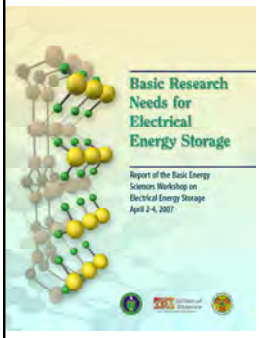
The electric economy: the fossil fuel century is over

- PHEV is way to go in USA
  - All electric drive
    - GM Volt
- Buses ideal market
  - Save 30% fuel
  - Fast acceleration
  - Clean air
- Renewable Energy
  - Demands storage
  - if not Pumped hydro
  - then Batteries

Beyond Lithium-Ion – 2010

FreedomCAR & Fuel Partnership

Energy Storage Materials – The Past and the Future



M. Stanley Whittingham,
Chemistry and Materials Science
State University of New York
Binghamton, NY, USA
http://materials.binghamton.edu

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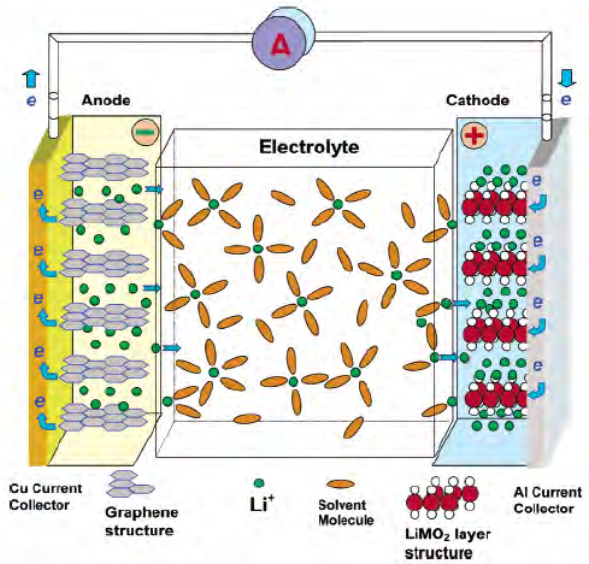
What happened 1967-1975?
Solid State Chemistry and Materials Science

- Ford Motor Company reported sodium **beta alumina** in 1967
  - ✓ High ionic conductivity
  - ✓ Na/S battery
- **Solid State Ionics** field begins in 1972
  - ✓ **Mixed conductors**
- Understand the mechanism of electrode reactions
  - 1970 situation
    - $Li + V_2O_5$ reacts to $Li_2O + V_2O_4$
    - Dry cell: MnO_2 reacts to Mn_2O_3
  - **Intercalation** Reactions are inherent to many cathodes:
    - $Li + V_2O_5$ reacts to give LiV_2O_5
    - $H + MnO_2$ reacts to give MnOOH
    - $Li + TiS_2$ reacts to give Li_xTiS_2 (no carbon diluent)
- **Message**
  - **Understand the chemistry**
    - **Essential for Li-air**

An Intercalation-based Lithium Battery Cell
1970s Technology



Redox Intercalation Cathodes for Lithium Ion Batteries

First Generation (1977):

Layered Sulfides.

TiS_2 - LiAl - Exxon

One Lithium to transition metal ratio

- 480 Wh/kg **(240 Ah/kg)**

First Commercial Success (1991):

Layered Oxides.

$LiCoO_2$ - **LiC_6** - SONY

0.5 Li to Co cycling - 480 Wh/kg

Today - 2010:

Mixed layered oxides.

$Li(NiMnCoAl)O_2$ – electronics, etc

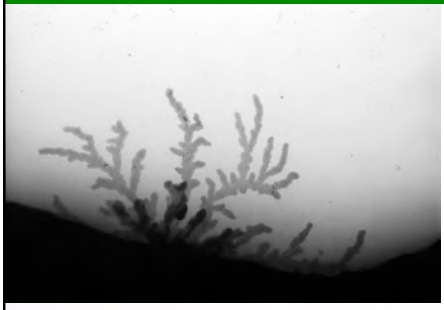
$LiFePO_4$ (& $LiMnPO_4$?)

BAE Systems, Binghamton
11 kWh Li-ion

Outline and Challenges for You

- **Where are we today?**
  - **Can we use pure metal anodes?**
  - **What is the status of intercalation oxides vs phosphates?**
- **What are tomorrow's needs?**
  - **Lower-cost higher energy batteries that are safe**
    - **Double the capacity of both the anode and the cathode**
    - **Use readily available elements (USGS studies)**
    - **Need more than one electron per redox center**
- **Can the grand challenge of a simple air battery be achieved?**
  - **Lithium/air, (or zinc, magnesium or aluminium)**
  - **Is it worth achieving (aka what is the real storage capacity)?**

Anode: Most Lithium rechargeables use intercalation electrode, e.g. carbon - why?



Russ Chianelli - Exxon

Avestor - AT&T

Exxon-MoliEnergy-Avestor

The Anode – Double Capacity to 1.4 Ah/cc

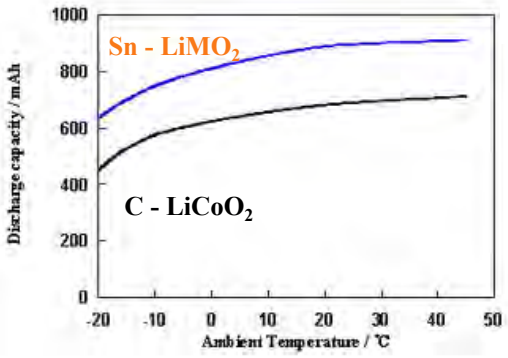
➢ **The Anode**

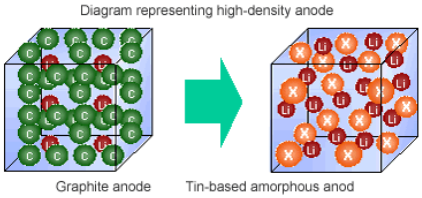
- **Make lithium metal work (Holy Grail)**
  - **+ High Energy, > 3000 Ah/kg**
  - **+ High discharge power**
  - **− Electrodeposition**
    - **− Dendrites "always" form**
- **Play it safe with carbon**
  - **− Low capacity**
  - **+ Extensive experience**
- **Move to tin or silicon**
  - **+ High capacity**
  - **− Large expansion leads to decrepitation, and loss of capacity**

Russ Chianelli, Exxon

Tin Anode: SONY's new Hybrid Lithium-Ion

- Capacity vs Temperature
  - $C/LiCoO_2$ vs $Sn/Li(MnNiCo)O_2$



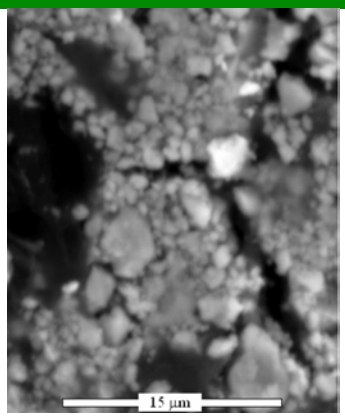


1. Tin-Based Amorphous Anode

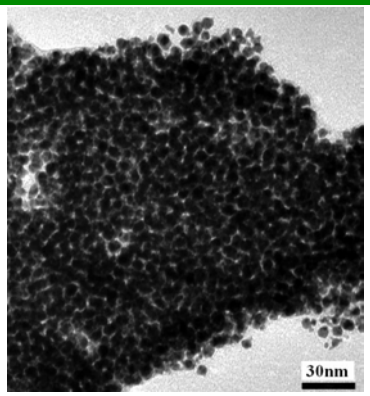
"The newly developed tin-based amorphous anode is a material consisting of multiple elements such as tin, cobalt, carbon, where the elements are mixed on a nanometer level. **Result is a 50% higher unit per volume ratio of lithium ion density.**"

SONY - February 15, 2005

SONY's Anode is a Smart Nanostructure



SEI layer only formed on surface of microstructure



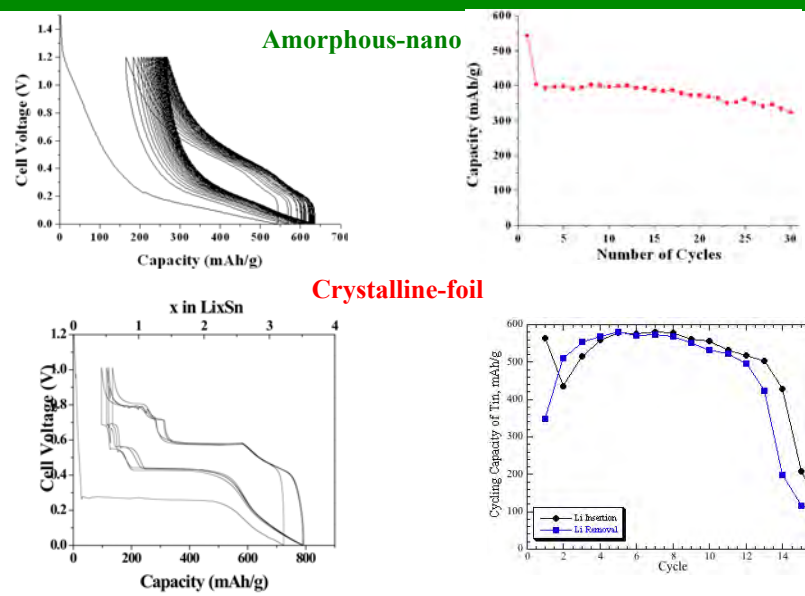
New composite
Sn-Co-Ti alloy anodes

23 % tin; 10.3 % cobalt; y % titanium

$Sn_{1.1}CoTi_y$ + carbon

Nano Amorphous Sn-Co has Promising Electrochemistry

ESL, 10, A274 (2007)

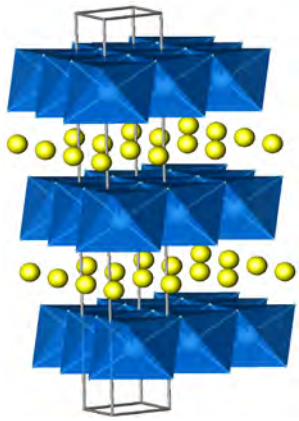


The Cathode – Double Capacity to 300 Ah/kg

- **The Cathode**
  - **Use only readily available elements, per USGS**
    - + **Fe, Ti, Mn, V as major component**
      - + **Fe, Mn and V have acceptable redox potential**
    - − **Eliminate most of the Co, and possibly Ni as major component**
    - + **Find low cost manufacturing methods**
  - **Expand capabilities of present intercalation systems**
    - + **Fully utilize 1 lithium in layered $LiMO_2$ systems**
    - + **Use 2nd lithium in phosphates**
    - − **Minimize use of inactive components**
  - **Move away from intercalation reactions**
    - + **Make oxygen, sulfur work**
      - − **Lower voltage, but much higher capacity (Ah/g)**

Cathodes - Oxides/Phosphates

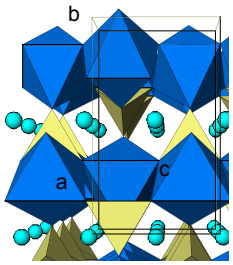
$Li(MnNiCo)O_2$



MO_6 octahedra

LiO_6 octahedra

$LiFePO_4$



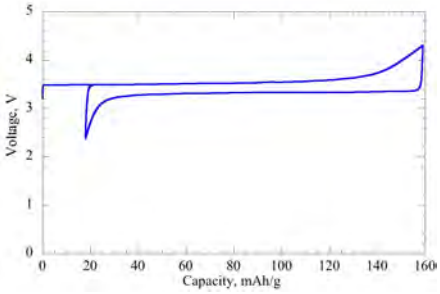
Up to 7% Iron on Lithium sites

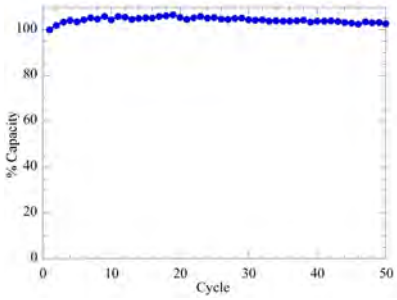
3 block structure (3 layers of $LiMO_2$) - $LiCoO_2$
Contrast Li_xTiS_2 - 1 block structure - CoO_2

Up to 10% Nickel on Lithium sites

$LiFePO_4$ Hydrothermal: Electrochemistry
(Electrochem. Commun., 8, 855 (2006))

- Electrochemical behavior of **ordered** Olivine
  - High capacity, even when not treated above 200°C
  - Vitamin C used as reducing agent
  - **Carbon nanotubes** added to hydrothermal reaction medium
  - Extremely stable on cycling
    - ✓ No capacity loss over 50 cycles





Solid Solution Behavior of $LiFePO_4$

$LiFePO_4$ can be substituted on both Fe and P sites

Vanadium substitution occurs on P site: $LiFeP_{1-y}V_yO_4$

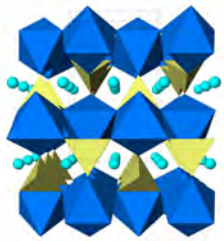
Gives a **nanostructured** material

50 nm crystallites in micron-sized particles

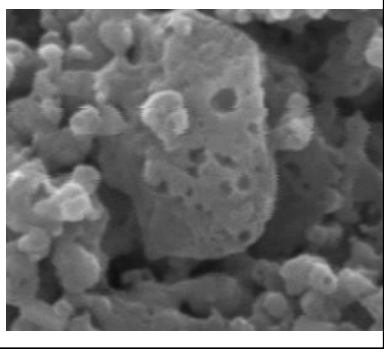
Leads to higher density

Higher capacity

Weight and volume basis



3 μm with 50 nm crystallites

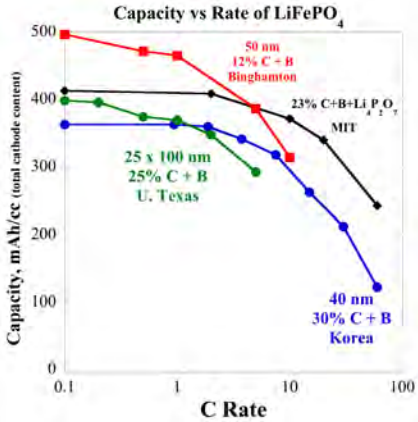


Collaboration with C-S Wang at U. Maryland

Cathode Morphology Critical to High Capacity
ESL 12, A33 (2009)

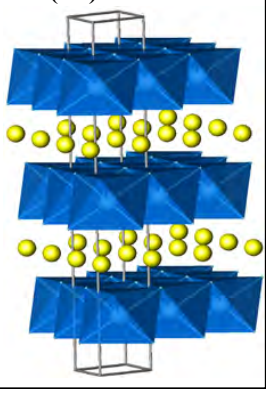
➢ **$LiFePO_4$**

- **Nanosize critical, but overall particles are micron-size**
  - **+ Higher density – g/cc – leads to lower carbon use**
  - **+ Still low energy storage capabilities**

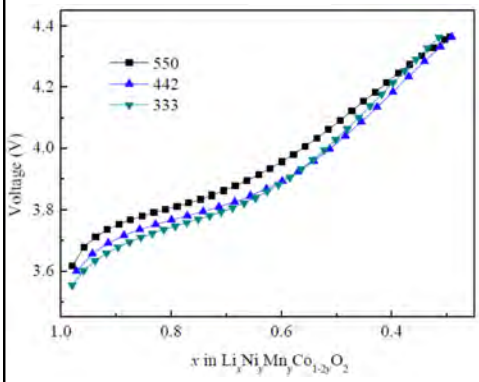


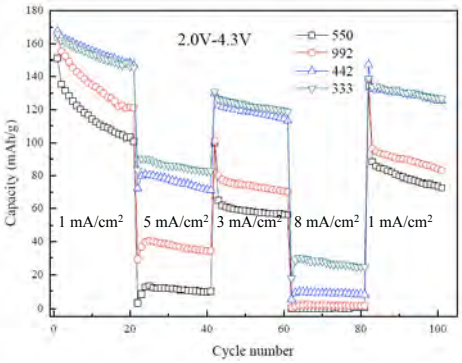
Complexity of Disordered $Li[LiNiMnCo]O_2$

- What is ideal chemical composition?
- Stoichiometric $Li[NiMnCo]O_2$
  - Always some Ni/Li exchange (except for high cobalt content)
    - Ni limits Li diffusivity, and cyclable lithium
    - Ni stabilized structure against conversion of one block (1T)
  - Minimize Li on Ni site, but allow 3-5% Ni on Li site.



What is best composition? Cycling at constant current suggests that 442 composition has best overall capacity





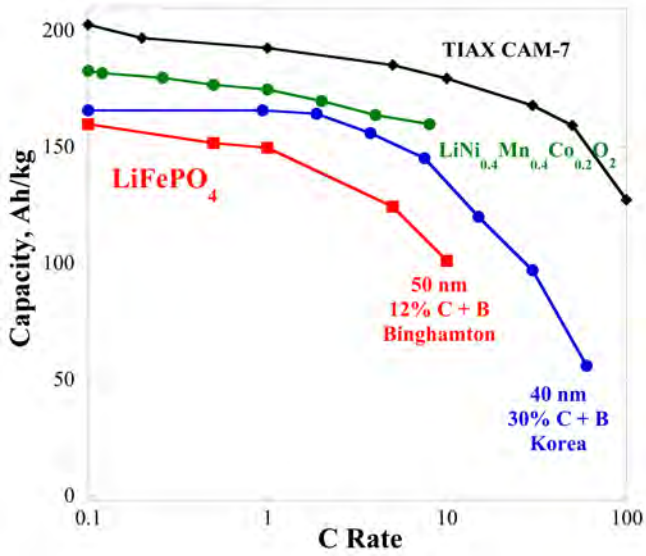
Maximum capacity at 4.4 volts is 197 Ah/kg and 180 at 4.3 volts charging

Increase nickel content and decrease cobalt content

Ni stabilizes structure against conversion to one block (1T)

20% Co maybe optimum; Mitsubishi going to 10% Co, 45% Ni

Metal Oxides higher Capacity than Phosphates
(Even more so on a Volumetric basis)



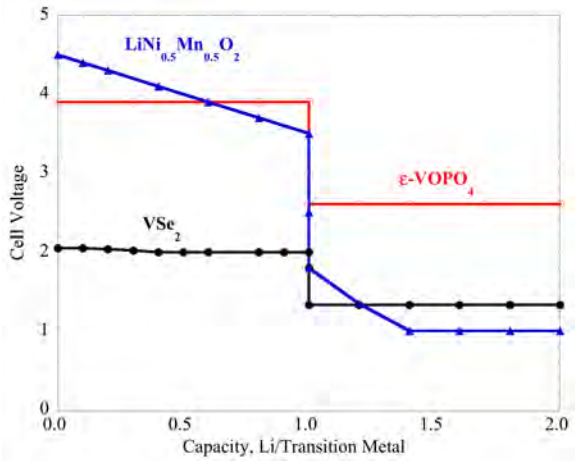
TIAX CAM-7:
$LiNi_{1-y}M_yO_2$

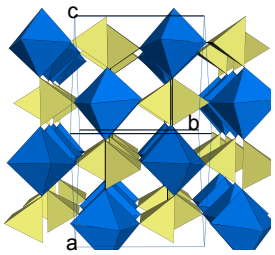
Binghamton/ NREL
$LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$

Korea – Kim
Solvothermal
$LiFePO_4$

Binghamton
Hydrothermal
$LiFePO_4$

Several Systems offer 2 Li per Redox Cation
(but, voltage difference too high)



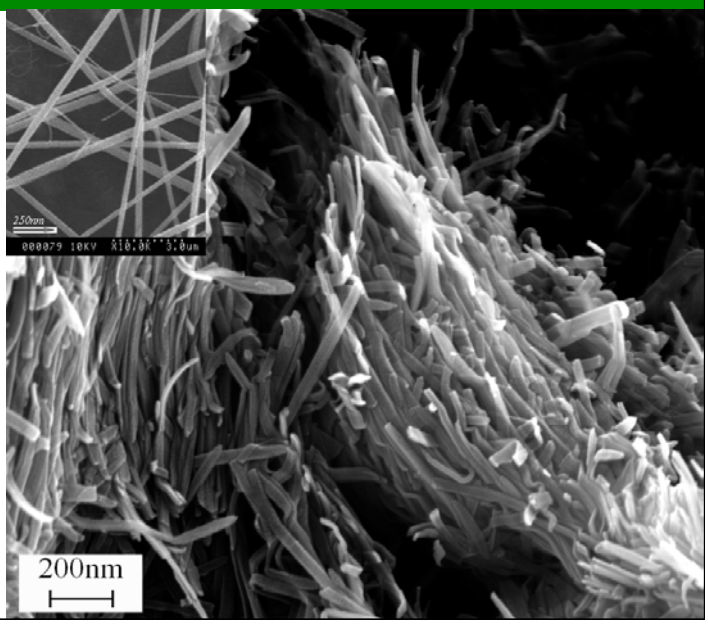


Electrospun VO_y
(Electrochem. Commun., 11, 522, 2009)

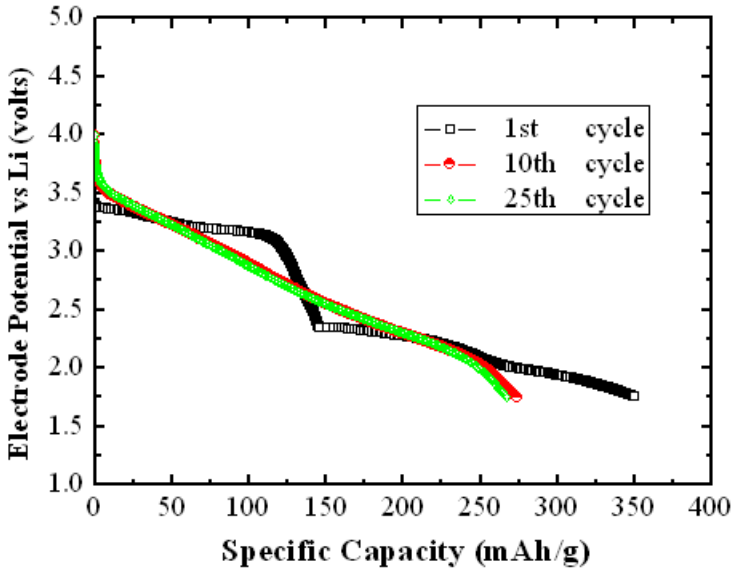
Cathodes

Electrospun Fibers

Hydrothermal
of
Electrospun Fibers



Electrochemistry of Electrospun VO_y
(Electrochem. Commun., 11, 522, 2009)



What is the status of Intercalation Batteries

- **Li-ion intercalation batteries**
  - **Approach 800 Wh/kg** (excluding C anode)
    - + **Lab experimental data**
      - + **Includes all active components (including oxygen)**
    - − **Cost is an issue**
      - + **Find low cost manufacturing methods**
  - **Volumetric capacity hurt by:**
    - − **Carbon anode**
    - − **Carbon and binder in cathodes**
    - − **Use of nanomaterials**

Intercalation Batteries can be Improved

"Lithium-ion cells have high energy density"

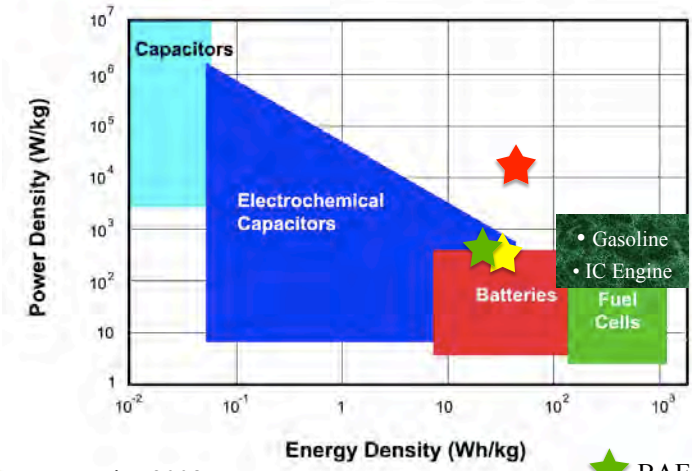
Where has it gone?

System	Cell	V	A-hr	Volume (mL)	Mass (g)	Wh/L	Wh/L Theory
A123 $LiFePO_4$	26650	3.3	2.3	35.5	70	215	1980
Panasonic Ni-MH	18670	1.2	3.2	17.0	60	225	
E-One Moli $LiMn_2O_4$	26700	3.8	2.9	37.2	101	232	2060
Panasonic $LiCoO_2$	18650	3.7	2.55	16.5	46.5	570	2950

(J. Dahn, Almaden Talk)

Batteries, Capacitors and Energy Storage

Computer/Cell phone Li-Ion 100-200 Wh/kg



Toyota Prius 2008

A123 Formula 1 cell

BAE Bus 2009

Materials and Systems: 40 Year Cycle 1970 - 2010

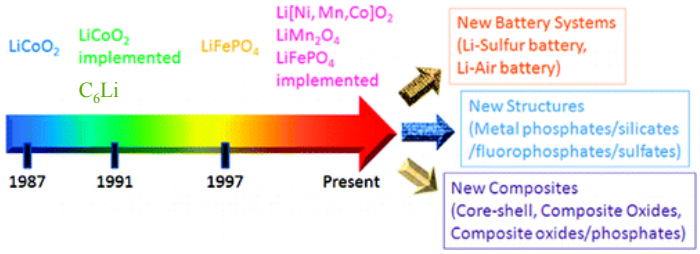
USA UK Japan Asia

Intercalation

(Nazar et al, Chem. Mater., 2010)

$LiTiS_2$

1970-1980



Other

Na/S – Ford Motor Co

Li/S – GM/ANL

Metal/air – NASA/ Lockheed

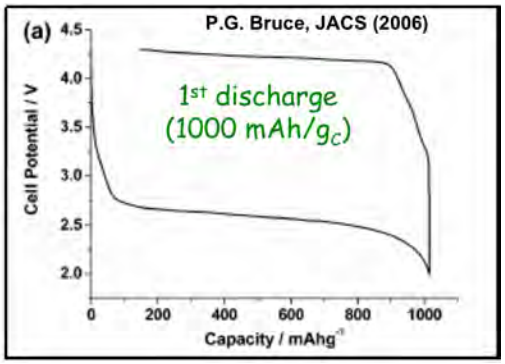
Zebra: $Na/NiCl_2$ – SA, Brazil, GE

Zn/air – low cost and safe

Can Lithium – Air be made to work?

One step and dream toward the Holy Grail

$$2\,Li + O_2 \overset{MnO_2}{\rightleftharpoons} Li_2O_2$$



Opportunities:

High capacity

Low cost

Challenges:

Energy Inefficient

Oxygen Electrocatalyst

Lithium protection

Lithium electrodeposition (key to all Li batteries)

If C_6Li is used energy advantage may be lost

Containment of electrolyte

What is the reaction mechanism?

What is the reaction mechanism of Li-Air?

- **Aqueous system**
  - **LiOH**
  - **Soluble, maybe more easily recharged**
- **Non-aqueous system**
  - **O_2 + Li gives LiO_2, then what?**
  - **Ideally Li_2O_2 then Li_2O**
  - **In reality, LiO_2 reacts with solvent, giving ?**
- **A thorough study of reaction mechanism essential**
  - **Can an electrocatalyst be developed that can change the reaction pathway**

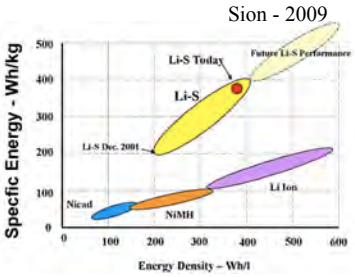
What is the real storage capacity of Li-Air?
(Following Dahn at Almaden)

- **Lab Energy density may be double that of Li-ion if all works out well**
  - **Lithium-ion: 450 Wh/kg**
  - **C-Lithium-air: 900 Wh/kg** (no catalyst, no carbon, etc)
- **Lab Volumetric energy density same as Li-ion**
  - **Li-air: 1250 vs 1450 Wh/L for Li-ion**
  - **LiC_6-air: 1880 Wh/L**

What is the real storage capacity of Li-Air?
(Following Dahn at Almaden)

- **Lab Energy density may be double that of Li-ion if all works out well**
  - **Lithium-ion: 800 Wh/kg**
  - **C-Lithium-air: 900 Wh/kg**
- **Lab Volumetric energy density same as Li-ion**
  - **Li-air: 1250 vs 1450 Wh/L for Li-ion**
  - **LiC_6-air: 1880 Wh/L**
  - **Li-S less than Li-ion**

Sion - 2009



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- Lab Volumetric energy density same as Li-ion
  - Li-air: 1250 vs 1450 Wh/L for Li-ion
  - LiC_6-air: 1880 Wh/L
  - Li-S less than Li-ion

There are no fundamental scientific obstacles to creating batteries with ten times the energy content - for a given weight - of the best current batteries.

From the program of the Almaden Institute

- Hype/overly raise expectations hurts everyone
  - We need to understand Li/air and Li/S
    - Lots of basic science needed
  - Zn/air may be superior
  - Flow systems may lead to lowest cost

Conclusions – The 2015 Battery System

- An anode with a lab capacity around 500 Ah/kg and 1.4 Ah/cc
  - Silicon or tin based nano-structured electrode
  - Issue is SEI layer on large expansion materials
  - Dream is pure lithium
- A cathode with a lab capacity of >200 Ah/kg at C rate (1 hour discharge)
  - Extension of present technology to 2 electrons
  - Dream is air
- A stable electrolyte
  - 5 volt charging stability
  - No formation of solubilizing agents, such as HF
- A 200-300 kWh/kg (1 kWh/L) actual system