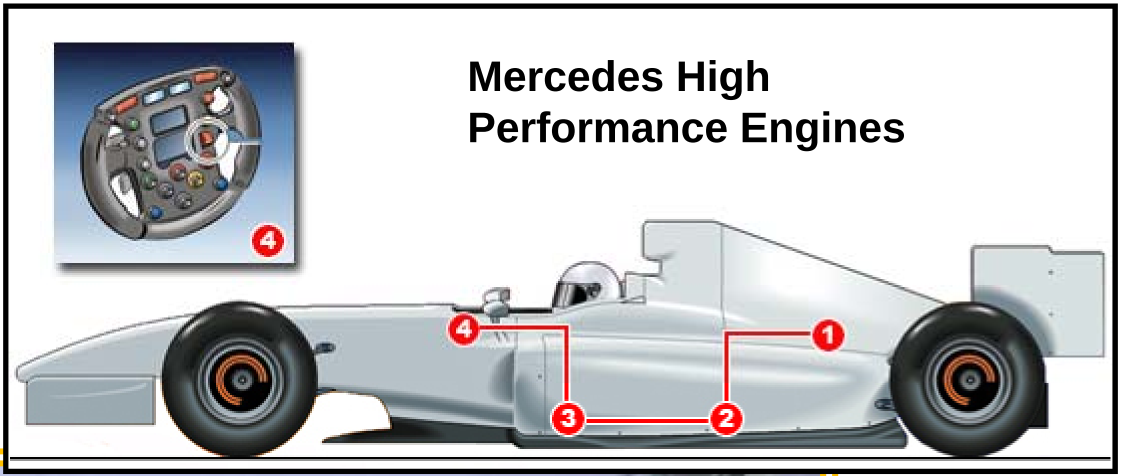


Sandia National Lab test chamber

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.)

Current Benchmark in High Power Li-Ion: Formula 1 Racing

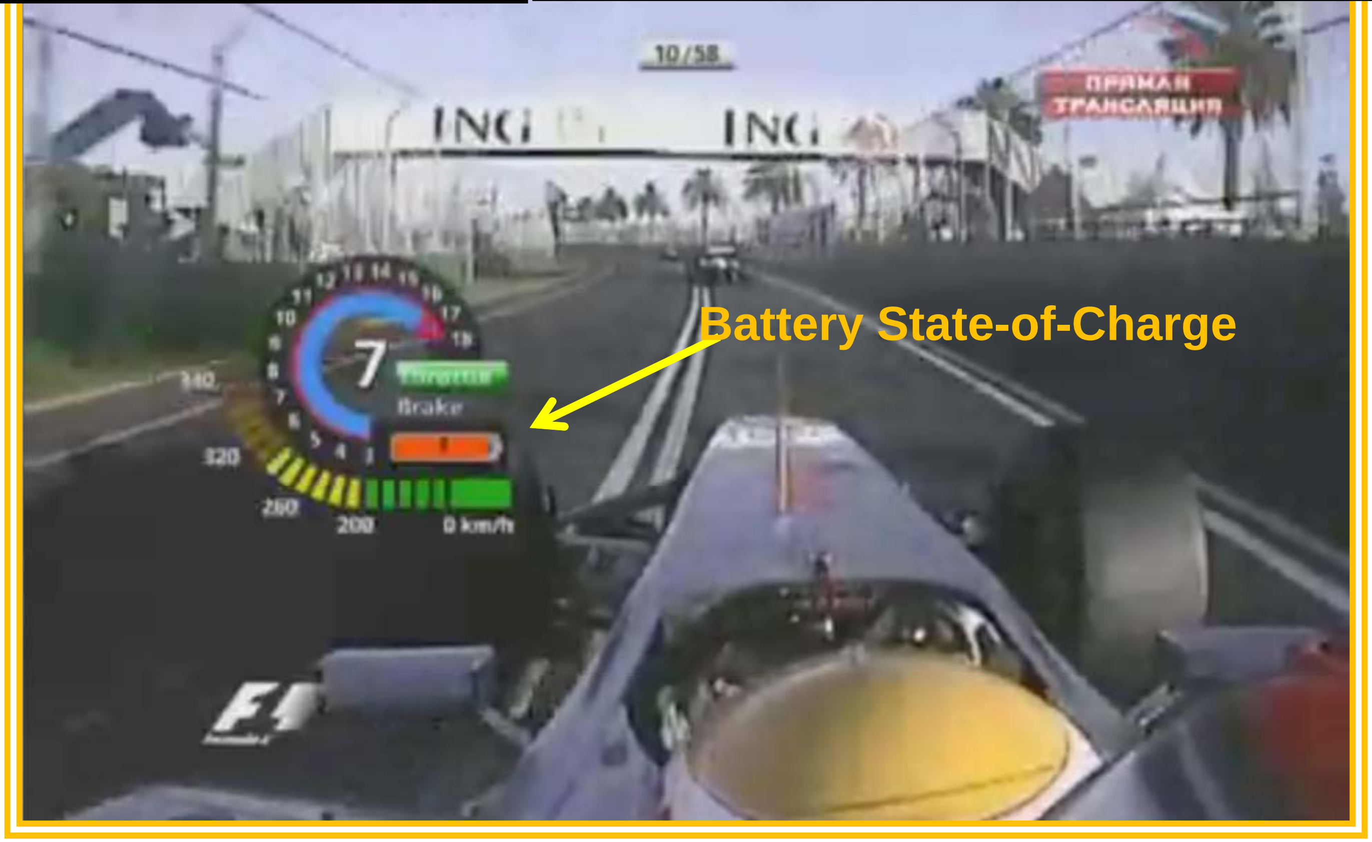




Mercedes High Performance Engines

Used over 6-8 sec discharge

Ultracap power with Li-ion energy



Battery State-of-Charge

Melbourne
March 2009

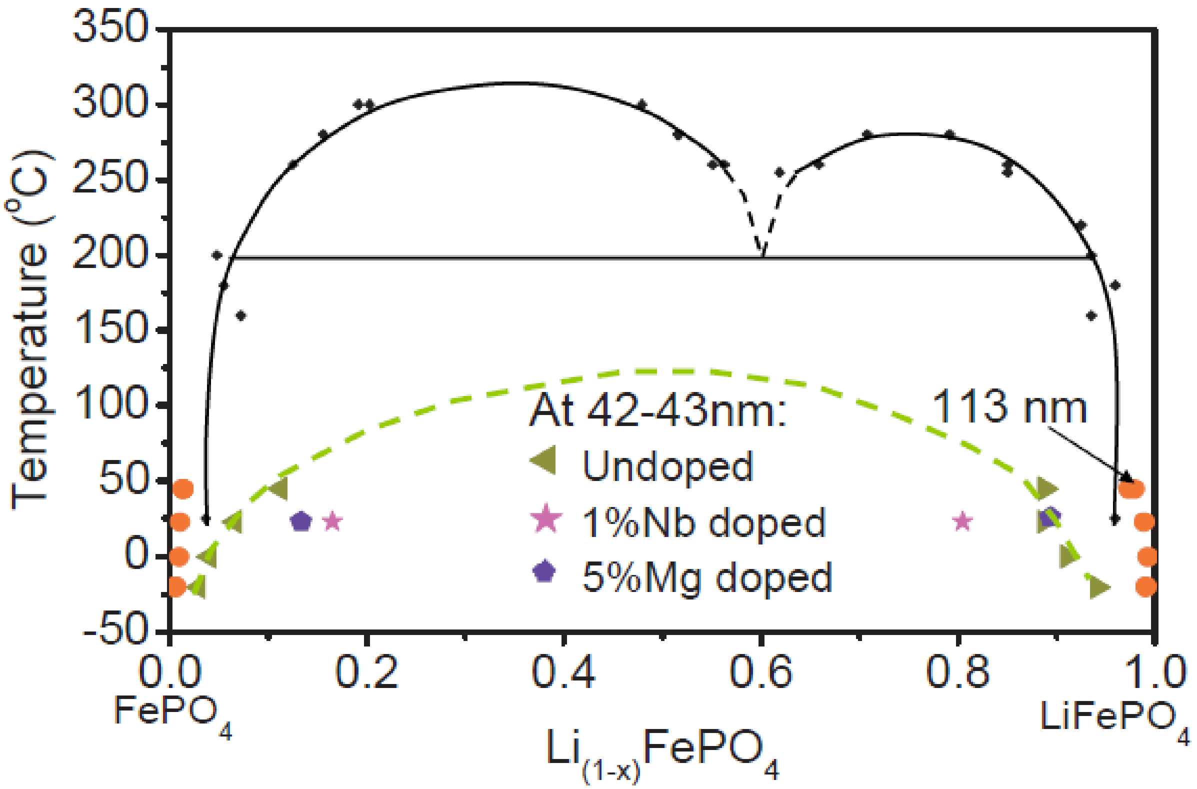
Kinetic Energy Recovery System (KERS) in Action
2009 Race Season

- **McLaren-Mercedes - A123 olivine based KERS system**
- **Opening race of 2009 season in Melbourne, AUS**
- **Lewis Hamilton, 2008 World Champion, starts in 18th position (out of 20) and finishes 4th**

Electric vehicles are not boring (4 kW/kg battery = 45C rate)

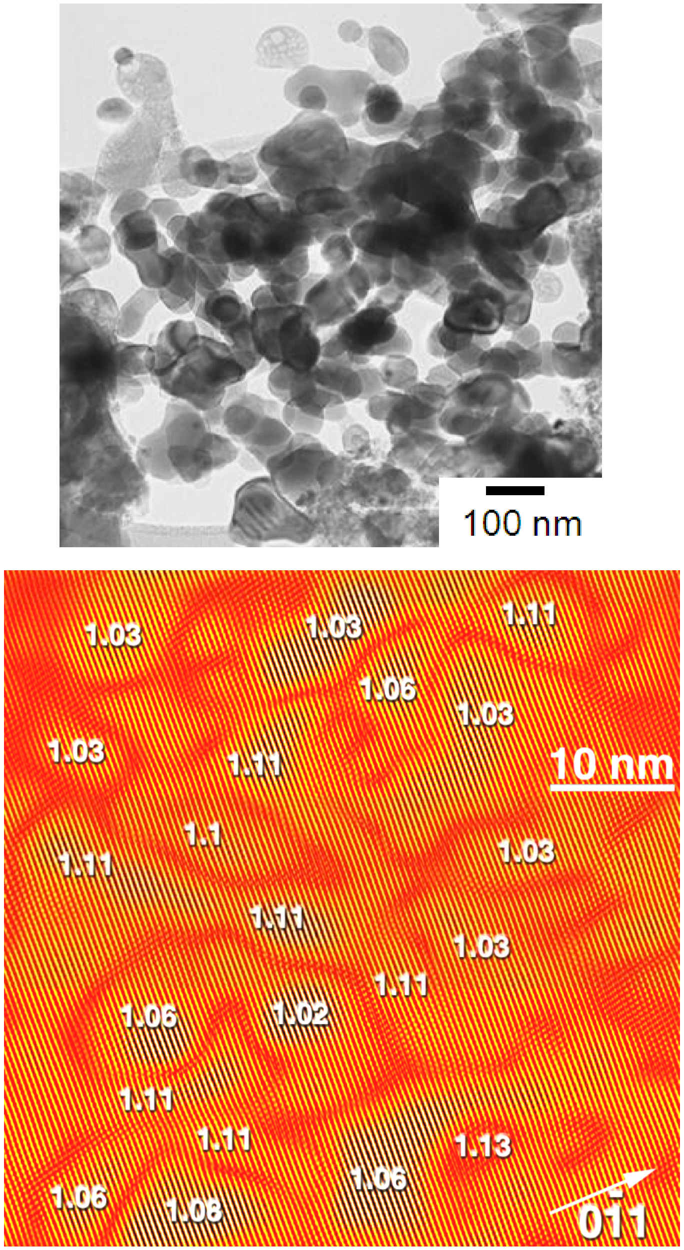
www.killacycle.com

Engineering phase stability and storage mechanisms for power and life in nanoscale olivines



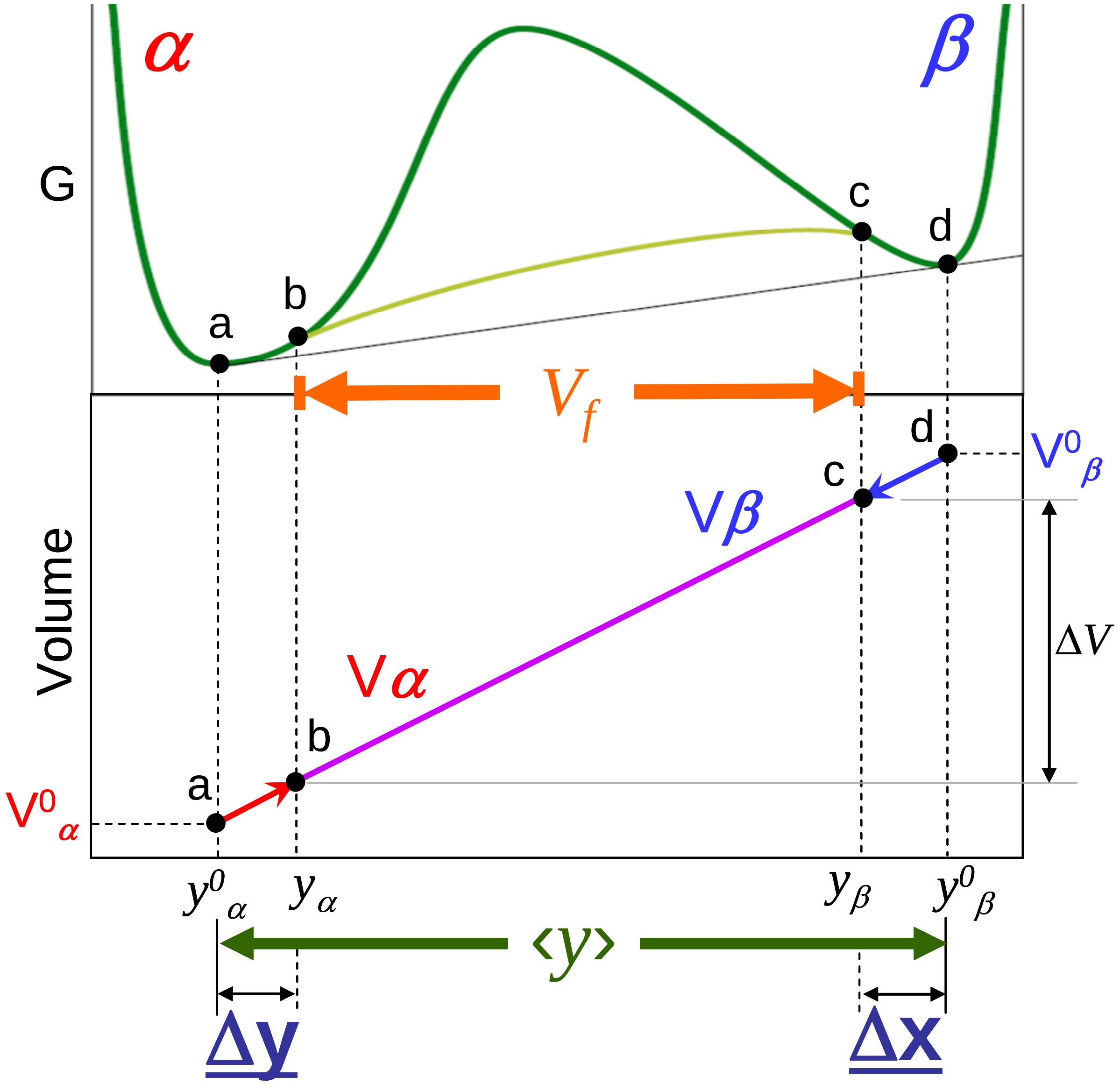
Composition- and Size-Dependent Phase Diagram – can achieve near-solid-solution at RT:

- **Reduced elastic misfit during electrochemically-induced phase transformation – lattice coherency**
- **Results in higher Li exchange rates, reduced fatigue over >10^4 cycles**



Strain accommodation in battery materials: Olivines (top) and spinels (bottom)

Coherent vs. Incoherent Miscibility Gap



New equilibrium compositions form to reduce elastic misfit energy

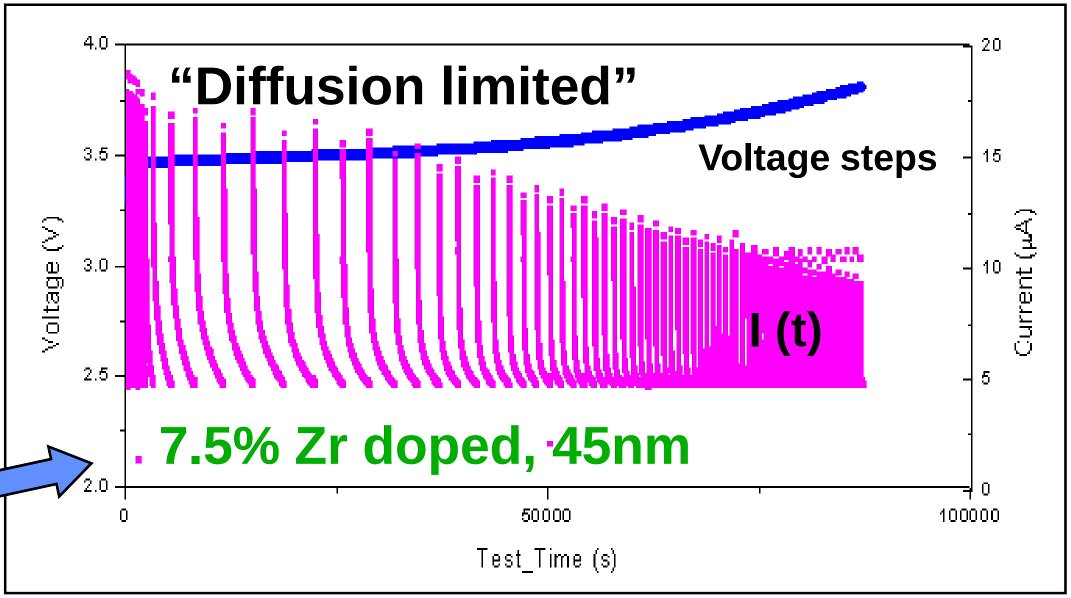
Result: Smaller miscibility gap, extended solid solutions of both phases

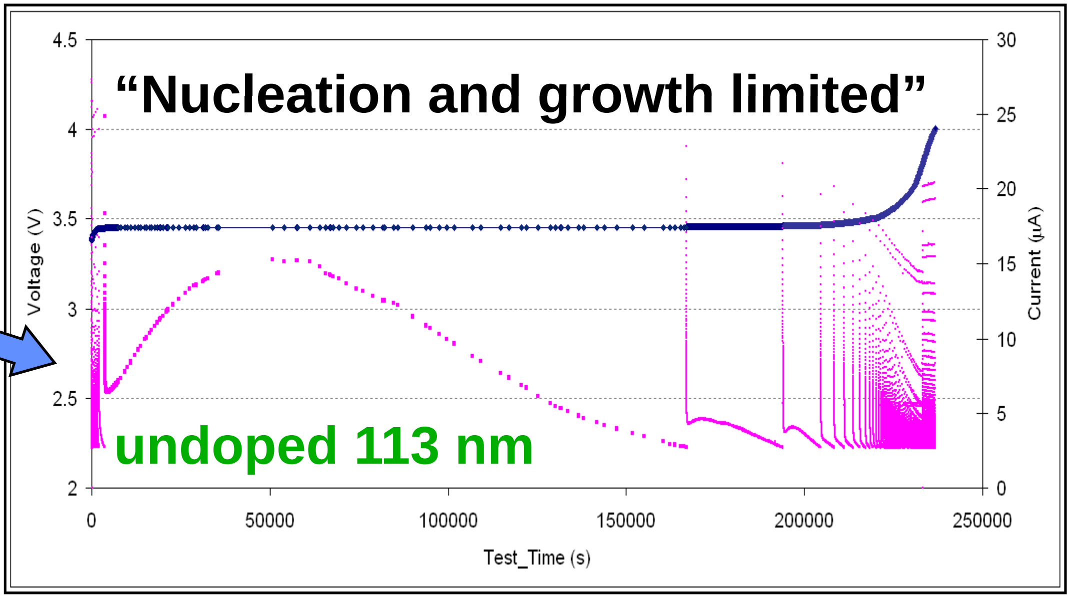
Changes in Li Storage Mechanism Observed in Time Dependence of Charging Current (Potentiostatic Titration, or PITT):

- **Two limiting cases dominated by diffusion and phase transformation limited contributions to capacity**

- **When diffusion limited, kinetic information such as diffusion coefficients can be obtained from PITT (by numerical fitting experimental *I(t)* curves)**

- **When nucleation and growth limited, current flow (red) upon stepwise change in voltage is *proportional to phase transformation rate***

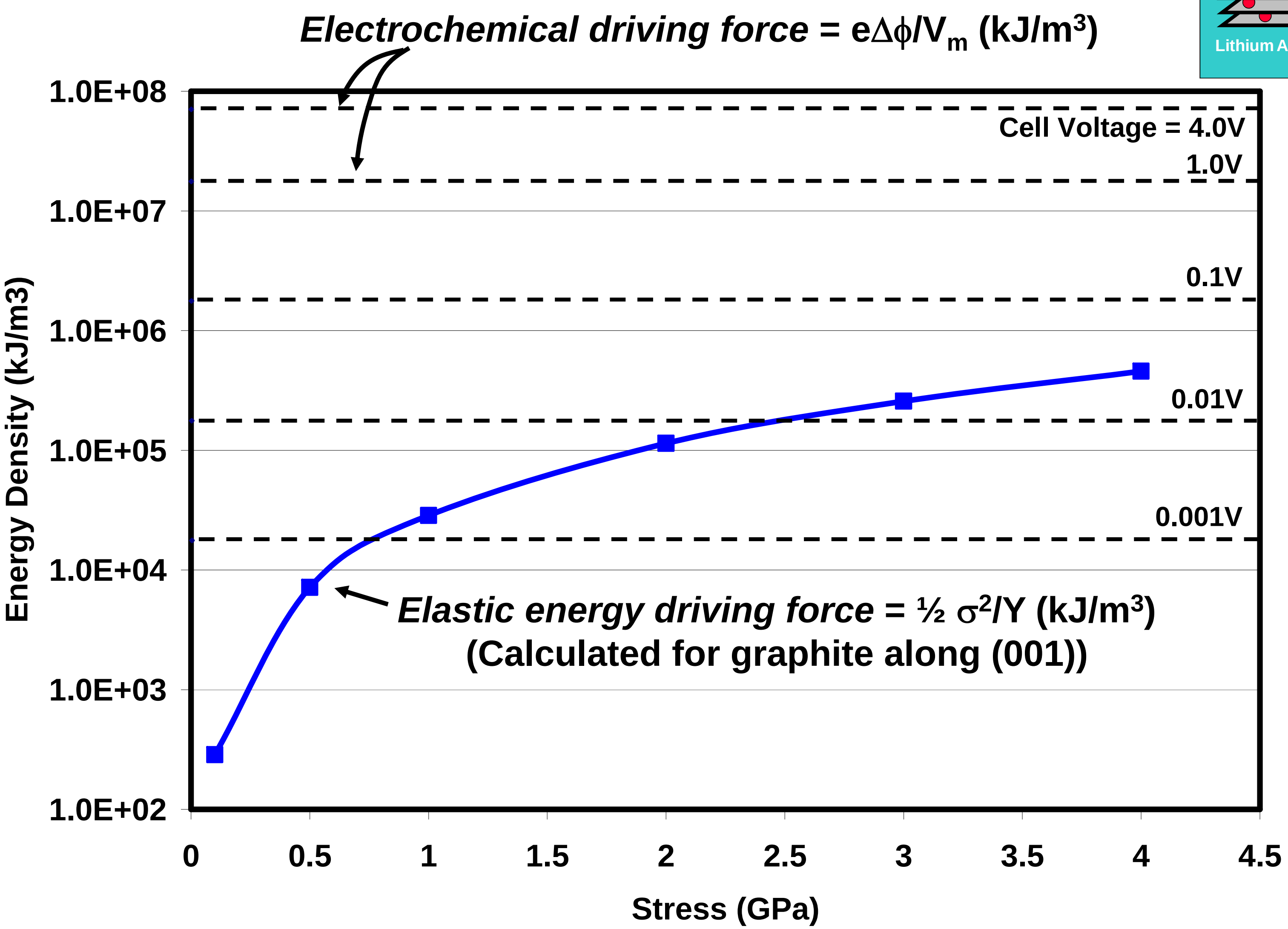




Meethong *et al*., *Chem. Mater.*, 2009

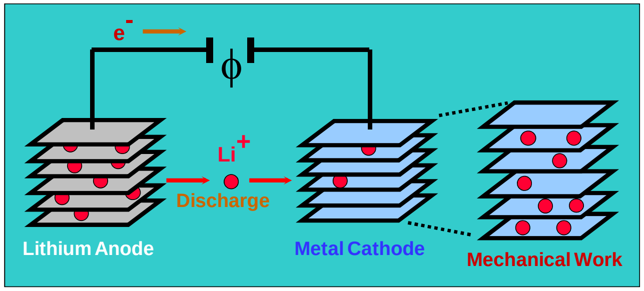
Electrochemical Energy vs. Mechanical Energy

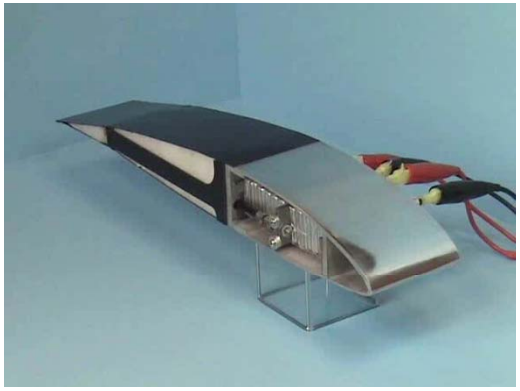
Comparison of elastic energy as fcn of stress vs. electrochemical equivalent at various cell voltages:


Electrochemical driving force = $e\Delta\phi/V_m$ (kJ/m^3)

Elastic energy driving force = $\frac{1}{2}\,\sigma^2/Y$ (kJ/m^3)
(Calculated for graphite along (001))

(Electrochemical energy calculated for Li$^+$ in graphite)





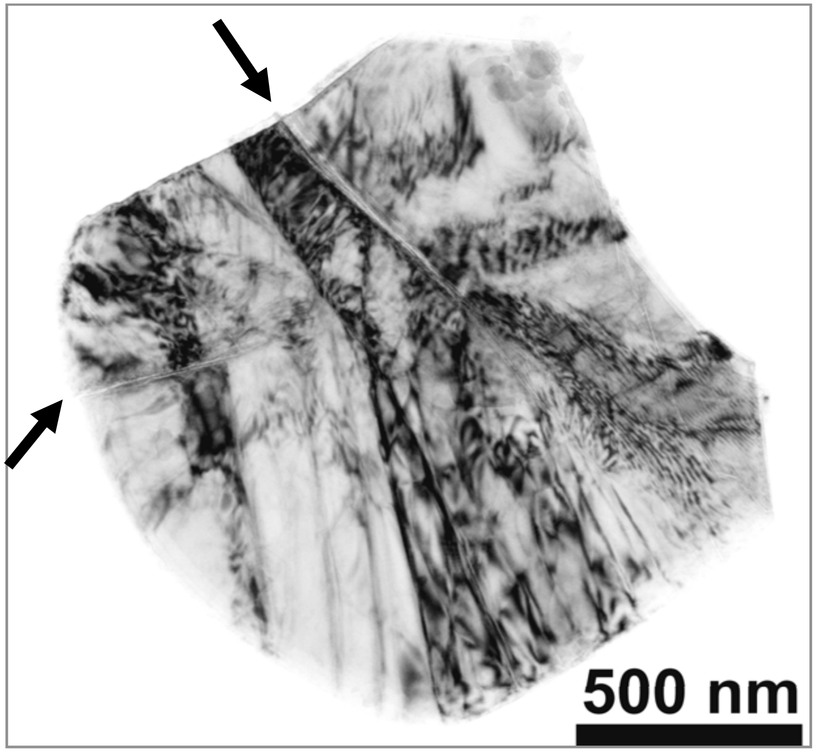
Use of electrochemical to mechanical energy conversion for actuation

Intercalation Volume Change

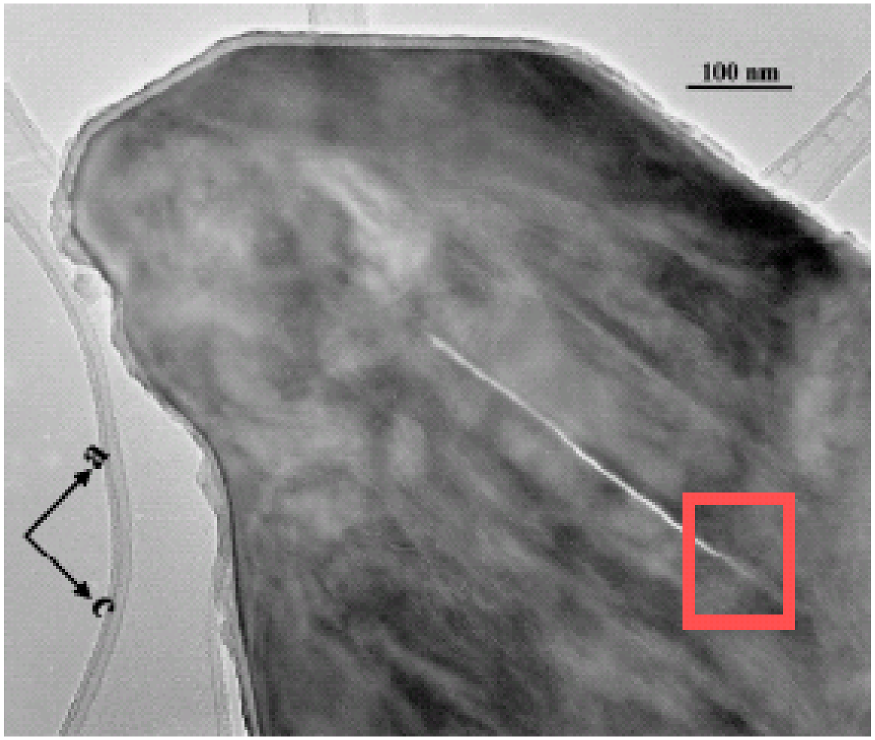
- Volumetric/linear strains exceed the failure strain of brittle ceramic compounds

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

Mechanical Failure is Common in Batteries



$LiCoO_2$: 50 charge/discharge cycles
H. Wang et al., *JECS* (1999)



$LiFePO_4$: 1st chemical delithiation
G. Chen et al., *ESL* (2006)

Volume change upon lithiation: +1.9% ($LiCoO_2$), -6.5% ($LiFePO_4$)

Pergamon

Available online at www.sciencedirect.com

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Acta Materialia 51 (2003) 1103–1113

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Metastable Phase Formation (Amorphization)

Electrochemically-driven solid-state amorphization in lithium-silicon alloys and implications for lithium storage

Pimpa Limthongkul [a], Young-Il Jang [b], Nancy J. Dudney [b], Yet-Ming Chiang [a]

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Received 24 June 2002; accepted 11 October 2002

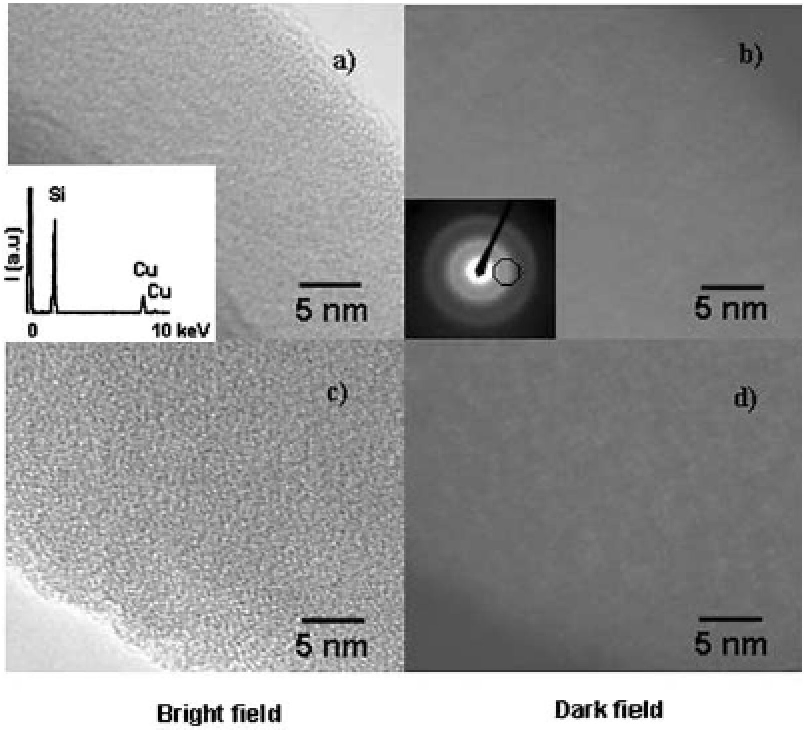


Fig. 5. HREM bright field images (a,c) and their corresponding dark field images (b,d) showing microstructure of Si after lithiation to 68 mole% Li, showing that electrochemical lithiation has resulted in production of an amorphous alloy.

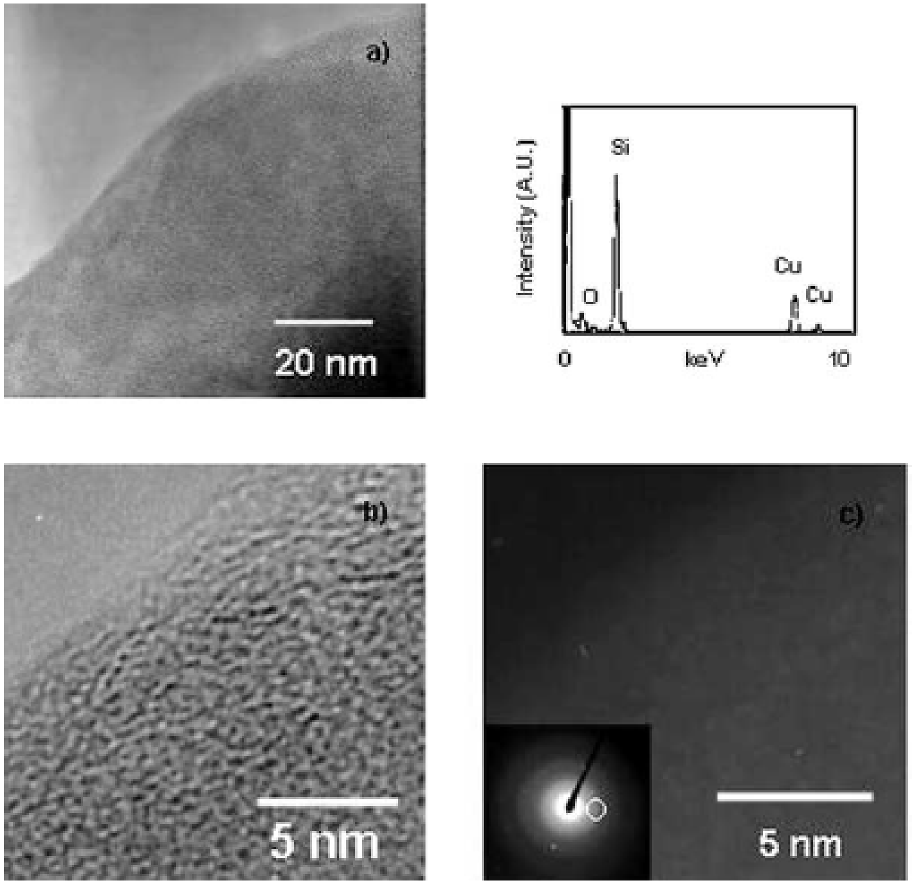
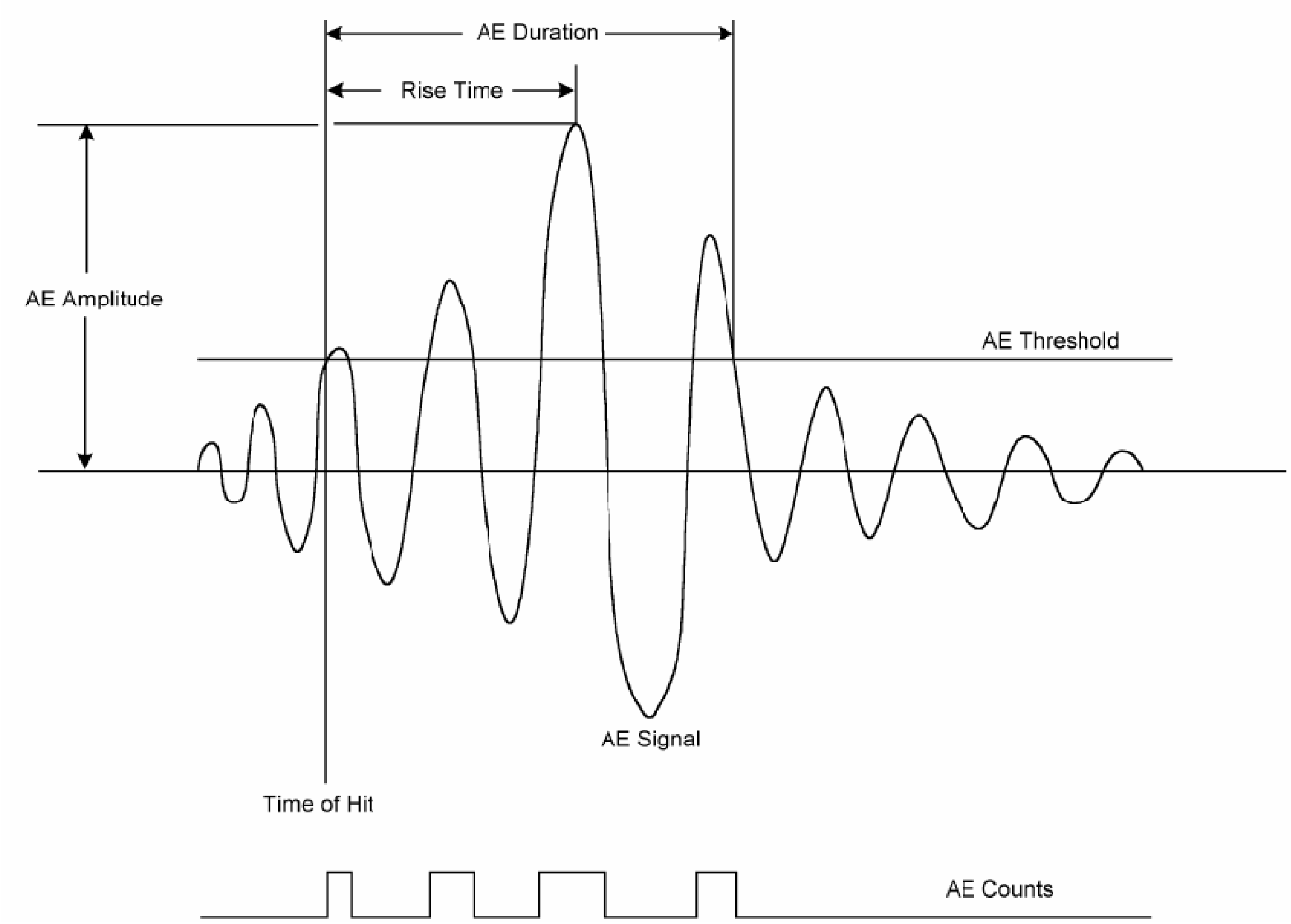


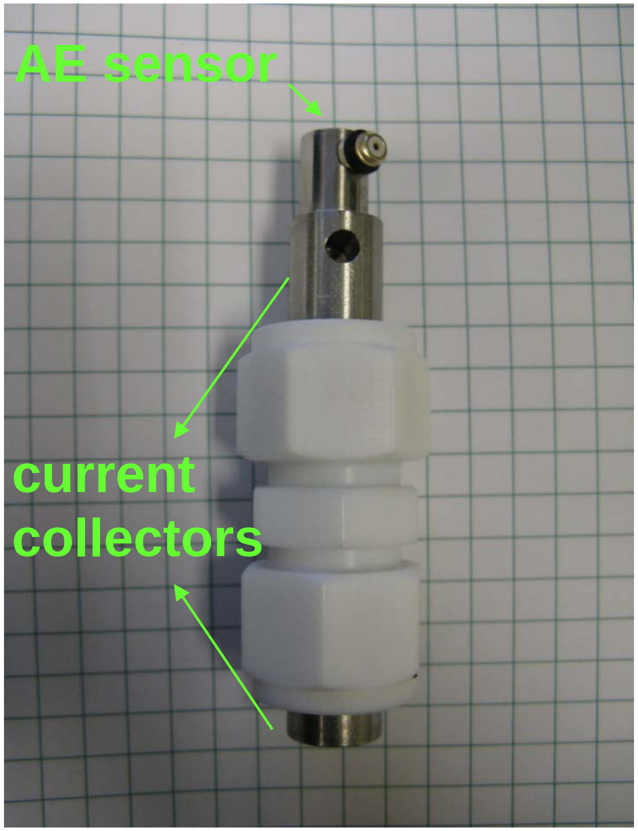
Fig. 7. HREM bright field image a) at low magnification, b) at high magnification, and c) a corresponding dark field image of (b), of Si lithiated to a higher concentration of 74 mole% Li, falling within the Li_7Si_3 and $Li_{13}Si_4$ equilibrium two-phase field. The lithiated composition instead consists predominantly of a Si based amorphous phase.

Acoustic Emission

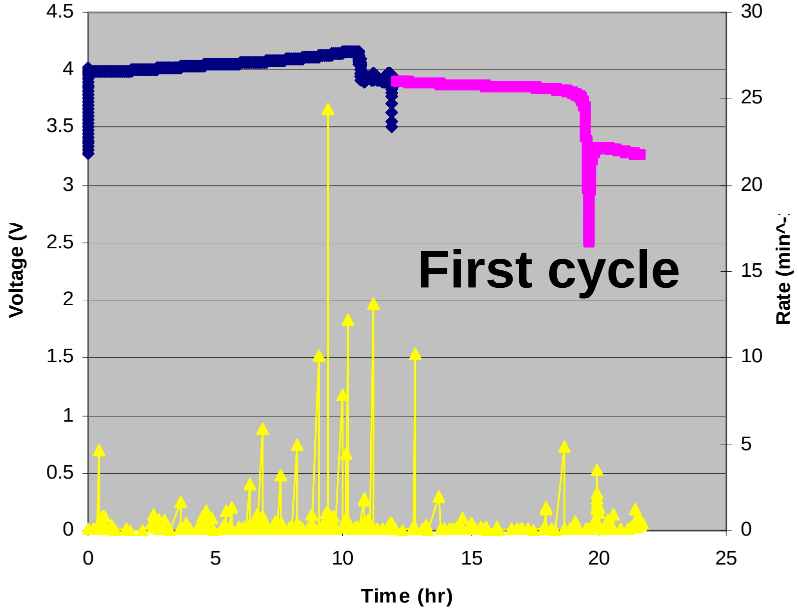
Transient elastic waves generated by the rapid release of energy within material

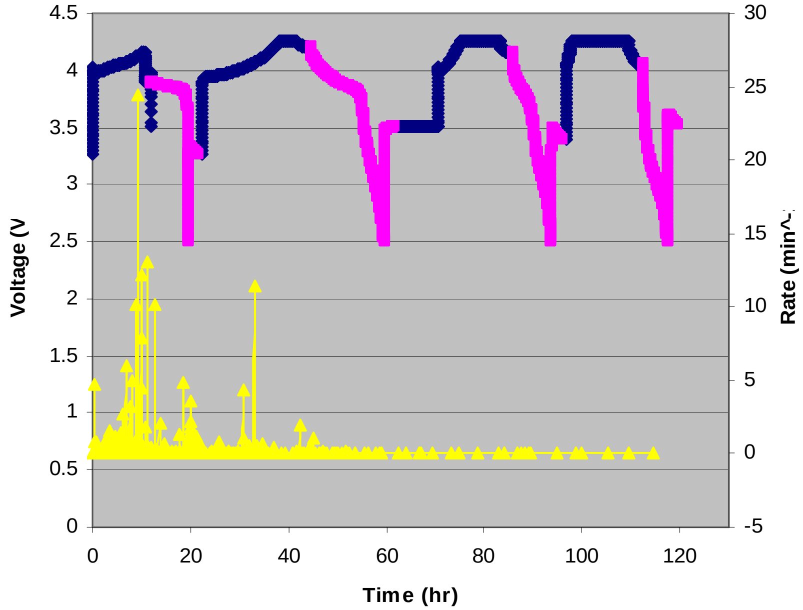


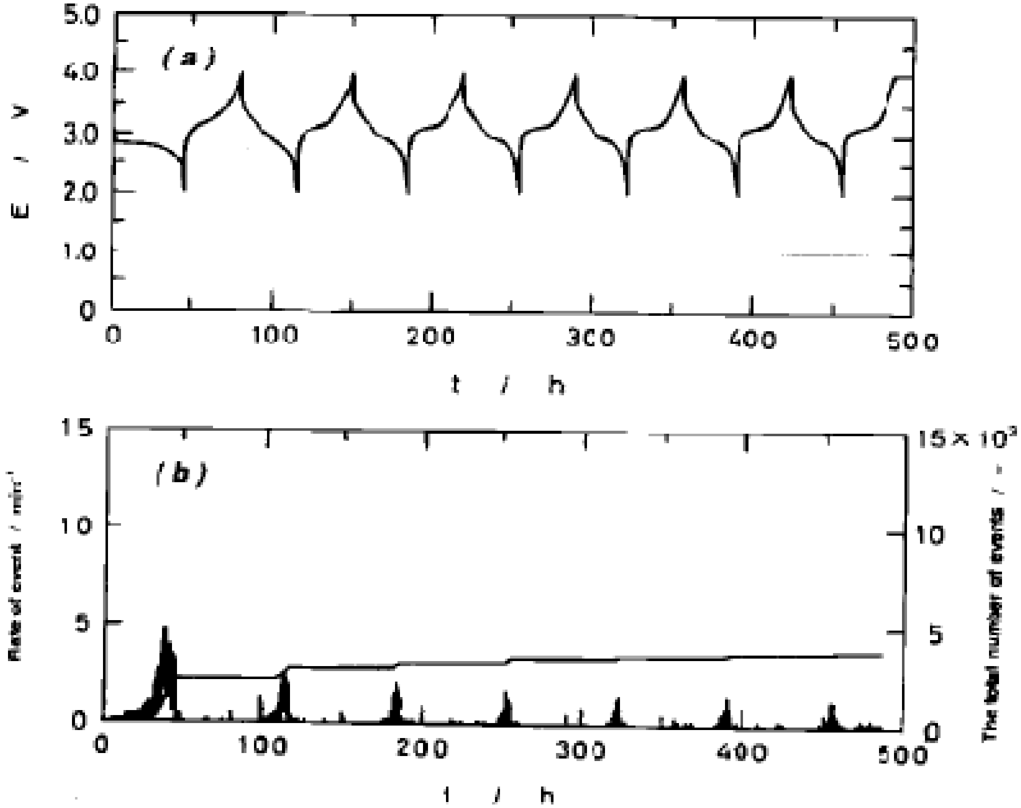
Waveform of an AE hit



AE data


First cycle

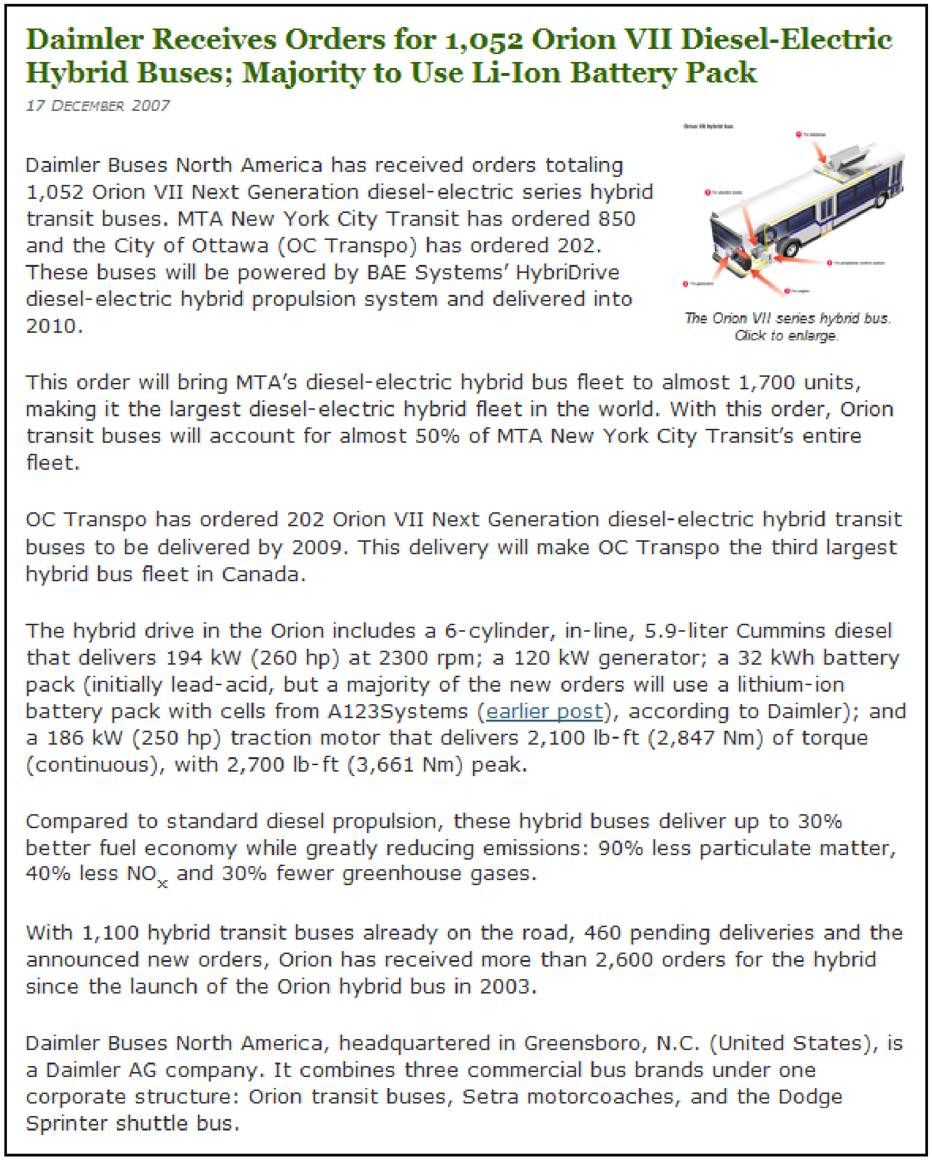




T. Ohzuku et al. J. Electrochem. Soc., (144)3496, 1997

Microcracking during cycling is analogous to thermal-shock in ceramic materials

Li-Ion Powered Hybrid Buses



Daimler Receives Orders for 1,052 Orion VII Diesel-Electric Hybrid Buses; Majority to Use Li-Ion Battery Pack

17 December 2007

Daimler Buses North America has received orders totaling 1,052 Orion VII Next Generation diesel-electric series hybrid transit buses. MTA New York City Transit has ordered 850 and the City of Ottawa (OC Transpo) has ordered 202. These buses will be powered by BAE Systems' HybriDrive diesel-electric hybrid propulsion system and delivered into 2010.

The Orion VII series hybrid bus. Click to enlarge.

This order will bring MTA's diesel-electric hybrid bus fleet to almost 1,700 units, making it the largest diesel-electric hybrid fleet in the world. With this order, Orion transit buses will account for almost 50% of MTA New York City Transit's entire fleet.

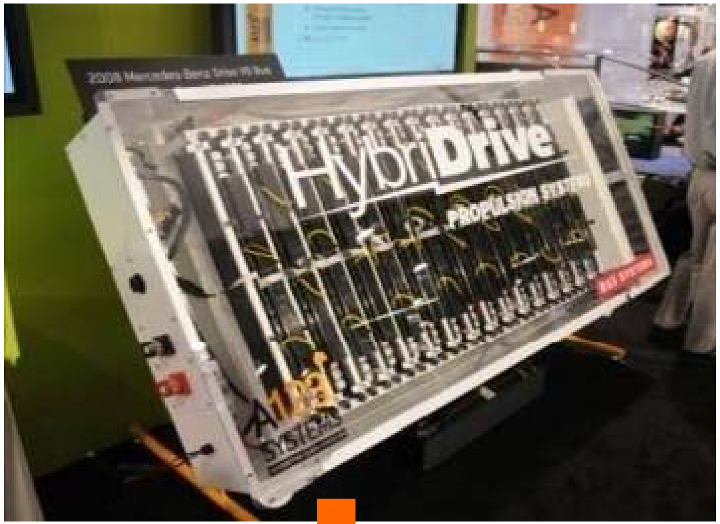
OC Transpo has ordered 202 Orion VII Next Generation diesel-electric hybrid transit buses to be delivered by 2009. This delivery will make OC Transpo the third largest hybrid bus fleet in Canada.

The hybrid drive in the Orion includes a 6-cylinder, in-line, 5.9-liter Cummins diesel that delivers 194 kW (260 hp) at 2300 rpm; a 120 kW generator; a 32 kWh battery pack (initially lead-acid, but a majority of the new orders will use a lithium-ion battery pack with cells from A123Systems (earlier post), according to Daimler); and a 186 kW (250 hp) traction motor that delivers 2,100 lb-ft (2,847 Nm) of torque (continuous), with 2,700 lb-ft (3,661 Nm) peak.

Compared to standard diesel propulsion, these hybrid buses deliver up to 30% better fuel economy while greatly reducing emissions: 90% less particulate matter, 40% less NO_x and 30% fewer greenhouse gases.

With 1,100 hybrid transit buses already on the road, 460 pending deliveries and the announced new orders, Orion has received more than 2,600 orders for the hybrid since the launch of the Orion hybrid bus in 2003.

Daimler Buses North America, headquartered in Greensboro, N.C. (United States), is a Daimler AG company. It combines three commercial bus brands under one corporate structure: Orion transit buses, Setra motorcoaches, and the Dodge Sprinter shuttle bus.



200 kW pack saves 3400 lb over Pb-acid

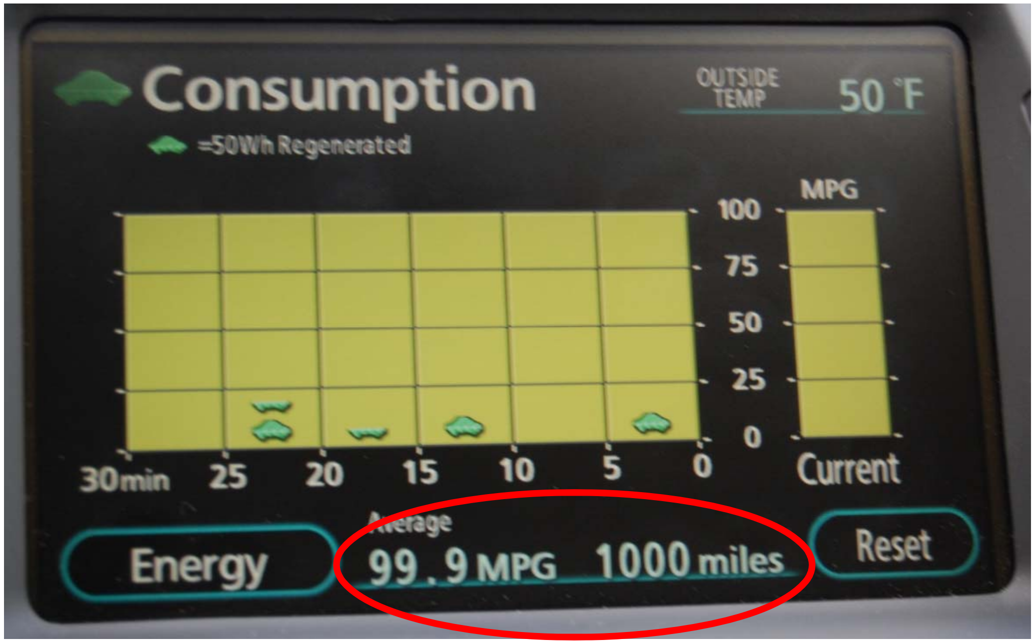
Manufactured in Hopkinton, Massachusetts

Daimler Orion VII Bus

1st Generation PHEV: Toyota Prius converted to use a 5 kWh Li-ion pack

Hymotion

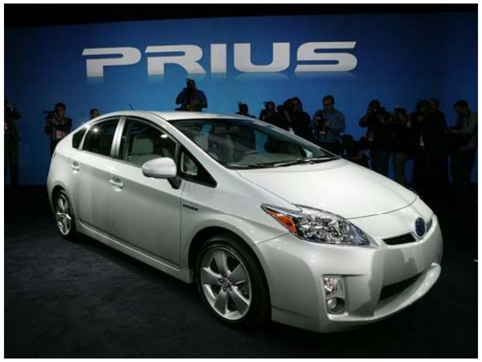
A123 SYSTEMS



1000.3 miles/8.33 gal
= 120 mpg

Current and Upcoming Factory XEVs:

HEVs:

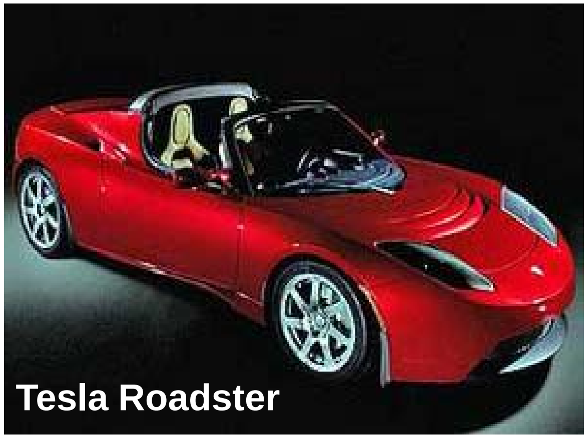


+ many others

PHEVs:

Fisker Karma

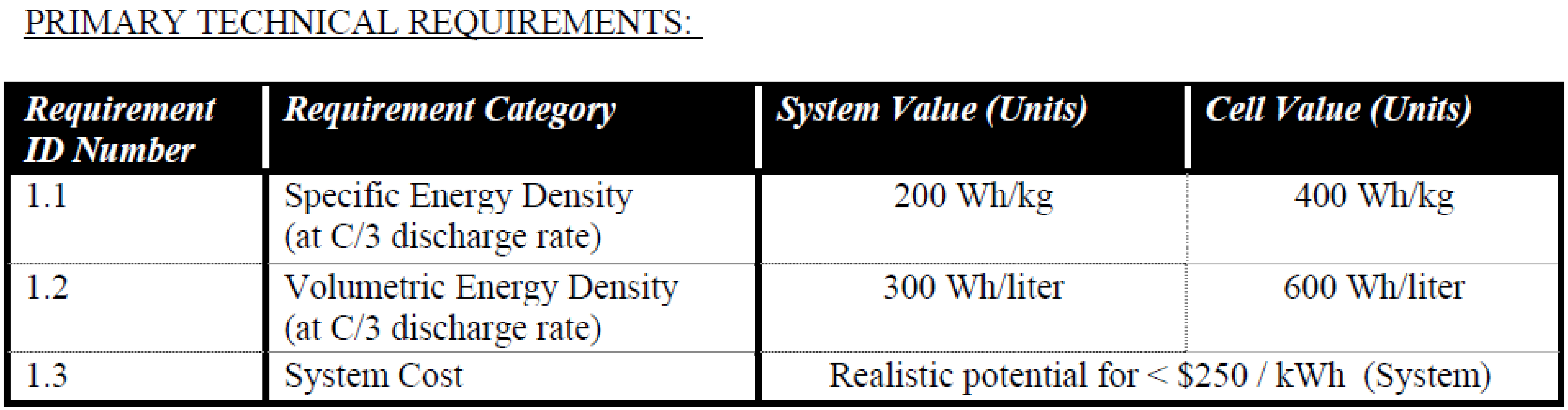
BEVs:



Tesla Roadster

Nissan Leaf

ARPA-E's view of requirements for widespread adoption of BEVs



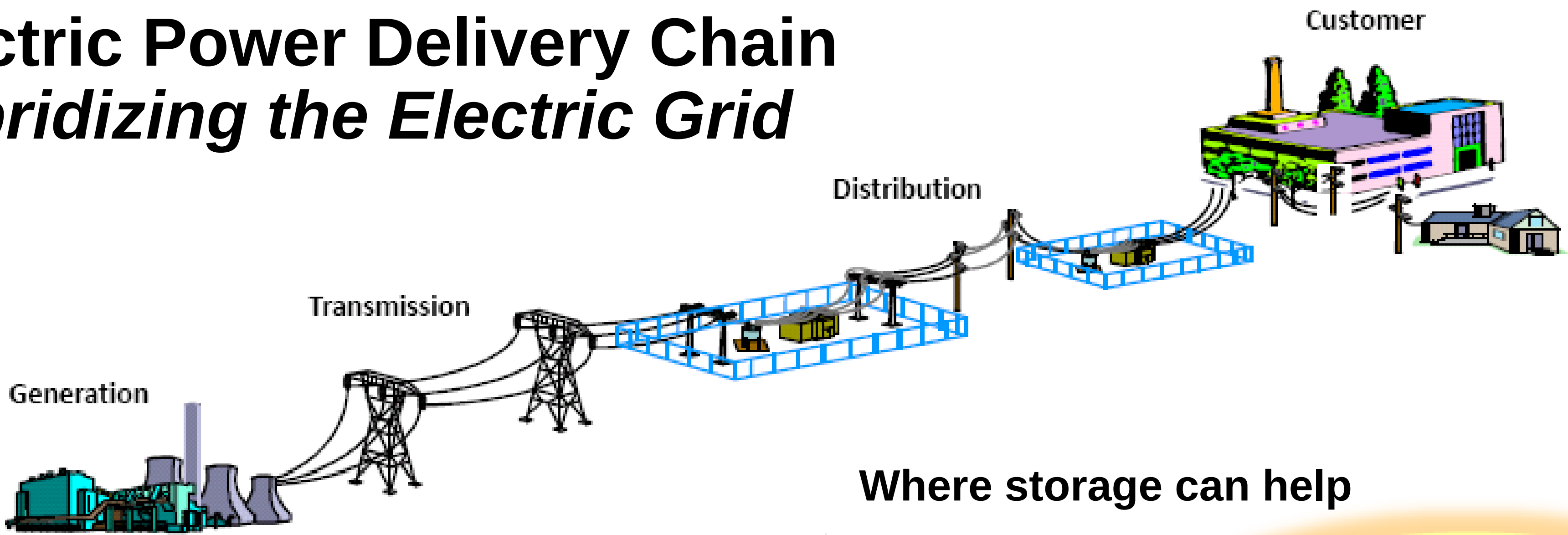
PRIMARY TECHNICAL REQUIREMENTS:

Requirement ID Number	*Requirement Category*	*System Value (Units)*	*Cell Value (Units)*
1.1	Specific Energy Density (at C/3 discharge rate)	200 Wh/kg	400 Wh/kg
1.2	Volumetric Energy Density (at C/3 discharge rate)	300 Wh/liter	600 Wh/liter
1.3	System Cost	Realistic potential for < $250 / kWh (System)	

(From ARPA-E FOA: "Batteries for Electrical Energy Storage in Transportation (BEEST)"), http://arpa-e.energy.gov/

Emerging Grid Applications

Electric Power Delivery Chain
Hybridizing the Electric Grid



US: 3% renewables

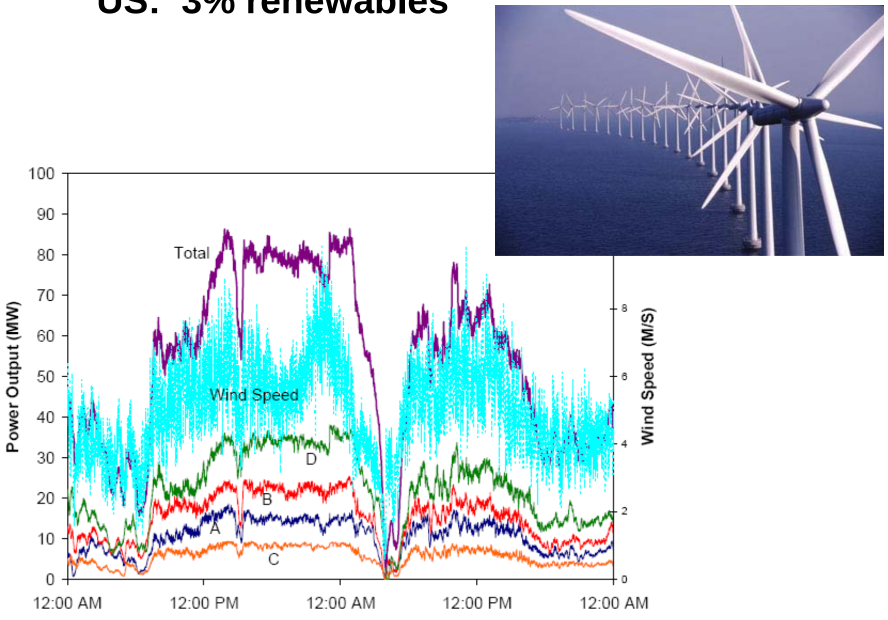
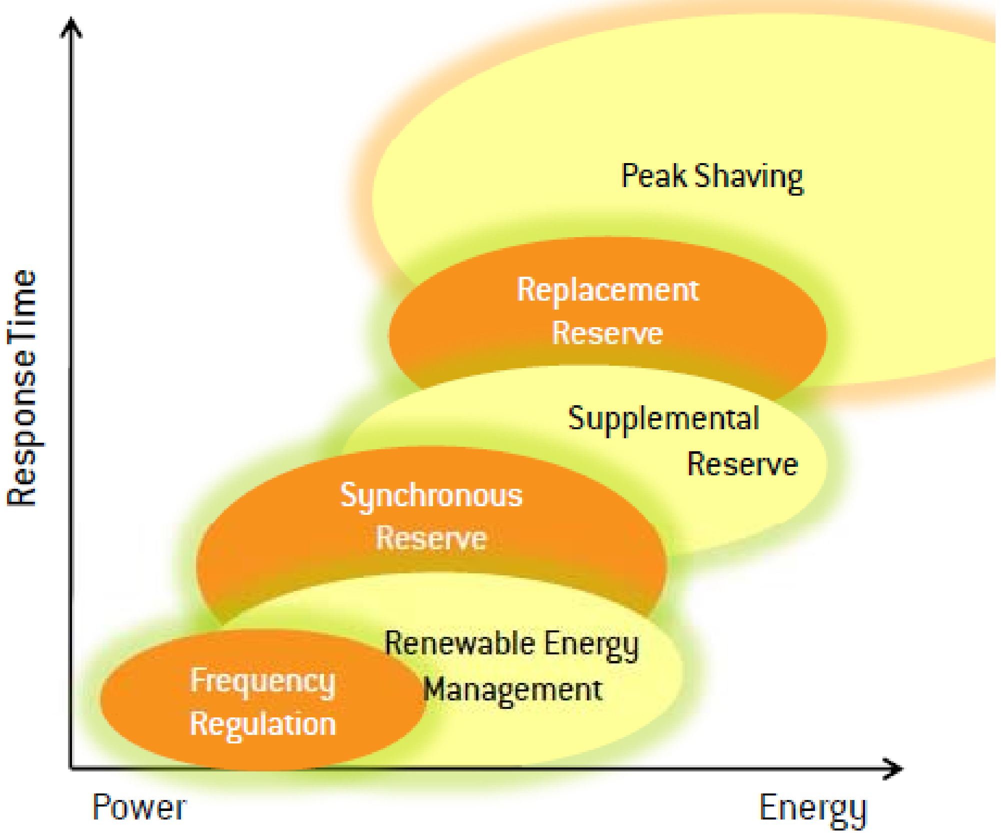


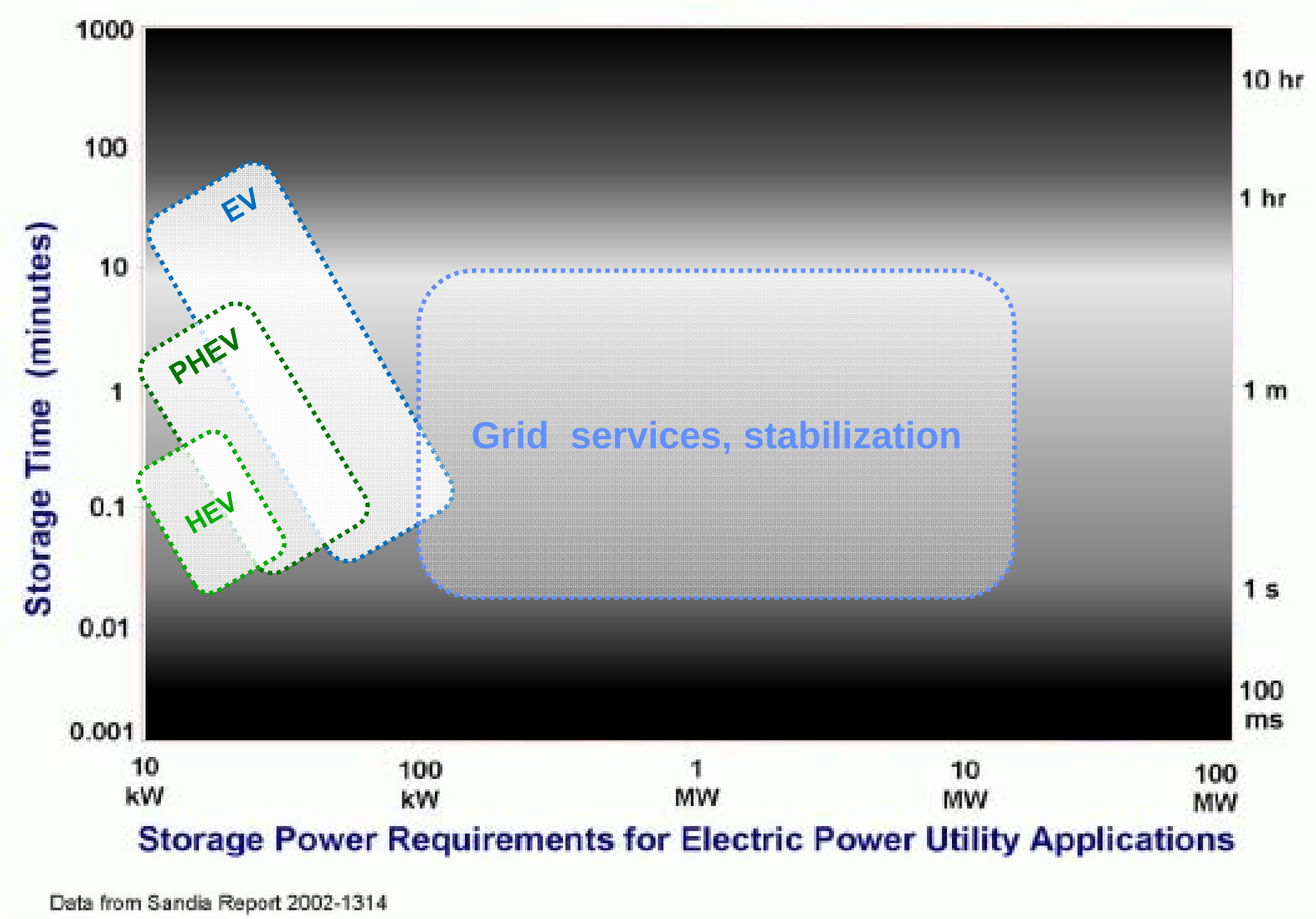
Fig. 8. Two days of output and wind speed from a four-section midwestern wind plant.

Wind and Solar are Intermittent Sources (not "dispatchable")

Where storage can help

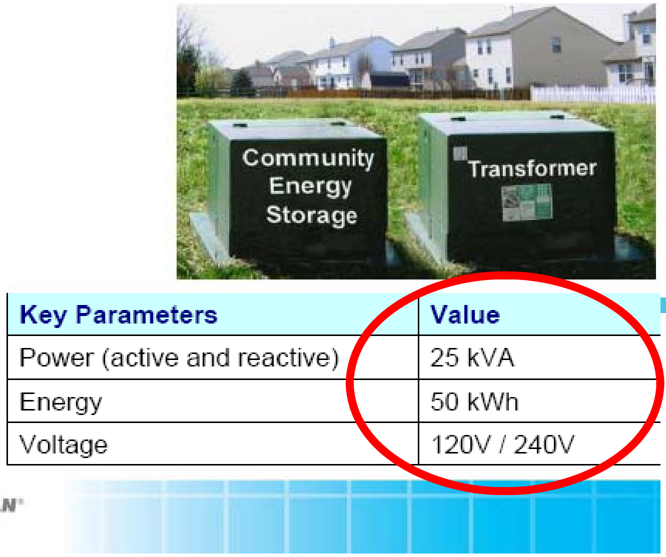


Comparison of Power Requirements for Automotive vs. Electric Grid



Data from Sandia Report 2002-1314

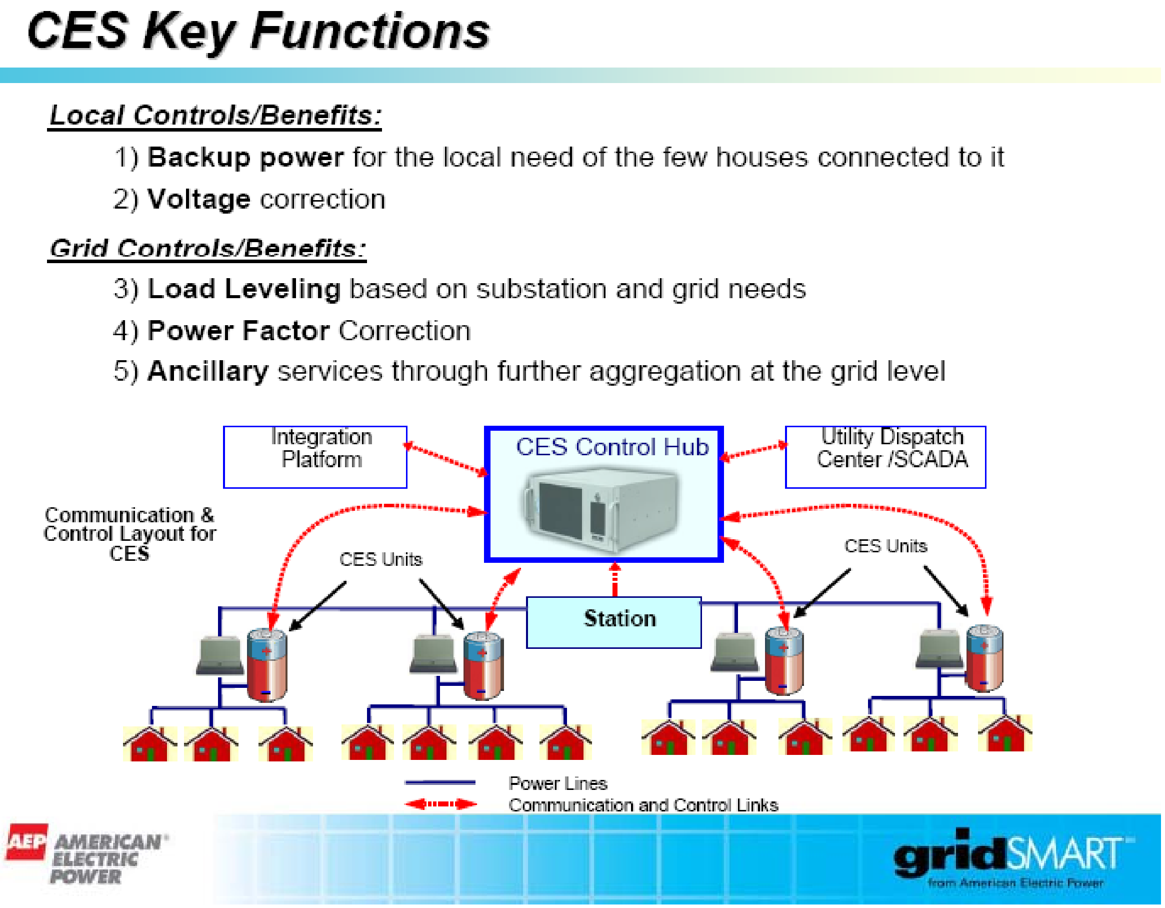
AEP's Community Energy Storage Vision



Key Parameters	Value
Power (active and reactive)	25 kVA
Energy	50 kWh
Voltage	120V / 240V

- *Lower power than an EV*
- *~Same energy as a BEV*

- *Massive in scale, distributed in nature*



CES Key Functions

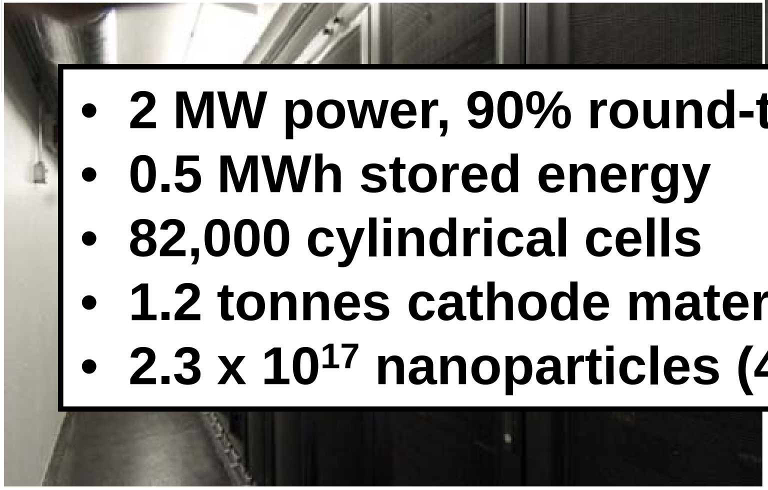
Local Controls/Benefits:

1) **Backup power** for the local need of the few houses connected to it
2) **Voltage** correction

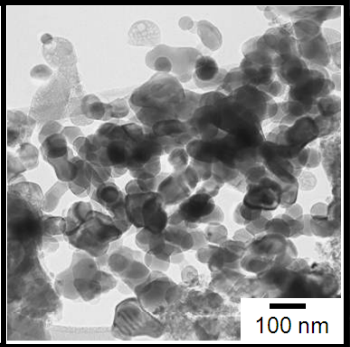
Grid Controls/Benefits:

3) **Load Leveling** based on substation and grid needs
4) **Power Factor** Correction
5) **Ancillary** services through further aggregation at the grid level

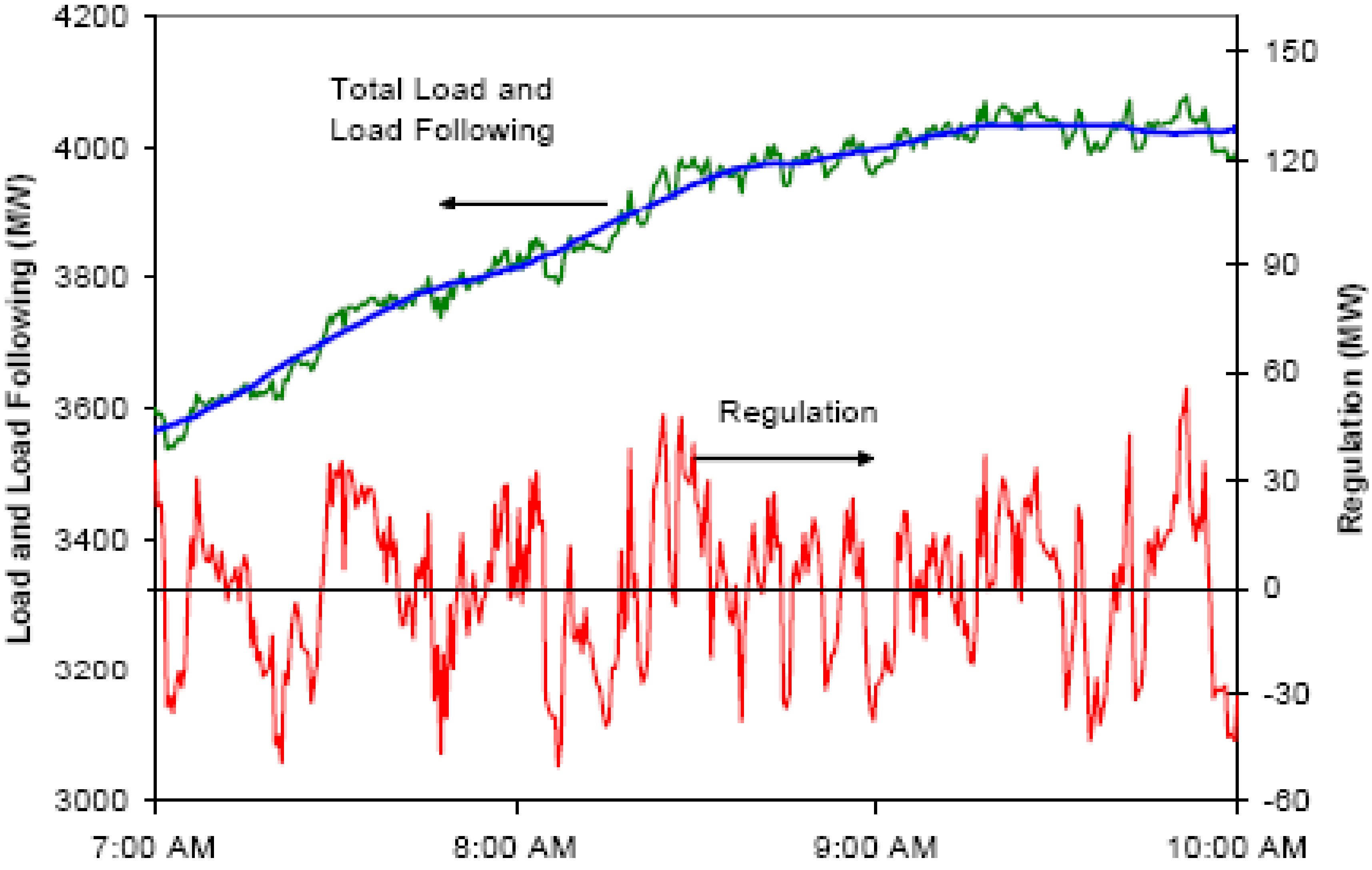
Megapower using Nanophosphates: Frequency Regulation with the World's largest Li-Ion Battery



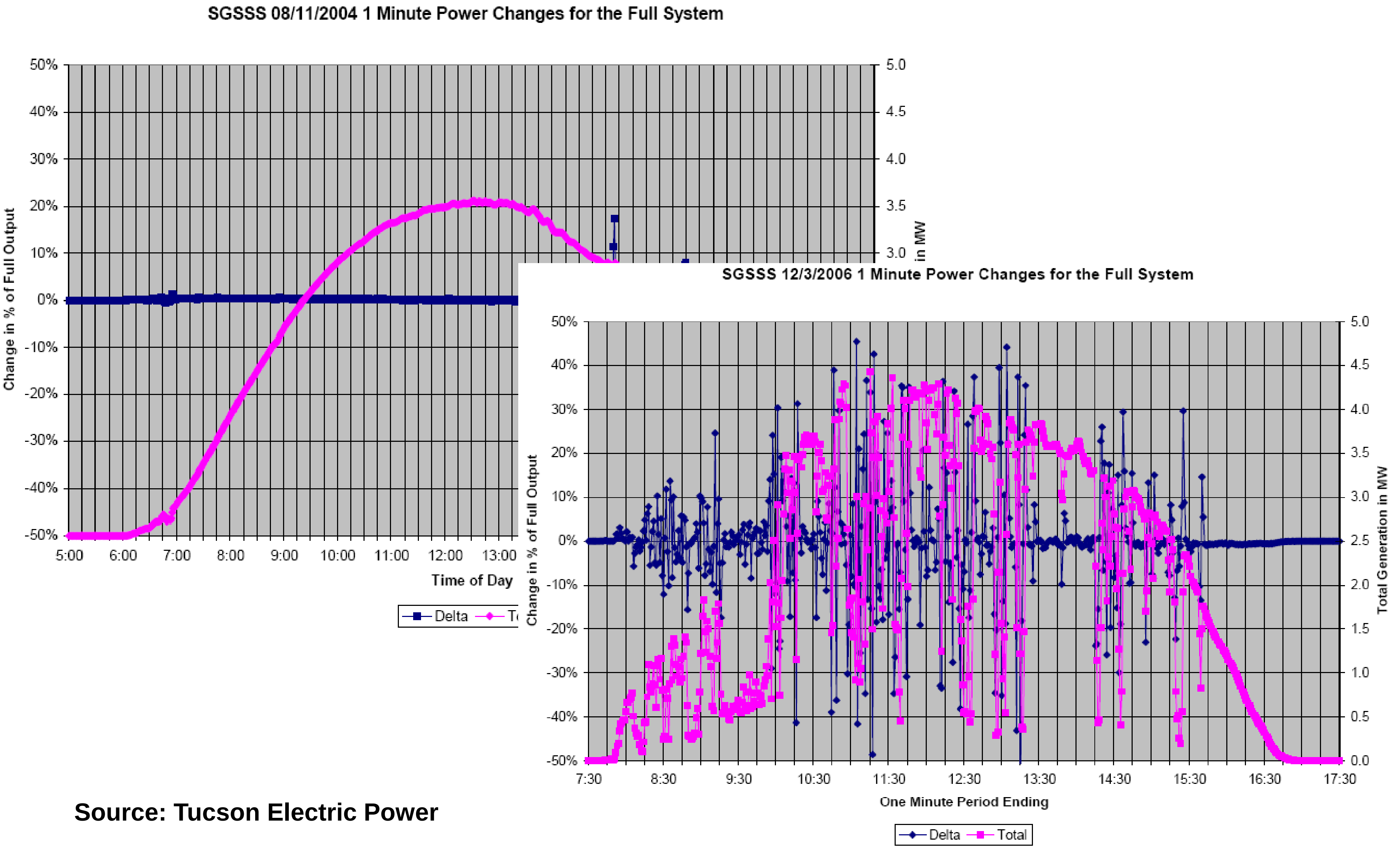
- 2 MW power, 90% round-trip efficiency
- 0.5 MWh stored energy
- 82,000 cylindrical cells
- 1.2 tonnes cathode material
- 2.3 x 10^{17} nanoparticles (40 nm dia.)



Frequency Regulation has HEV-like Profile



Why PV Needs Storage

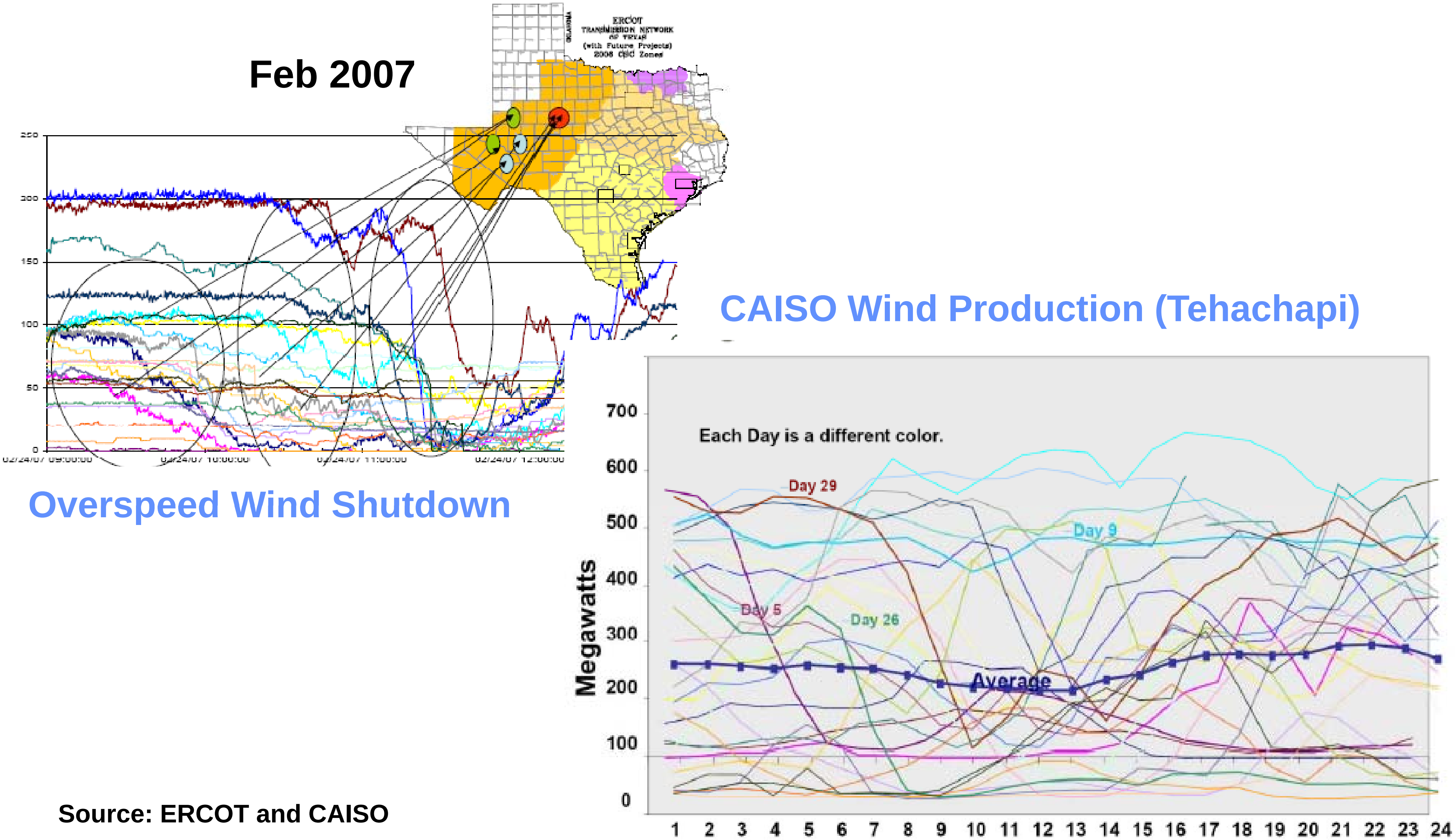


Source: Tucson Electric Power

What it looks like when not smoothed

Why Wind Needs Storage

Feb 2007

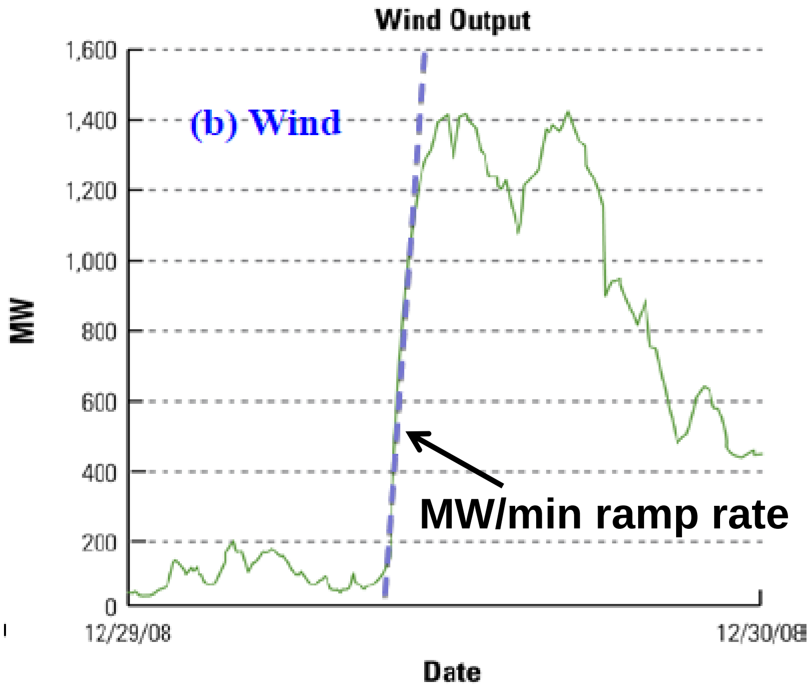


CAISO Wind Production (Tehachapi)

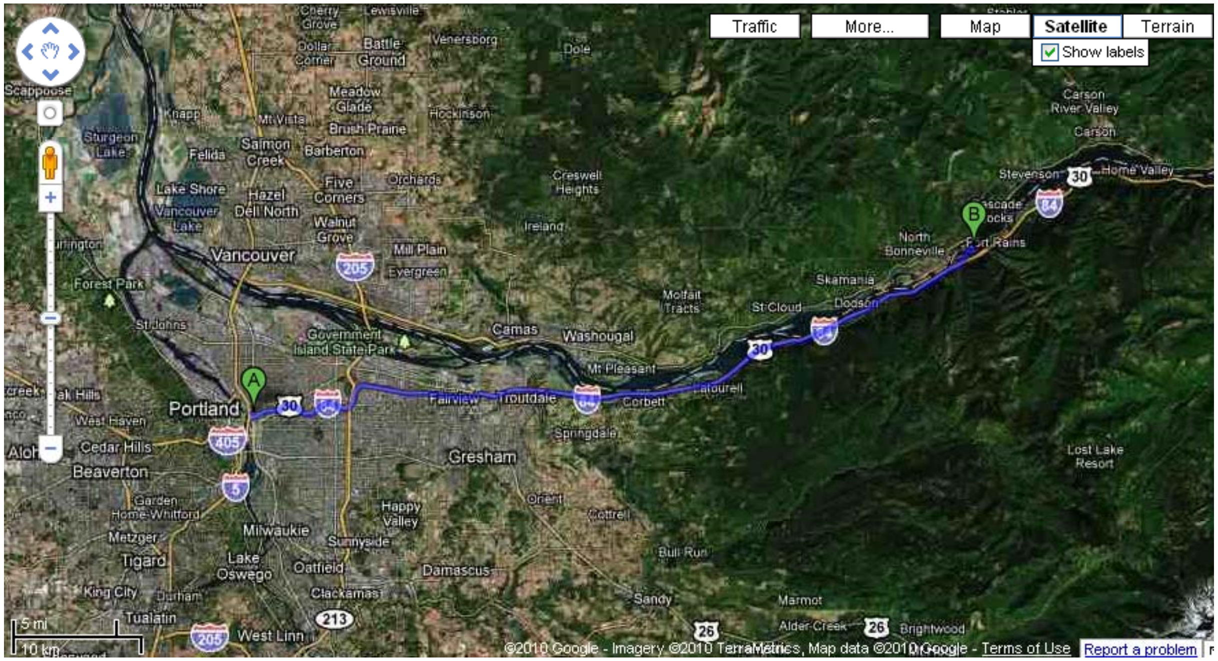
Overspeed Wind Shutdown

Source: ERCOT and CAISO

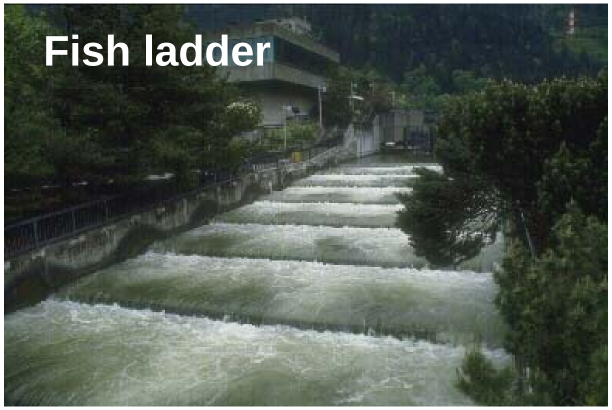
ARPA-E Program GRIDS (http://arpa-e.energy.gov/): Grid-Scale Rampable Intermittent Dispatchable Storage



MW/min ramp rate



40 miles from here: Bonneville Dam on the Columbia River



Pumped Hydroelectric Storage: How do we do this everywhere?

- 1872 MW output
- 15,000 MWh stored energy
- 2.5 x 1 mile, 842 acres

Questions?