BATTERIES: THE SEARCH FOR A PERFECT CHEMISTRY

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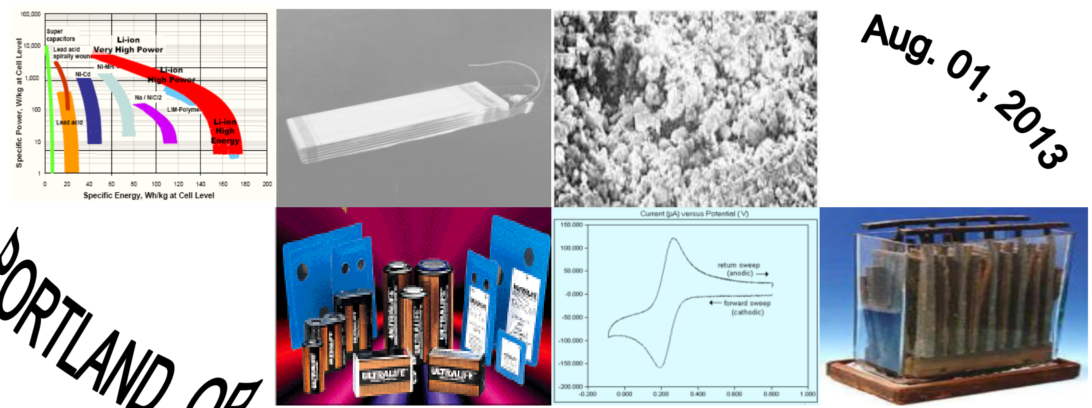
OregonTech



Aug. 01, 2013

PORTLAND, OR

SusTech 2013

Where is this going ?

Lithium iron phosphate

Cobalt-oxide nanowires from genetically modified virus

Electro-plated tin

Solid-state plated copper antimonide nanowire

Nanomatrix structure

Lithium purpurin

Manganese spinel (

Silicon whisker on carbon nanofiber composite

Lithium Managnese Oxide/NMC

Silicon/titanium dioxide composite nanowires from genetically modified tobacco virus

Hard carbon

Lithium iron fluorophosphate

Silicon nanowires on stainless steel

Silicon oxycarbide-coated carbon nanotubes

5% Vanadium-doped lithium iron phosphate olivine

Fe_3O_4-plated copper nanorods

Boron-doped silicon nanoparticles

Three-dimensional (3D) porous particles composed of curved 2D nanolayers

Iron-phosphate nanowires from genetically modified virus

Silicon nanopowder in a conductive polymer b

...on nanotubes (or silicon ...eres) confined within rigid carbon outer shells

Silicon/conducting polymer hydrogel

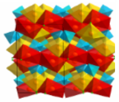
Metal hydride

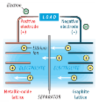
Lithium vanadium oxideLithium vanadium o

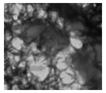
Lithium/titanium/oxide

Lithium manganese dioxide on porous tin

Silicon oxide-coated double-walled silicon nanotubes

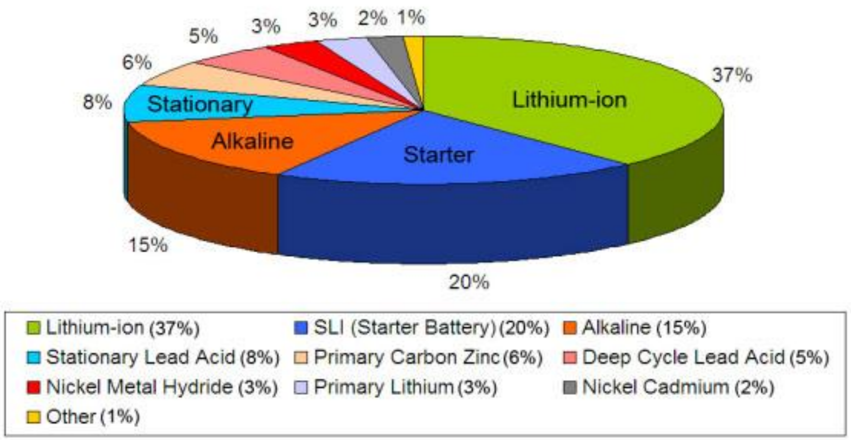


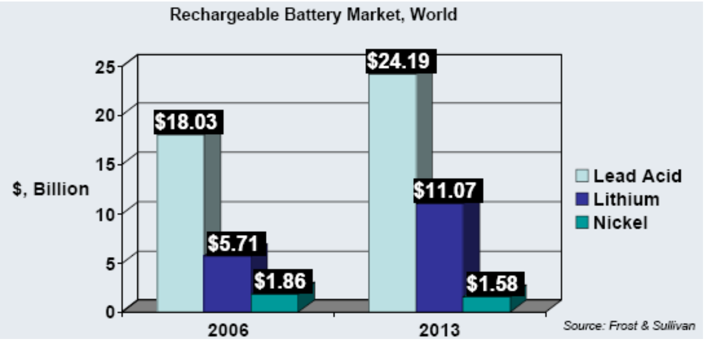


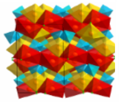


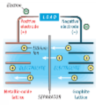
Outline

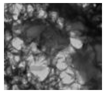
- Energy storage: the challenge of the century
- Markets
- Battery applications
- Battery history
- Electrochemistry
- Common battery types
- Lithium batteries
- New directions
- From concept to production
- Conclusion











Technological Challenge of the Century

Wh

Portable

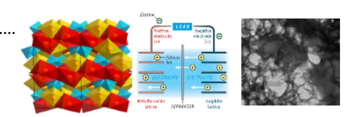
kWh

MWh

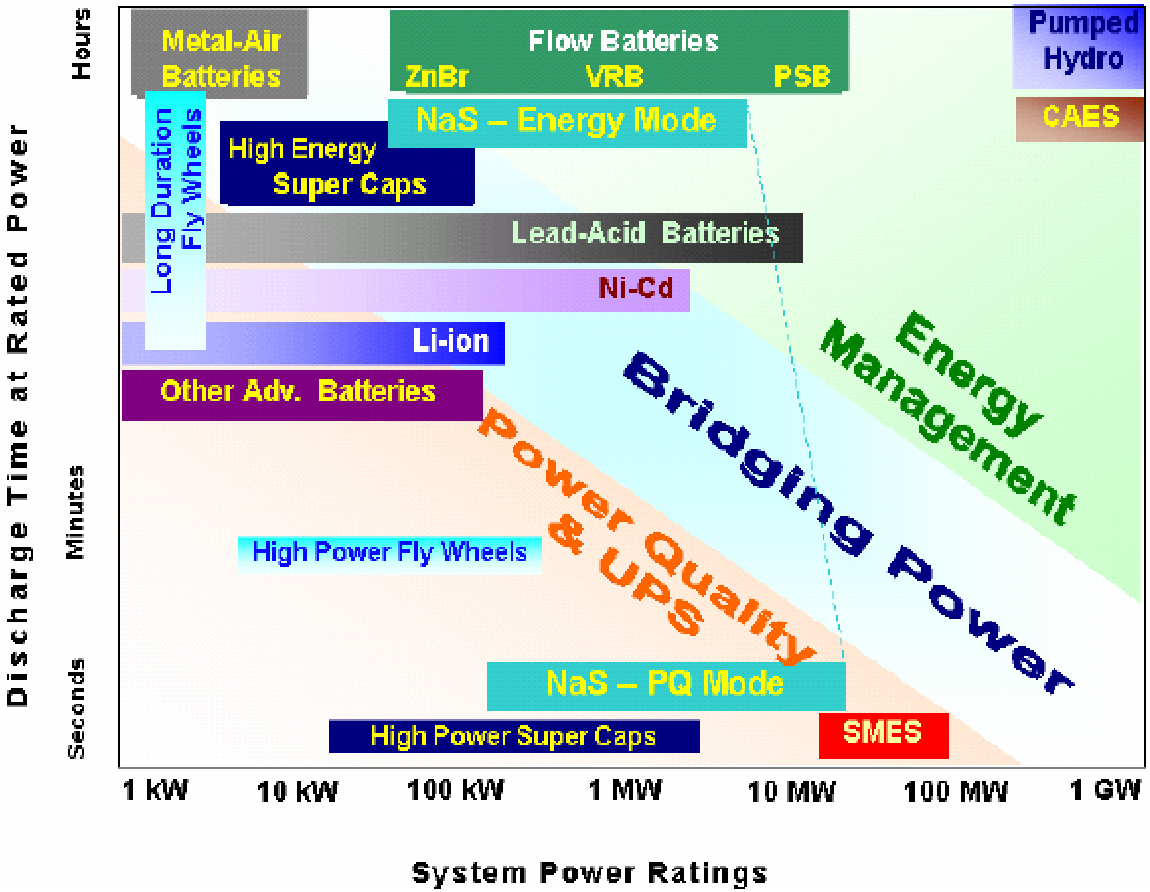
Automotive

Stationary

2 MW Li-ion storage



Energy Storage Technologies



Redox flow batteries

Sodium based batteries

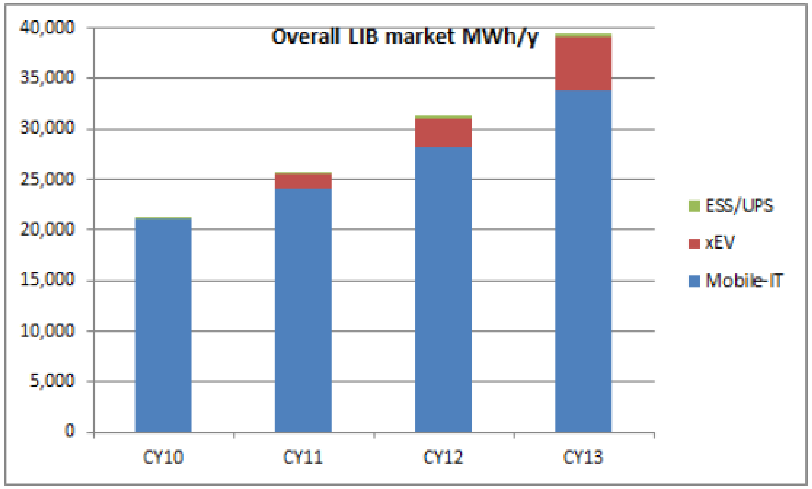
Lithium-ion batteries

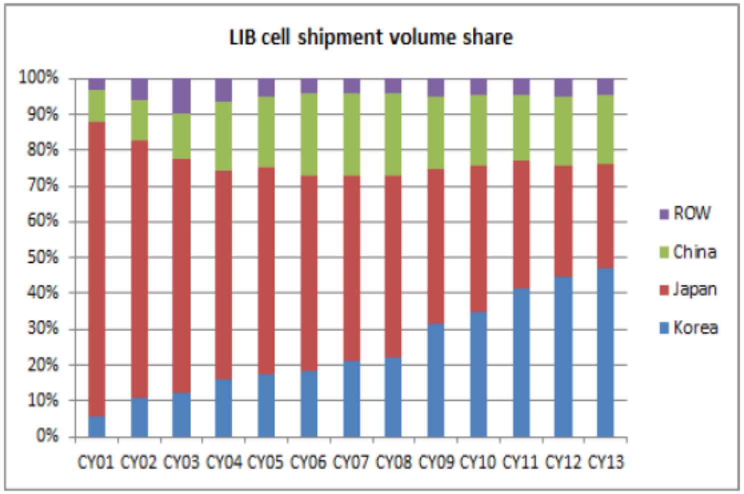
Nickel-based batteries

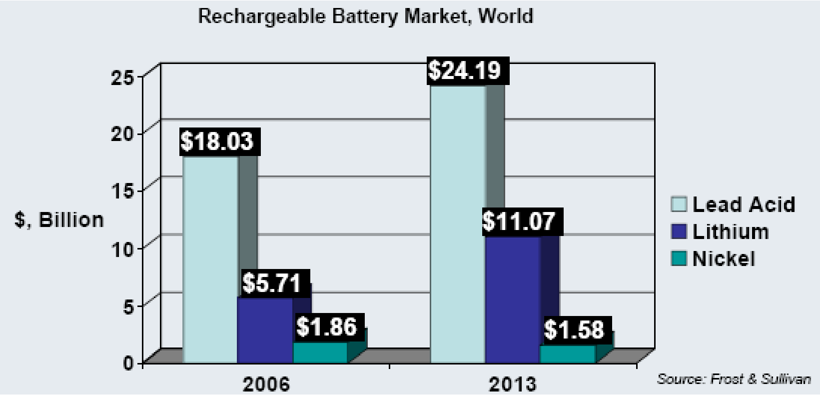
Advanced lead-acid

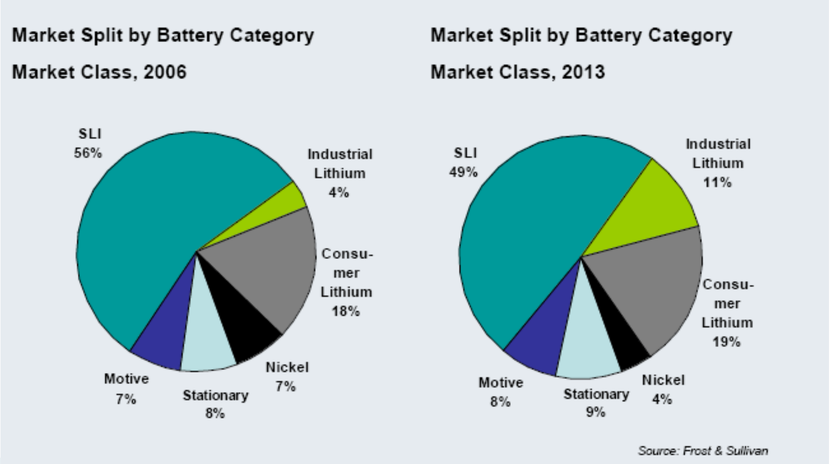
batteries

Markets

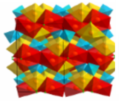


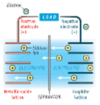


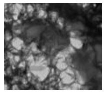




Mobile Applications Dominate Li Ion Applications Today







Automotive Applications

At what point do batteries become truly capable of replacing thermal engines?

	Gasoline	Li Ion
Specific Energy (kWh/kg)	2300	150

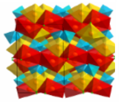
Cost of batteries
$650/kWh → $300 → $125

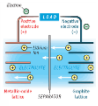
- Hybrid Electric Vehicle (HEV):
  - Small battery
  - Low electric power
  - Local energy generation

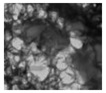
- PlugIn-Hybrid Electric Vehicle (PHEV):
  - Medium battery
  - External energy injection possible

- Full Electric Vehicle (FEV):
  - Big battery
  - Only external energy injection (or local energy generation via hydrogen fuel cell)

1 Million electrical vehicles by 2015





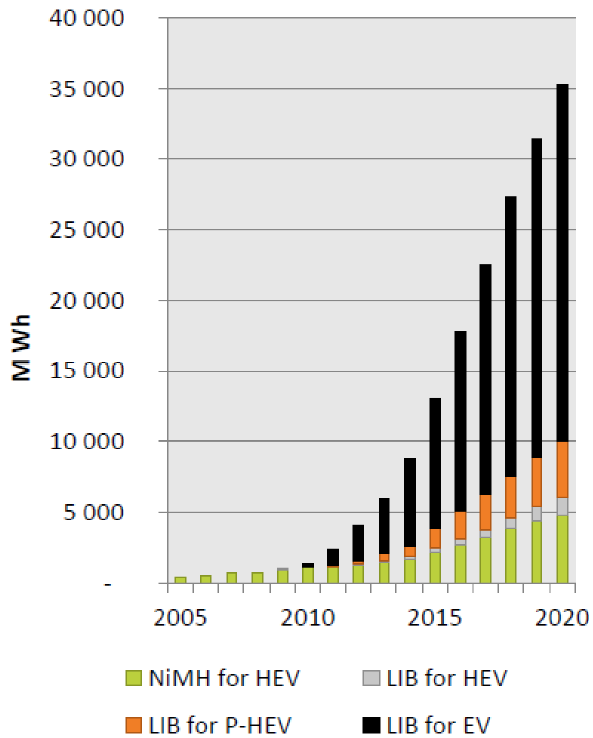


Electrical Vehicles

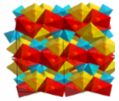
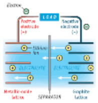
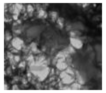
Examples:

Manufacturer/Model	Range/miles	Battery type
Bolloré Bluecar	160	Li Polymer
BYD e6	120	75 kWh ($LiFePO_4$)
Chevrolet Spark EV	82	21 kWh nano ($LiFePO_4$)
Ford Focus Electric	76	23 kWh lithium ion
Honda Fit,	100	Lithium ion
Nissan Leaf	200	24 kWh lithium ion
Tesla Model S	265	60-85 kWh lithium ion

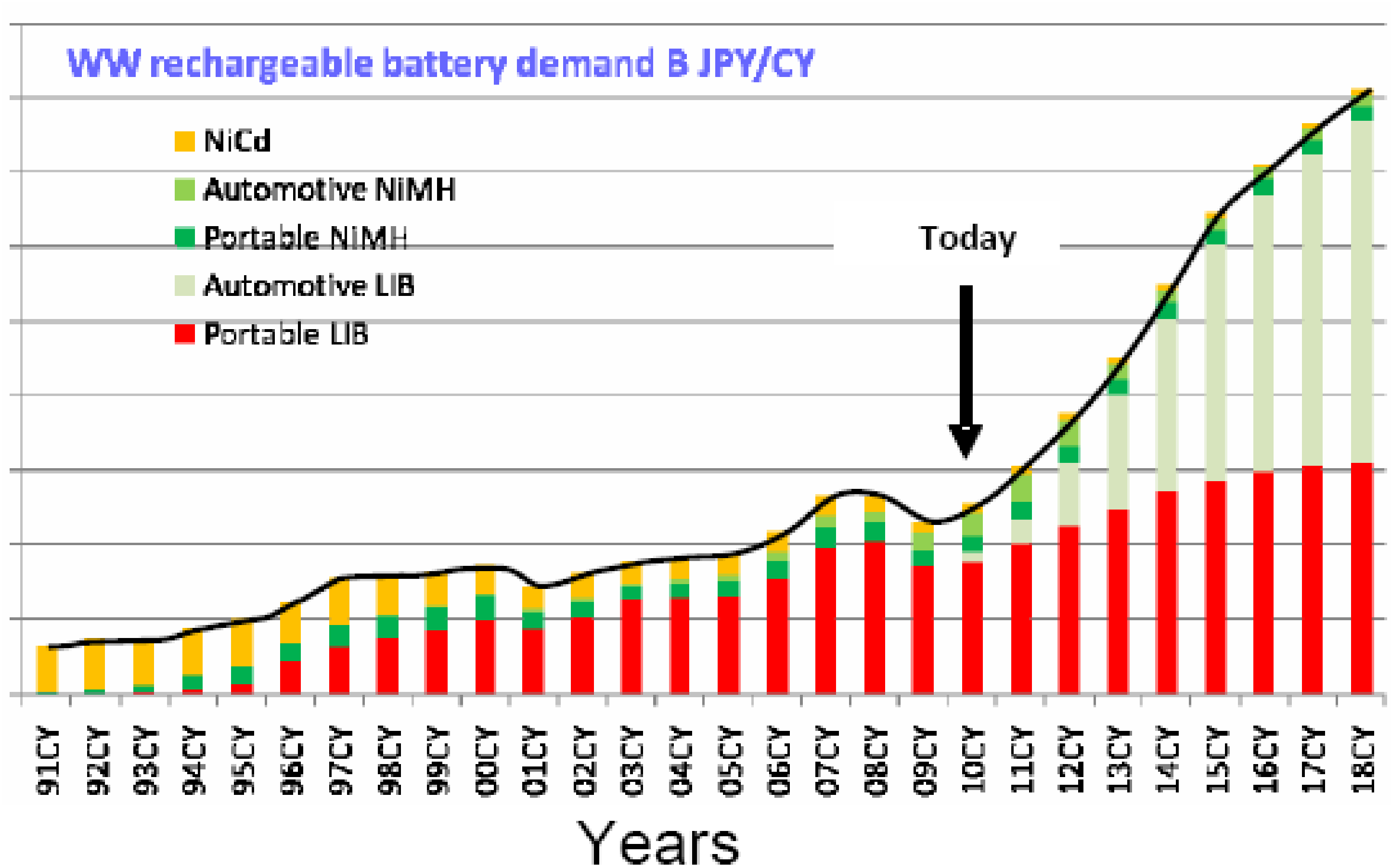
EV, HEV & P-HEV Battery needs (M Wh) 2005 – 2020



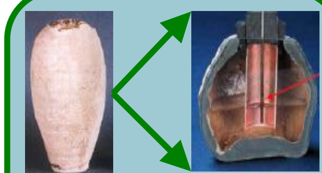
Electrical vehicle market is dominated by Li ion batteries!

Expanding Battery Market

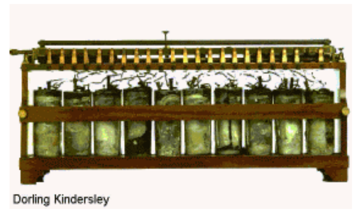


History of Batteries



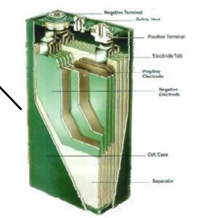
The Batter of Baghdad
ca. 200 BC

Voltaic Pile
1800



Gaston Plante
Lead Acid
Battery 1859

Li Ion Battery
1991



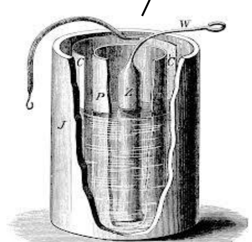
NiMH Battery
1989

200 BC

1800-1850

1850-1900

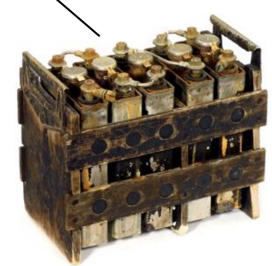
1901-present



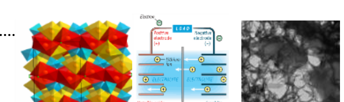
Daniel Cell
1836

Lechlanche Cell
1866

NiCd Battery
1899



NiFe Battery
(Edison) 1905

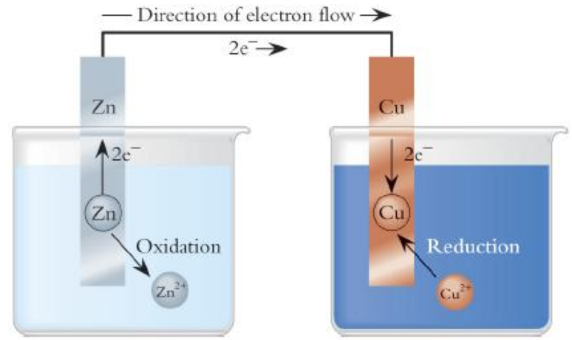


Electrochemistry

Standard Reduction Potentials at 25°C

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

Redox potentials determine the viability of a redox couple as energy producing galvanic cell

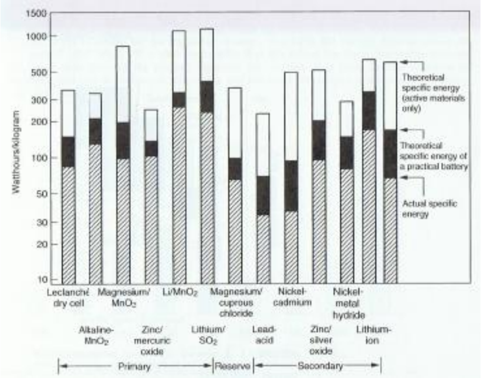


Walther Nernst
Nobel Prize in chemistry 1920

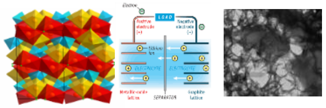
$$E = E^\circ - \frac{0.059}{n}\log\frac{[C_{products}]}{[C_{reactants}]}$$

$$E^\circ_{cell} = E^\circ_{red}(\text{cathode}) - E^\circ_{red}(\text{anode})$$

What are reaction mechanisms?



$$\Delta G = -nFE$$

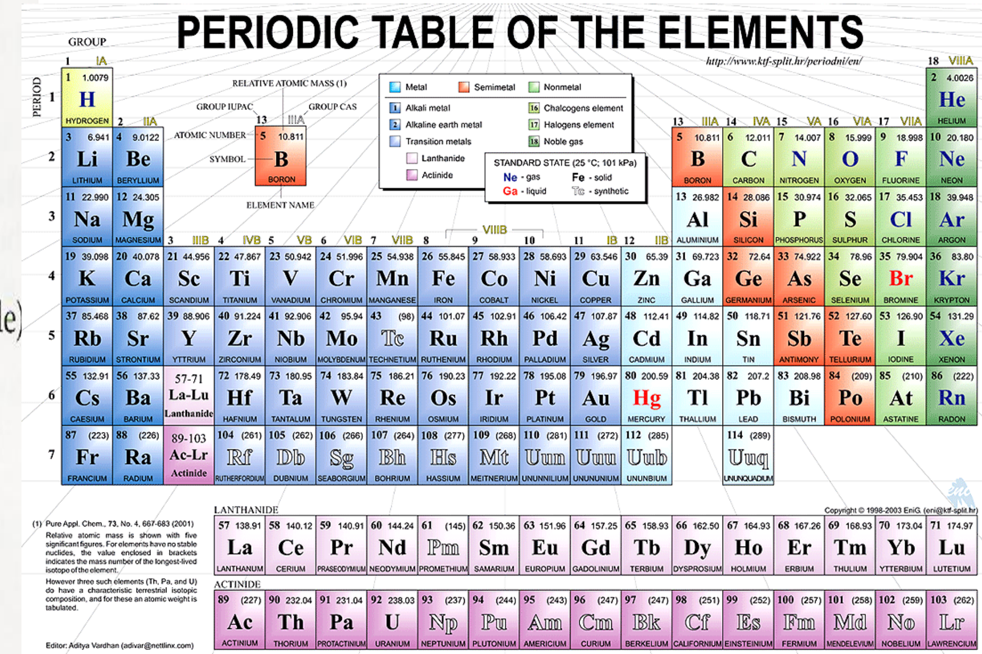


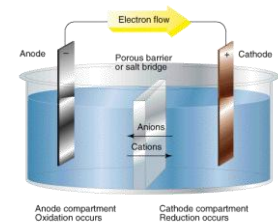
Search for Electrode Materials

Tendency to be reduced (gain electrons)

- Gold
- Mercury
- Silver
- Copper
- Lead
- Nickel
- Cadmium
- Iron
- Zinc
- Aluminum
- Magnesium
- Sodium
- Potassium
- *Lithium*

Tendency to oxidize (lose electrons)

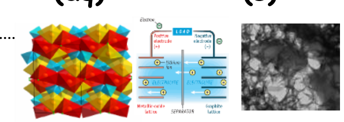




$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

$Cu^{+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

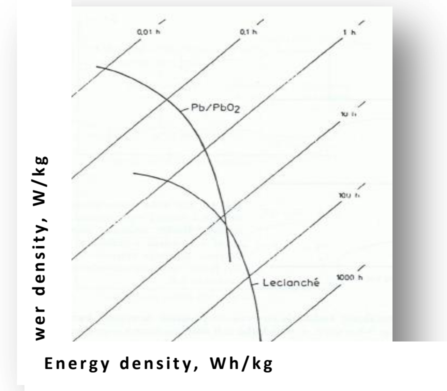
$Zn_{(s)} + 2Cu^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Cu_{(s)}$



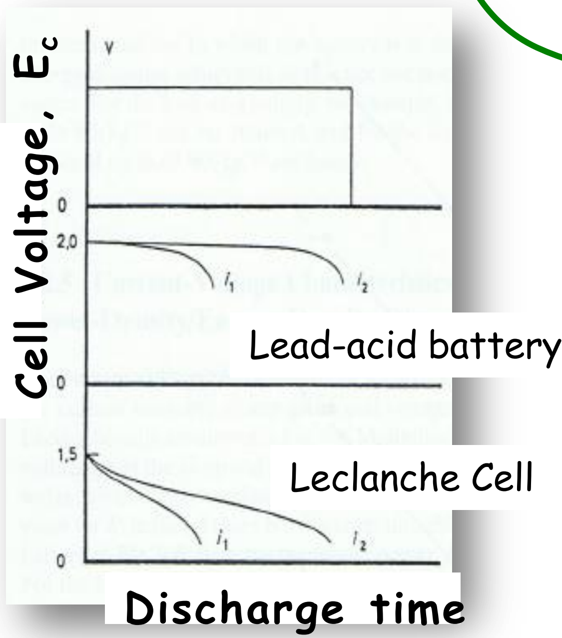
Battery Performance

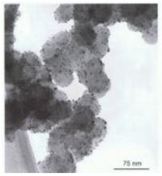
- Storage capacity or *charge density*, C/L or C/kg
- *Energy density*, J/kg or Wh/kg
- *Power density*, W/kg
- *Voltage efficiency*, E/E°
- Lifetime: *shelf-life* or *charge/discharge cycles*

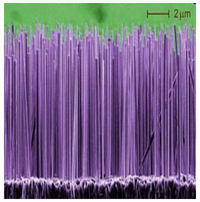
Performance attributes



Batteries

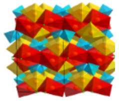


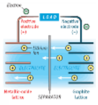


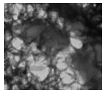


Performance Limitations

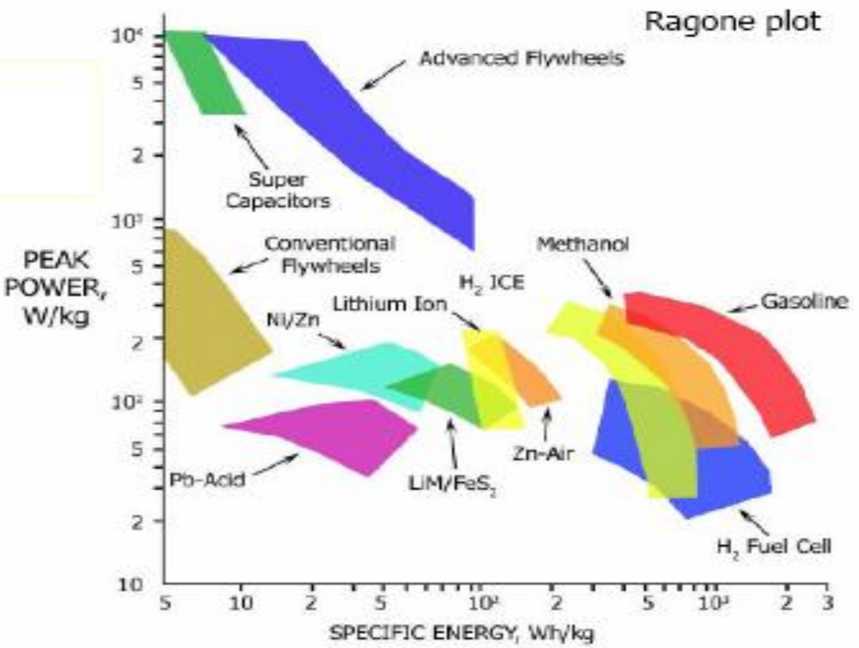
- Effective surface area of electrodes
- Catalytic activity of electrodes
- Diffusion of electroactive species through electrolyte
- Side reactions and reversible processes

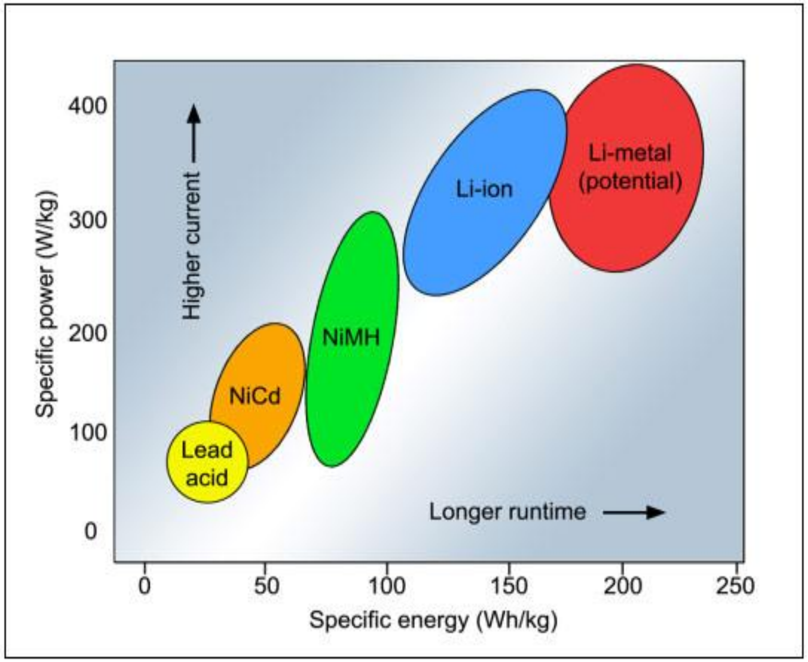






Common Rechargeable Battery Systems

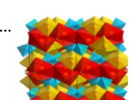
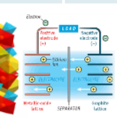
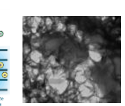




SYSTEM	VOLTAGE	ANODE	CATHODE	ELECTROLYTE
Lead acid	2.0	Lead	PBO_2	Aq. H_2SO_4
Nickel-cadmium	1.2	Cadmium	NiOOH	Aq. KOH
Nickel-metal hydride	1.2	MH	NiOOH	Aq. KOH
Lithium Ion	4.0	Li (C)	$LiCoO_2$	$LiPF_6$

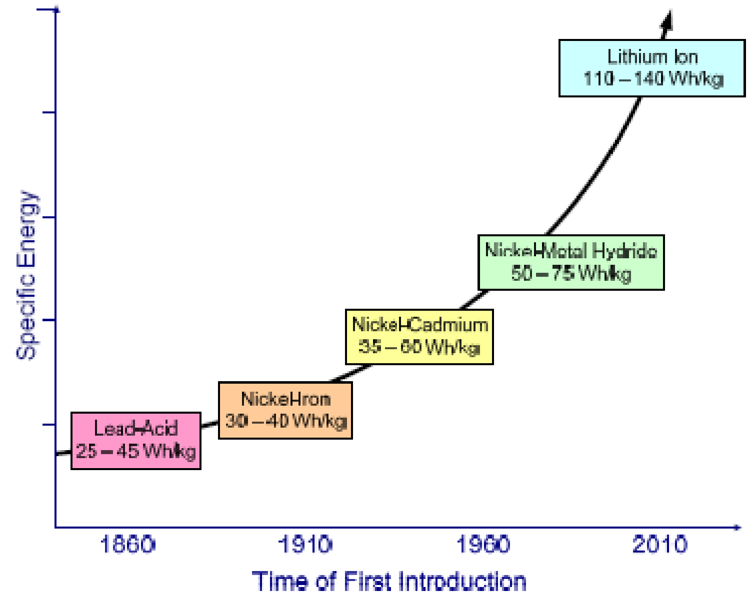
Performance Comparison

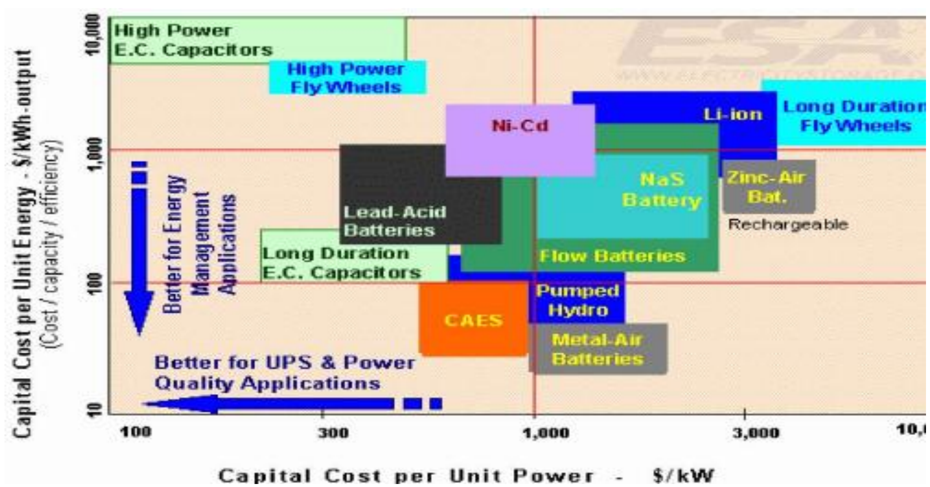
PARAMETER	NiCd	NiMH	SLA	Li Ion	Li Ion Polymer
Energy Density (Wh/kg)	40 - 60	60 - 80	30	80 - 160	100 - 160
Cycle life (end of life @ 80% capacity)	800 - 1500	500	200 - 500	300 - 1000	300 - 1000
Optimum charge time (h)	1.5	2 - 4	8 - 16	2 - 4	3 -5
Overcharge tolerance	Moderate	Low	High	Very high	Very low
Deep discharge tolerance	Moderate	Moderate	Low	Very low	Very low
Self-discharge/month (@ 25°C)	20%	30%	5%	3-5%	3-5%
Cell voltage (nominal)	1.2 V	1.2 V	2 V	3.7 V	3.7 V
Load current (continuous)	> 2 C	0.5 - 1 C	0.2 C	0.8 - 2 C	0.8 - 2C
Operating Temperature	-20 to +60°C	0 to +60°C	-20 to +60°C	-40 to +60°C	-20 to +60°C
Maintenance requirement	30 dayts	30 days	3 -4 months	6 -12 months	6 - 12 months
Environmental impact	Recycle Cd	Cd-free	Recycle Pb	No heavy metals	No heavy metals
Typical cost per Wh (US $)	0.48	0.79	0.45	1.04	1.84
In commercial use since	1950	1990	1970	1991	1999

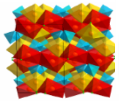
Energy Storage Methods Comparison

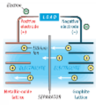
	ENERGY DENSITY (Wh/kg)	ENERGY DENSITY (MJ/kg)
Lead-acid	35	0.13
NiCd	45	0.16
NaS	80	0.28
NiMH	90	0.28
Li Ion	150	0.54
Gasoline	12000	43

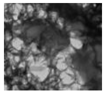




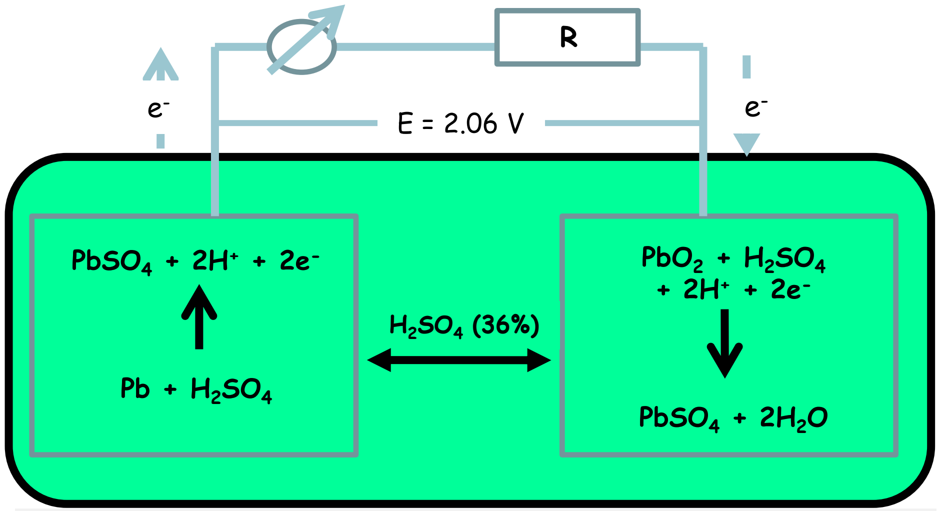
- For large scale storage underground thermal, pumped hydro and compressed air energy storage systems are preferable.
- Superconductors can store energy with negligible losses.
- Fuel cells are a viable alternative to petrol engines due to their high efficiency.





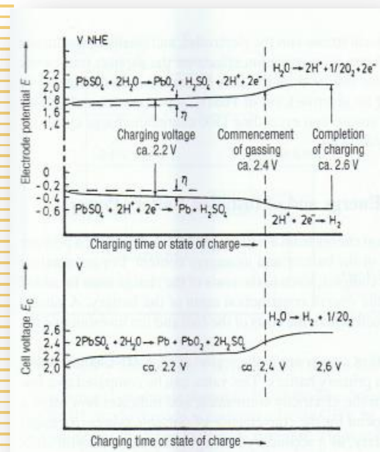


Lead Acid Batteries



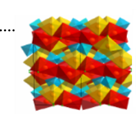
Sulfation of electrodes is a problem

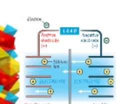
$$Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O$$

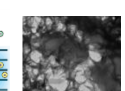


	Fully Charged	Completely discharged
SoC	100%	0%
DoD	0%	100%
Cel	~ 6 M	~ 2 M
ρ	~ 1.3	~ 1.1
OCV	12.7 V	11.9 V

- •Oldest type of rechargeable battery
- •Low energy and specific power (25-30 Wh/kg; 60-120 Wh/L)
- •Inferior cycle life and temperature performance
- •Low cost, industrial batteries
- •Useful battery for ICE vehicles

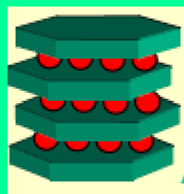






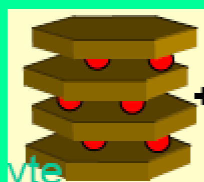
Nickel-Based Batteries

Insertion Positive Electrode



$Ni(OH)_2$

$+ OH^-$



NiOOH

The host structure is maintained

Nickel-Cadmium Cells (E=1.3V)

$Cd(OH)_2 + 2e^- \dashrightarrow Cd + 2OH^-$

Invented by W. Junger, 1899
Commercialized in 1947

45 – 65 Wh/kg

Nickel-Zinc Cells (E=1.7V)

$Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^-$

70 Wh/kg

Nickel-Metal Hydride Cells (E=1.3V)

$M + xH_2O + xe^- \rightarrow MH_x + xOH^-$

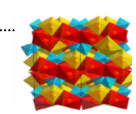
Invented ca. 1975, commercialized 1988

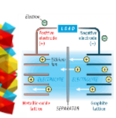
60 – 80 Wh/kg

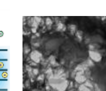
Nickel-Hydrogen

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

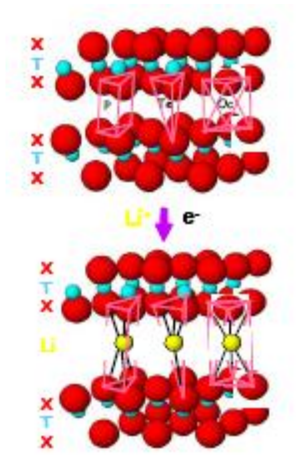
80 Wh/kg



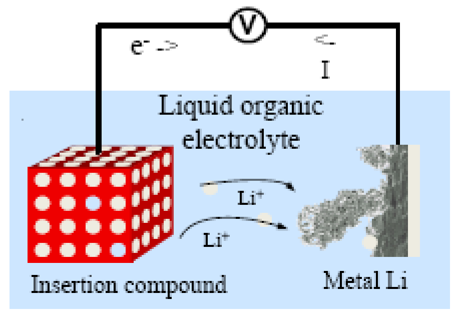




Li Metal Batteries



First intercalation compounds: TiS_2, MoS_2: 1970-1973



Metal Li: 1975 -

Formation of Li dendrites on charge

Short circuit through separator

Short circuit through separator

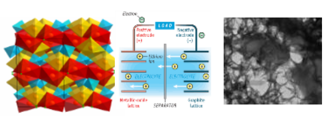
1980

1989

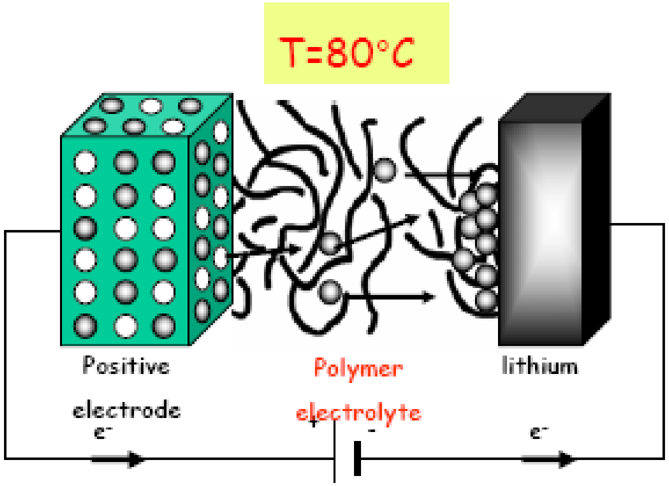
Commercialization of Li/MoS_2 Batteries by Moli Energy

Incidents on Cellular phones

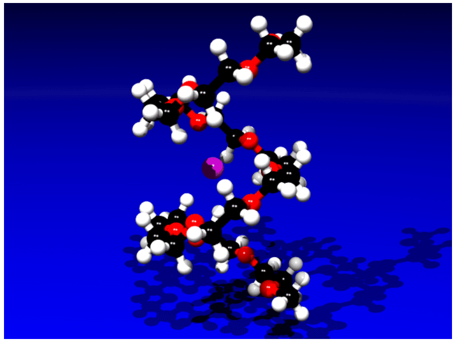
End of metal Li rechargeable batteries

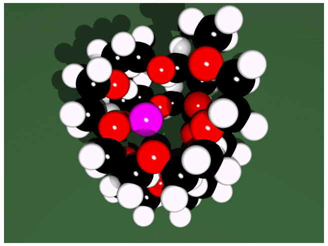


Li Polymer

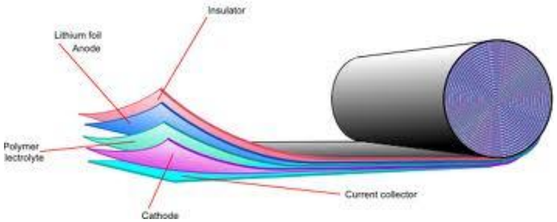


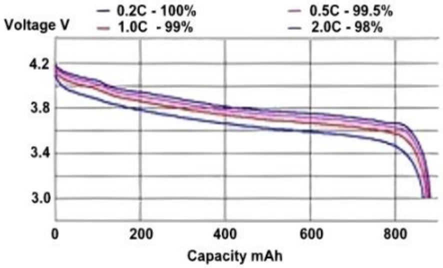
- Thin, polymer membrane – no free electrolyte
- Very thin - 1mm; light weight and flexible
- More resistant to overcharge
- High internal resistance
- Better performance at higher temperatures
- Gelled electrolyte for better conductivity
- Hybrid lithium polymer or lithium ion polymer

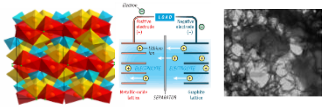




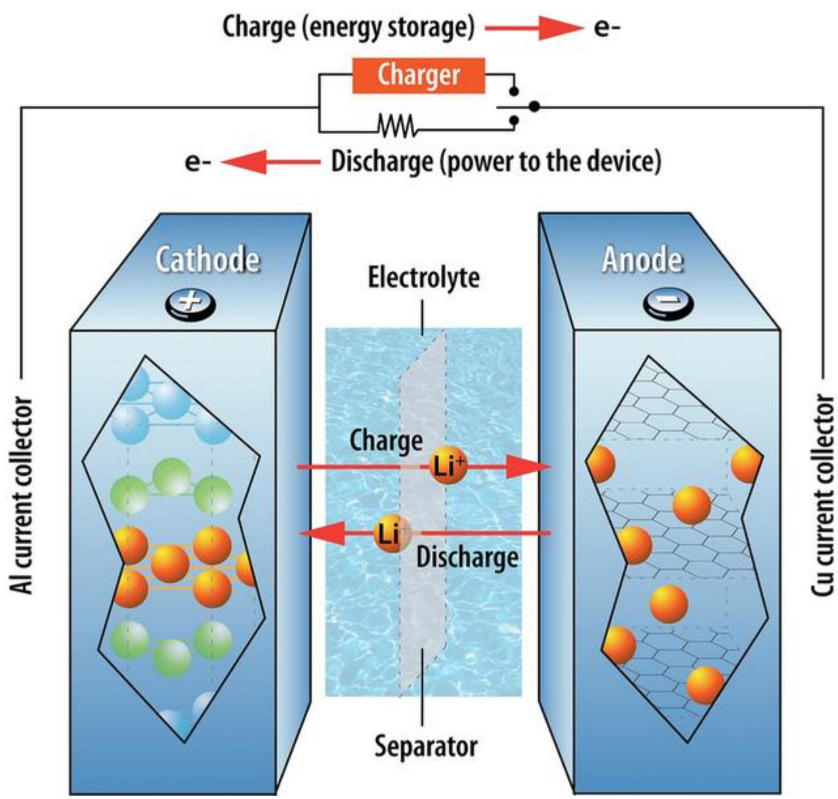
A helix of crystalline PEO , poly (ethylene oxide), with a lithium cation inside







Rechargeable Li Ion Batteries



$$\text{Theoretical Specific Capacity} = \frac{26.8Ah}{6.9\times10^{-3}kg} = 3884\frac{Ah}{kg}$$

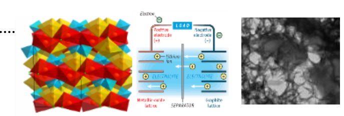
1980 → **1990**

Concept — **Commercialization**

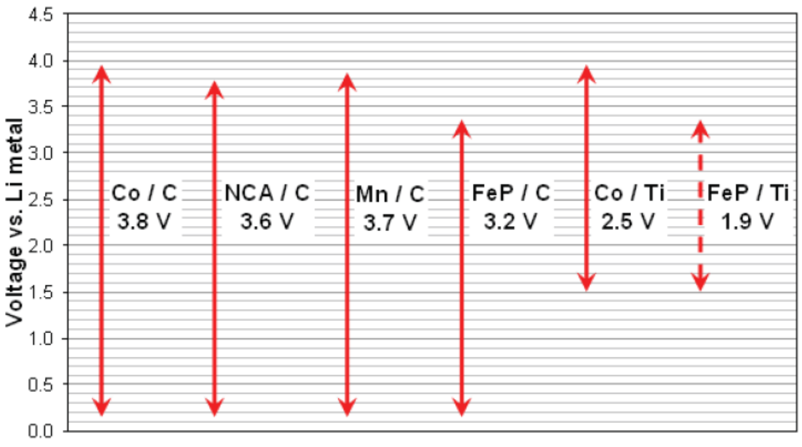
$xLi^{+} + MO_y + xe^{-} \rightarrow LixMO_y$; ca. 1 V vs. NHE; 180 Ah/kg

$Li \rightarrow Li^{+} + e^{-}$; - 3.045 V vs. NHE; 3862 Ah/kg

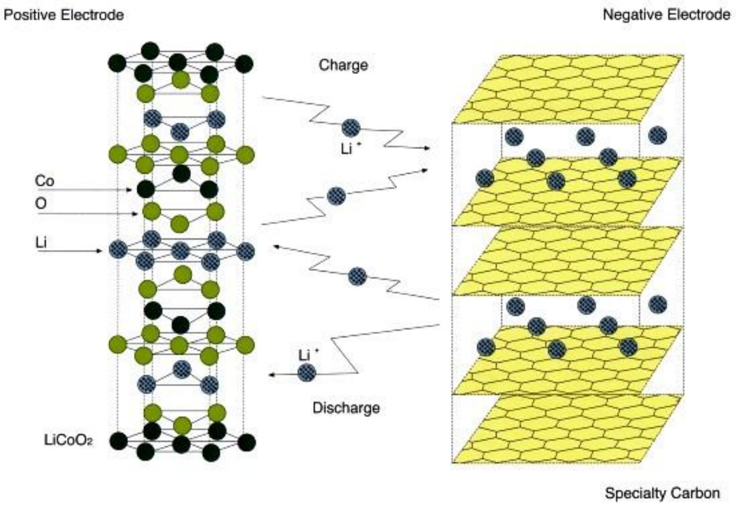
$xLi + MO_y \rightarrow LiMO_y$; ca. 3.5 V (ocv 4.1 V); 750 Wh/kg

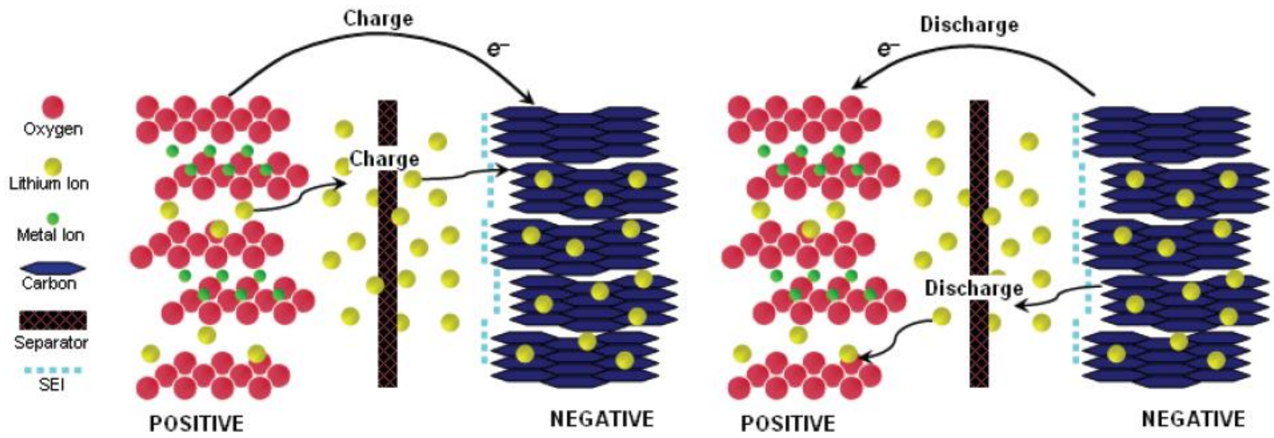


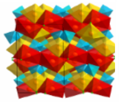
Rechargeable Li Ion Batteries

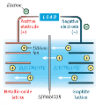


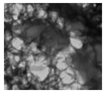
Voltage indicates approximate mid-point value.
Co = $LiCoO_2$; Mn = $LiMn_2O_4$; FeP = $LiFePO_4$; C = Graphite; Ti = lithium titanate





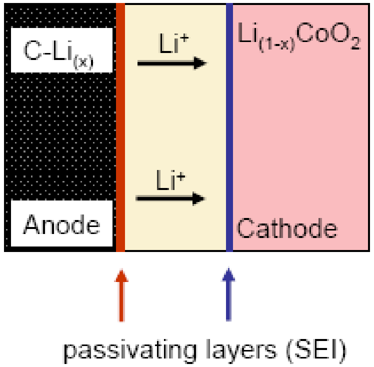


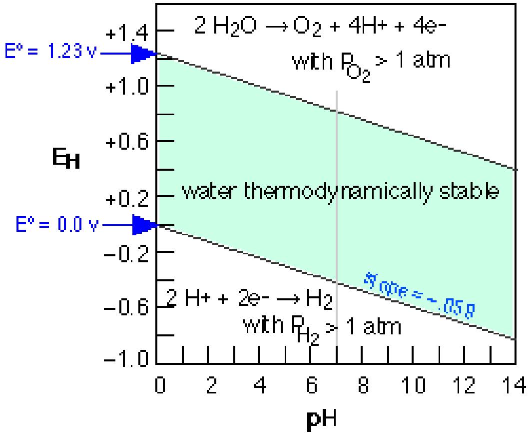




Electrolyte

Nonflammable liquid with good Li-ion conductivity
Large expanded electrochemical stability window (5 V)
Low cost, non-toxic
Good low temperature performance

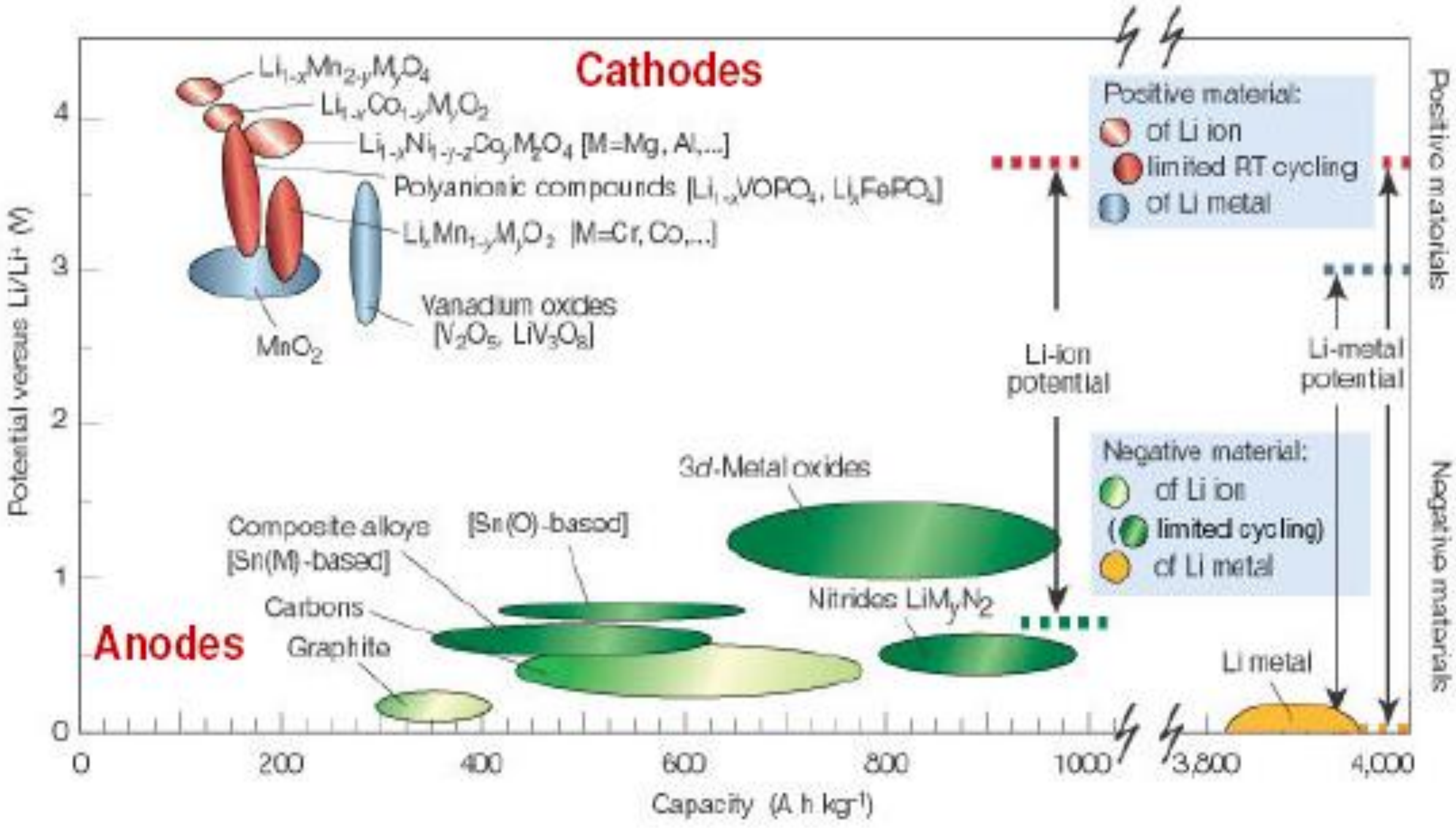




SEI Layer

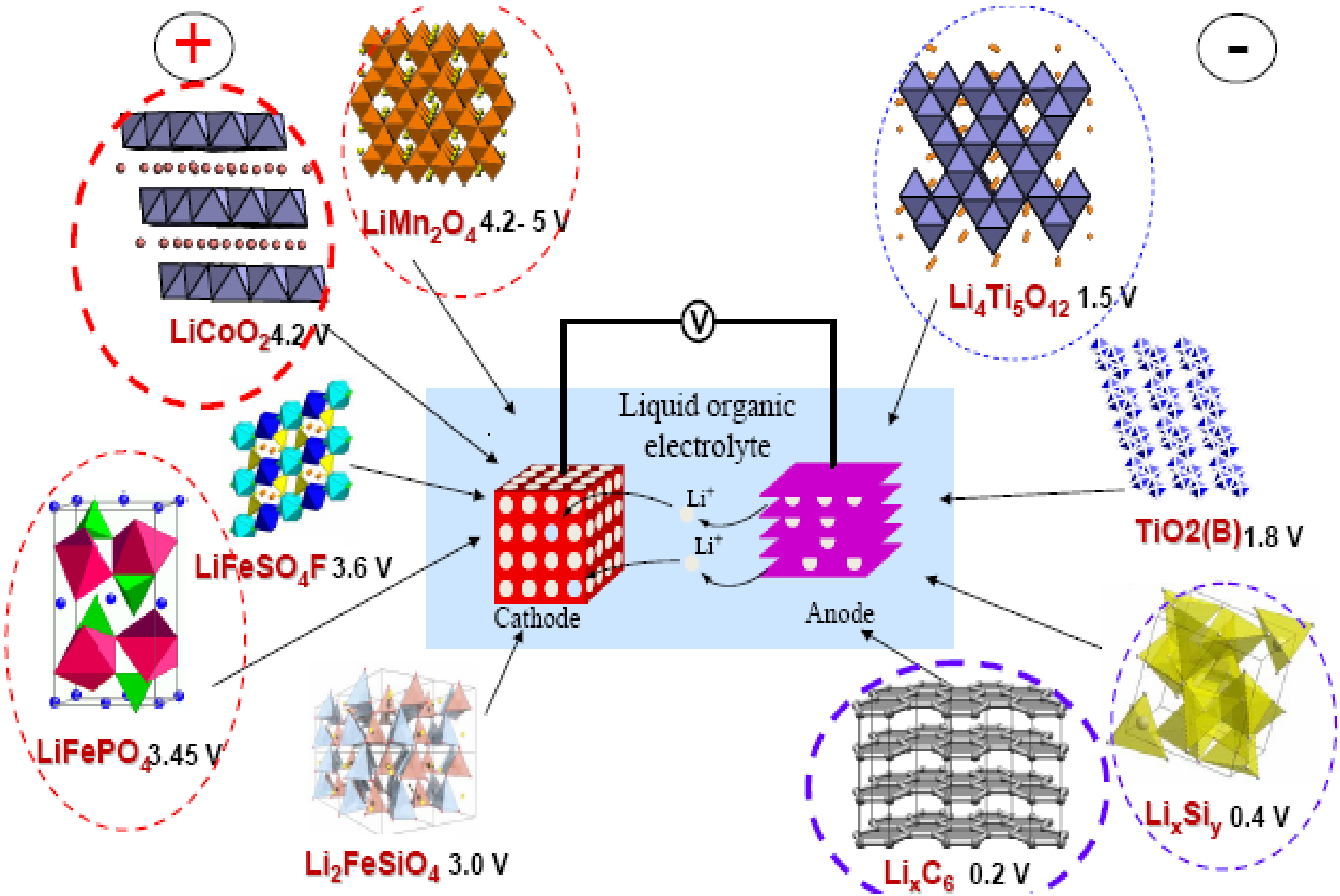
- Graphite, soft carbon, and hard carbon are good electrical conductors
- The SEI (solid-electrolyte interphase) layer on the carbon surface is created during formation – it is electrically insulating but conducts Li+
- The SEI layer is essential to the longevity of the battery because it prevents further reaction with the electrolyte
- Its formation contributes to irreversible capacity - it consumes Li+
- Formation of the SEI layer occurs at about 0.7 V vs. Li/Li+

Search for New Materials



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

Endless Possibilities



Cathode Trends

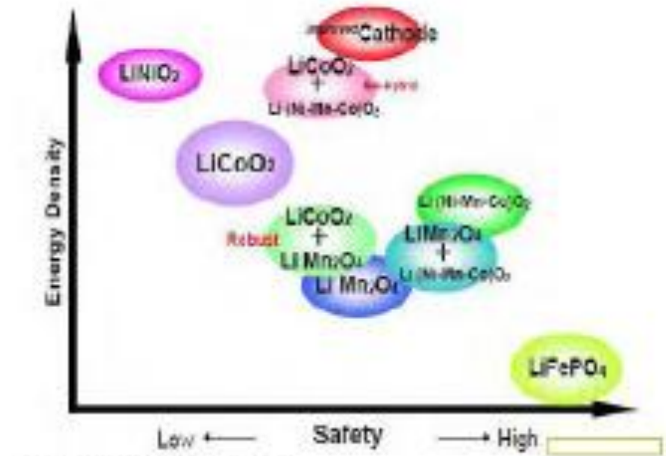
$LiCo_2$ (LCO)

$LiMn_2O_4$ (LMO)

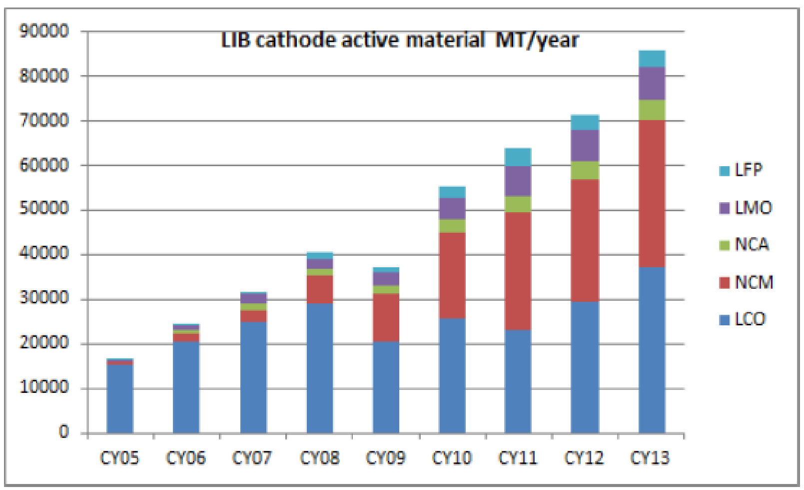
$LiMPO_4$ (LFP)

$Li[Ni_xMn_yCo_z]O_2$-NMC

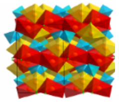
$Li[Ni_xCo_yAl_z]O_2$-NCA

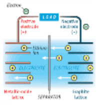


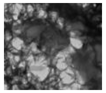
Source: SANYO, March 2011



Manganese spinel (LMO), Lithium iron phosphate, Lithium nickel manganese cobalt (NMC), Lithium Managnese Oxide/NMC, Lithium iron fluorophosphate, 5% Vanadium-doped lithium iron phosphate olivine, Lithium purpurin, Lithium manganese dioxide on porous tin, Air

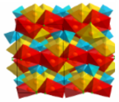


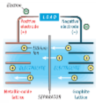


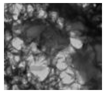


Anodes in Li Ion Batteries

- Lithium-titanate battery (LT), Lithium vanadium oxide, Cobalt-oxide nanowires from genetically modified virus, Three-dimensional (3D) porous particles composed of curved 2D nanolayers, Iron-phosphate nanowires from genetically modified virus, Silicon/titanium dioxide composite nanowires from genetically modified tobacco virus, Silicon whisker on carbon nanofiber composite, Silicon nanowires on stainless steel, Silicon oxide-coated double-walled silicon nanotubes, Metal hydrides, Silicon nanotubes (or silicon nanospheres) confined within rigid carbon outer shells, Silicon nanopowder in a conductive polymer binder, Silicon oxycarbide-coated carbon nanotubes, Electro-plated tin, Solid-state plated copper antimonide nanowire, Boron-doped silicon nanoparticles, Hard carbon, Silicon/conducting polymer hydrogel, Nanomatrix structure, Carbon-encased silicon nanoparticles, Lithium/titanium/oxide, Fe_3O_4-plated copper nanorods, Nanophosphate, Nickel/Tin on porous nickel,







Anode Trends

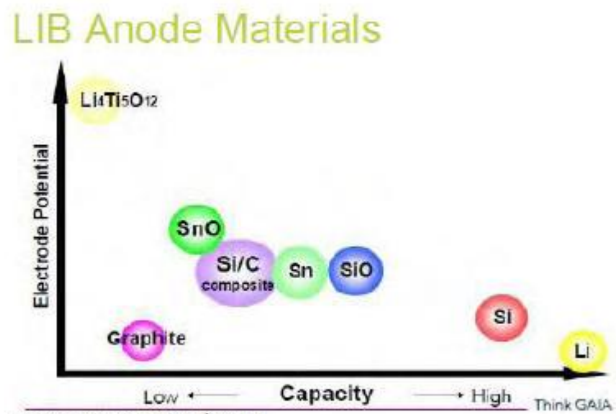
Specialization and optimization is the key for individual product applications

Current Materials

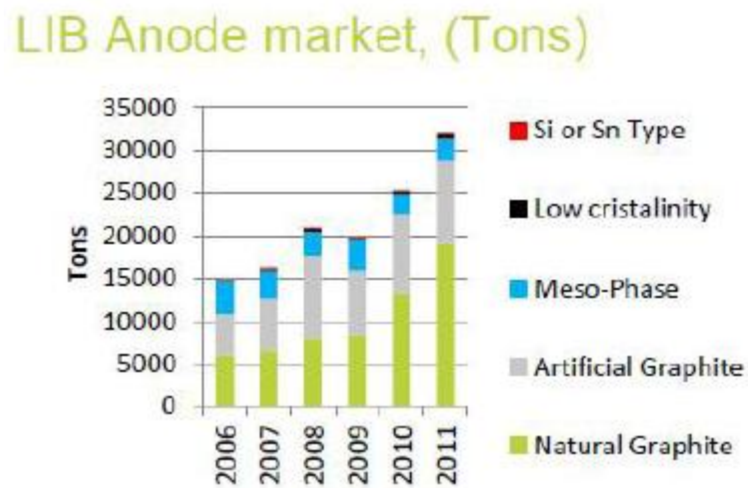
- Carbonaceous
  - Graphite
  - Hard Carbon
  - Soft Carbon
- Lithium Titanium Oxide (Li_4Ti5O1_2, or LTO)

Future Materials

- Silicon
- Nanomaterials
- Other

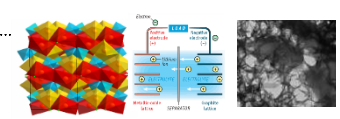


Source: Sanyo, March 2011




Source: Hitachi Chemical

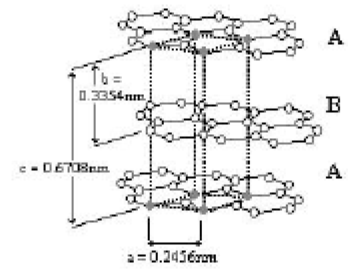
Courtesy of Polaris Battery Labs



Anode Trends

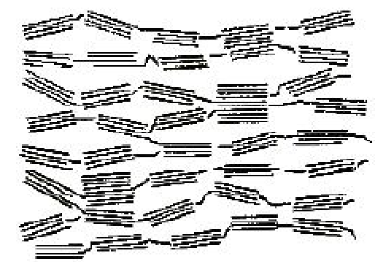
Graphite

- Stacked graphene layers, crystalline, anisotropic
- 0.335 nm spacing between planes
- About 10% volume expansion upon Li
- intercalation
- Theoretical maximum capacity 372 mAh/g (LiC6)



Soft Carbon

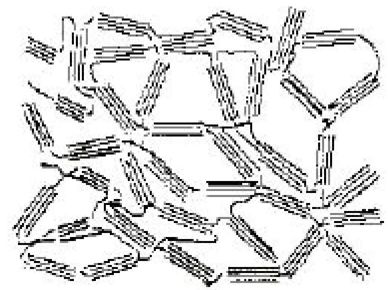
- The graphene layers are neatly stacked but there is less long-range order
- 0.375 nm spacing between planes (variable)



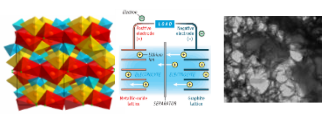
graphitizing

Hard Carbon

- The layers of carbon atoms are not neatly stacked, non-crystalline, macroscopically isotropic
- > 0.38 nm spacing between planes means almost no volume change upon intercalation and potentially better cycleability

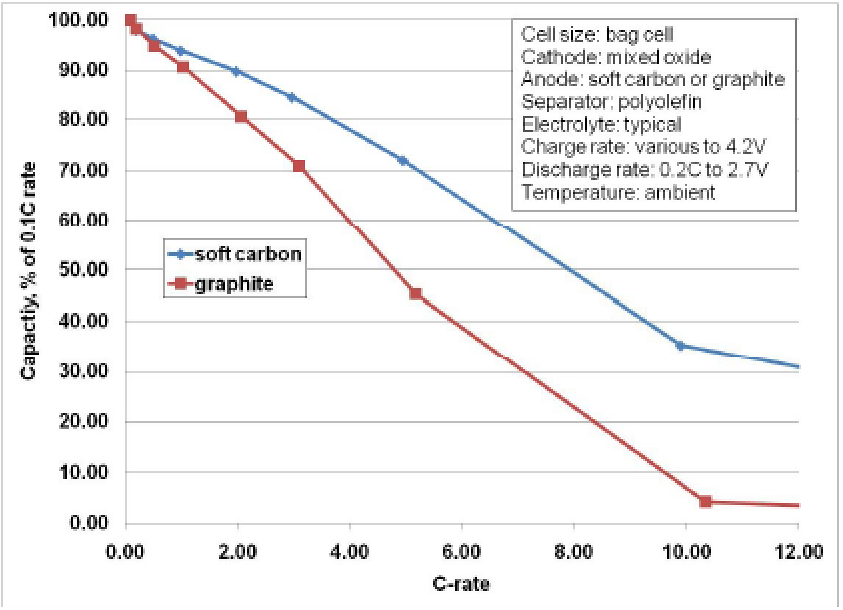


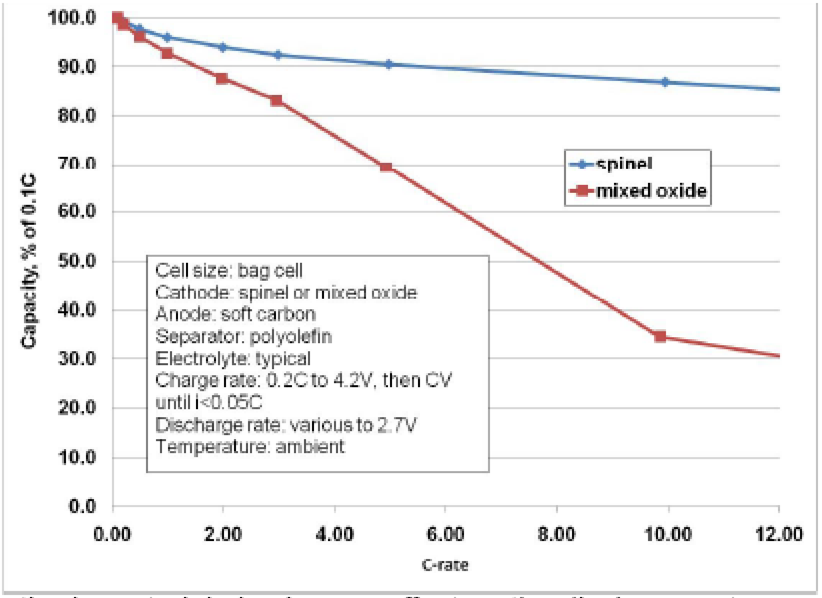
non-graphitizing

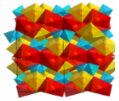


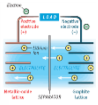
Anodes: Performance Comparison

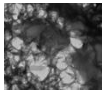
Material	Initial Capacity, mAh/g	Reversible Capacity, mAh/g	Irreversible Capacity, mAh/g	First cycle efficiency, %
Graphite	390	360	30	92
Hard Carbon	480	370	90	77
Soft Carbon	275	235	40	85







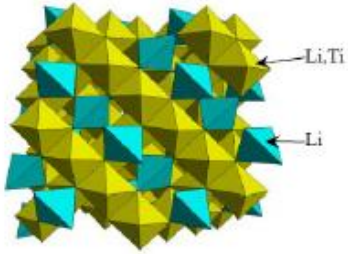


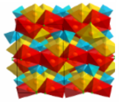


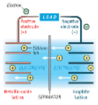
Promising Anode Materials: Titanate

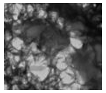
Lithium Titanate Anode $Li_4Ti_5O_{12}$ or LTO

- Theoretical capacity of 175 mAh/g
- Operating voltage is 1.5V vs. Li
- No SEI layer is formed - irreversible capacity is low
- Less than 0.2% volumetric change from fully discharged $Li_4Ti_5O_{12}$ to fully charged $Li_7Ti_5O_{12}$
- Safety, long cycle life
- Excellent power and low temperature performance



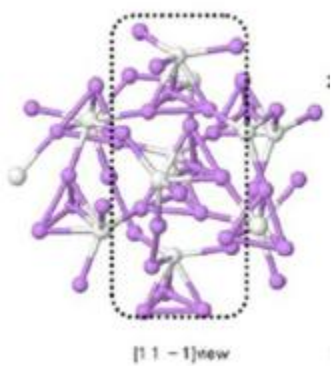


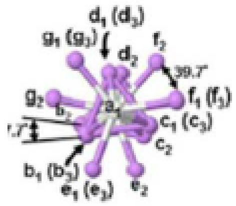




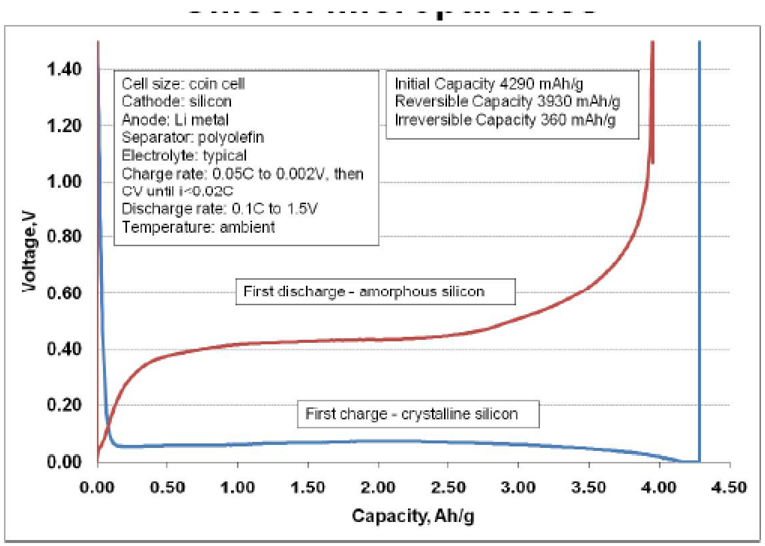
Promising Anode Materials: Silicon

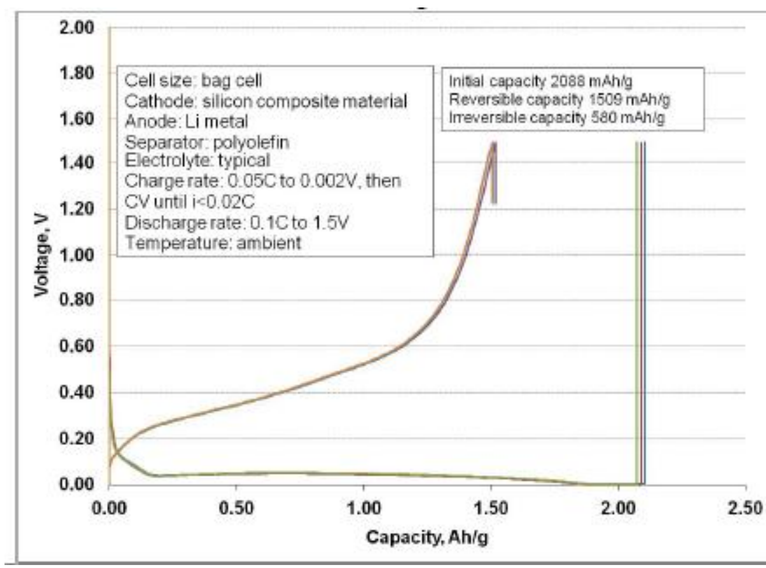
- Silicon has a theoretical capacity of 4200 mAh/g
- High capacity batteries or lighter, smaller batteries can be produced using Si anodes
- But it also has large volume changes associated with lithium intercalation (up to 300%)
- Graphite is only 10%
- The large volume change can mechanically disintegrate the material and result in particles that are not electrically connected, and battery failure occurs
- Nano sized particles mitigate the effects of the volume change and promote cycling stability

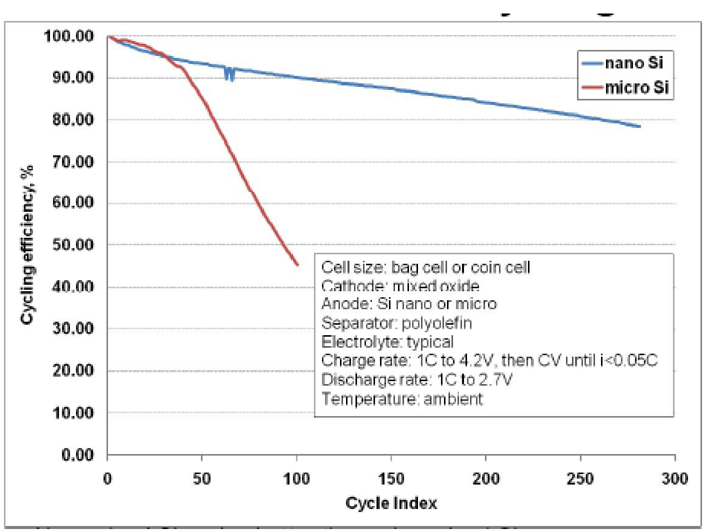




Promising Anode Materials: Silicon

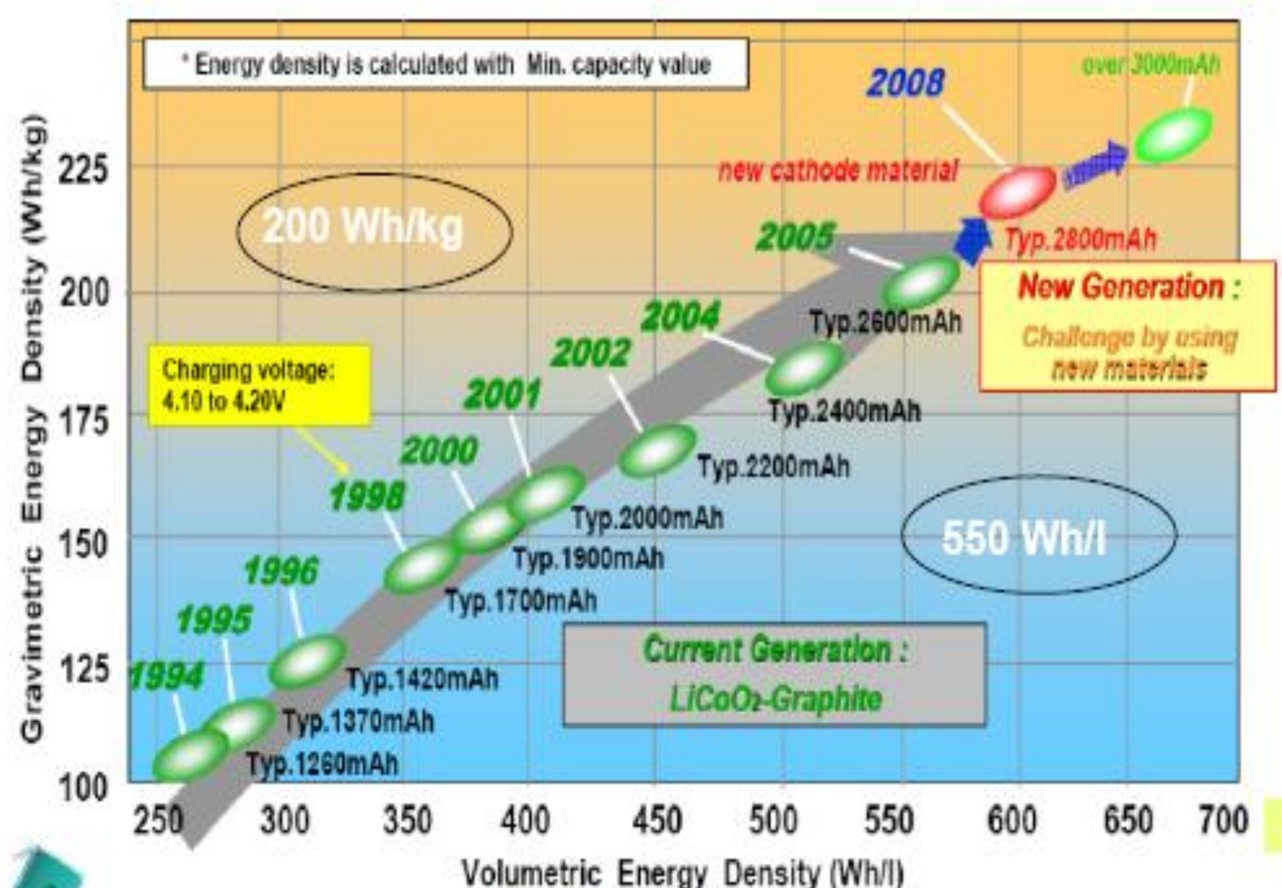






Anode Materials for Lithium Ion Batteries, Mary L. Patterson, Ph.D., Indiana University Battery Workshop, November 13, 2009

Li Ion Technology Evolution

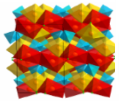


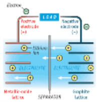
18650
5-10Wh

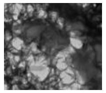
Batteries for EVs
30-100kWh

MWh Li-ion batteries

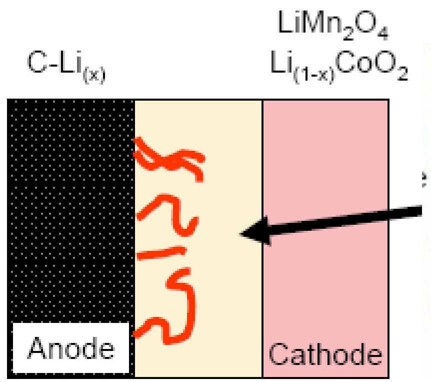
Per J.M. Tarascon, 2011

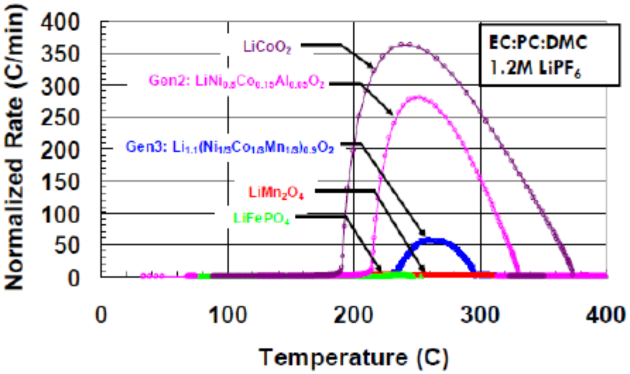






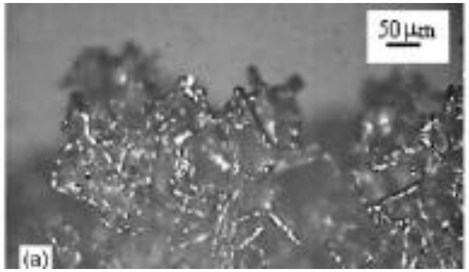
Li Ion Battery Safety

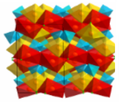


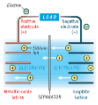


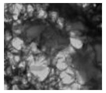
Due to Reaction Between Cathode & Electrolyte.

- Overcharging leads to dendrite growth
- Dendrites lead to shorts
- Shorts lead to heat, fire
- Most organic solvents are unstable









Lithium Availability

Two main sources:
- Saline deposits
- Minerals
- Sea water (0.2 ppm)


Global Reserves: 13 million tons

160 000 tons Li_2CO_3 annual production

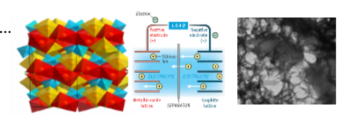
20-25% for battery sector (>32 000 tons)

Roughly 0.5 kg of Li_2CO_3 per 1kWh battery

10 % of the 60 million cars are pure EVs (25kWh)

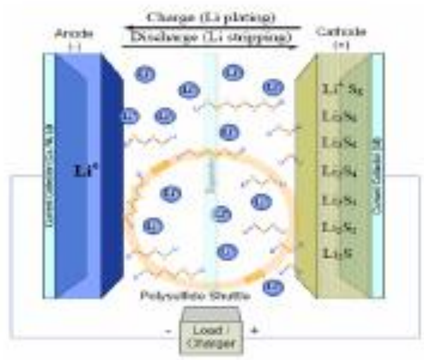
75 000 tons = ~ half of today's total production

Total current Li Production → ~ 10 Million EVs

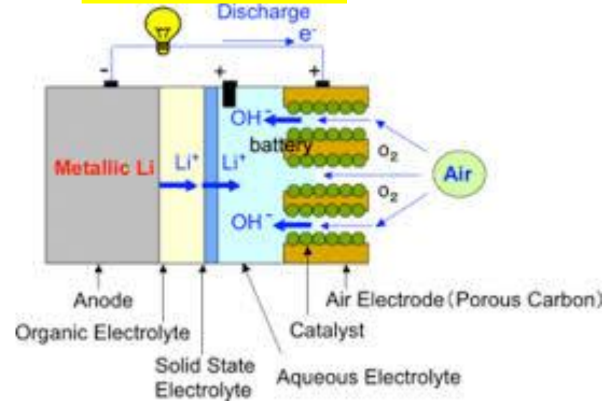


LiS and Li Air

Lithium Sulfur



Lithium Air



Natural, abundant, and cheap feedstock

$2Li^{+}+2e^{-}+S \rightarrow Li_2S$ ($E°= 2,27$ V)

Specific energy = 3802 Wh/kg

$2Li^{+}+ 2e^{-} + O_2 \rightarrow Li_2O_2$ ($E°= 3,14$ V)

Specific energy = 5259 Wh/kg

$0,5Li^{+} + 0,5e^{-} + Li_{0,5}CoO_2 \rightarrow LiCoO_2$

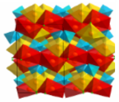
Specific energy = 550 Wh/kg

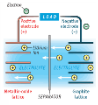
~ 380 Wh/kg

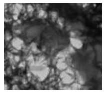
~ 180 Wh/kg

~ 500 Wh/kg

Per J.M. Tarascon, 2011

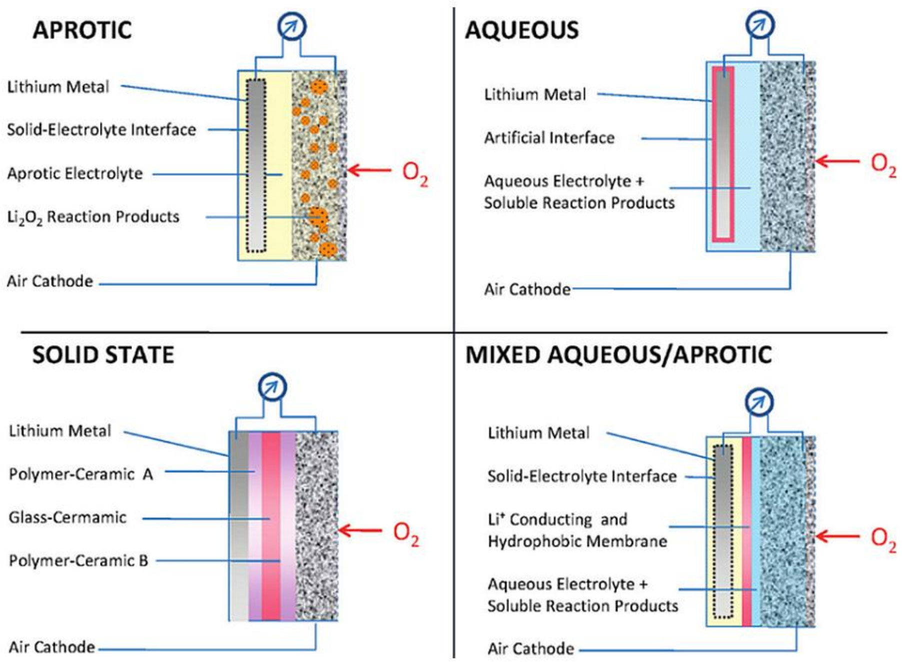


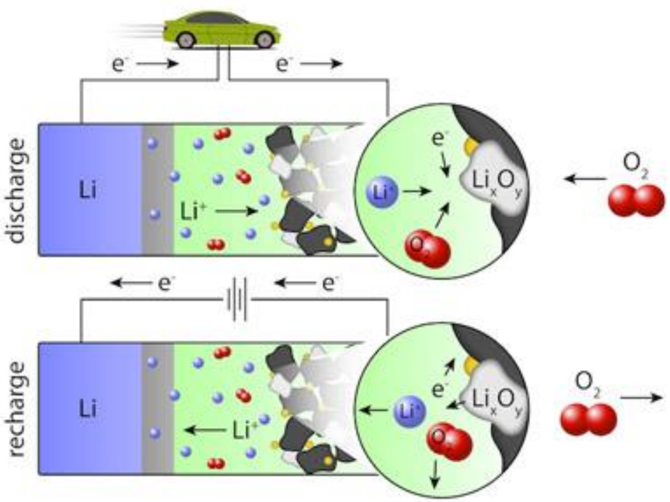




Li Air: "Holly Grail of Batteries"

- Opportunities:
  - High capacity
  - Low cost
- Challenges:
  - Energy inefficient
  - Oxygen electrocatalyst
  - Lithium protection
  - Lithium electrodeposition
  - Containment of electrolyte
  - Reaction mechanism?





Reactions:

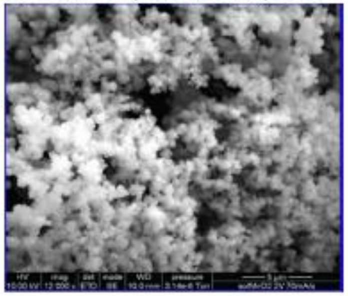
$2\ Li^+ + 2e^- + O_2 \rightarrow Li_2O_2$

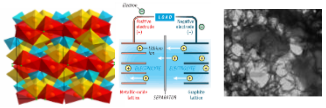
$O_2 + e^- \rightarrow O_2^{\cdot -}$

$Li^+ + O^{2\cdot -} \rightarrow LiO_2$

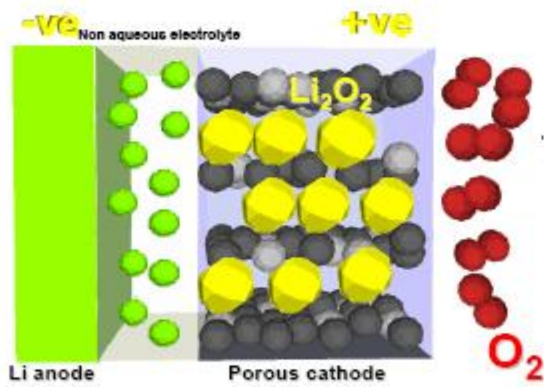
$2\ LiO_2 \rightarrow Li_2O_2 + O_2$

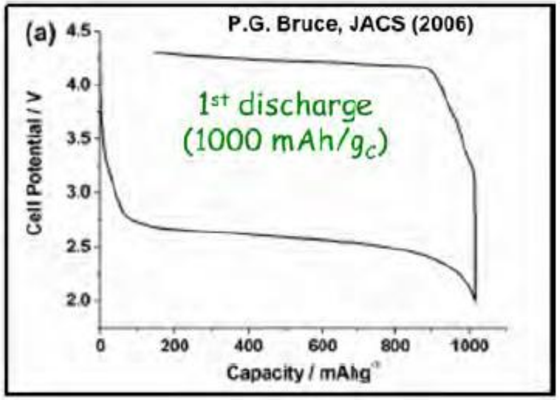
Positive = porous composite

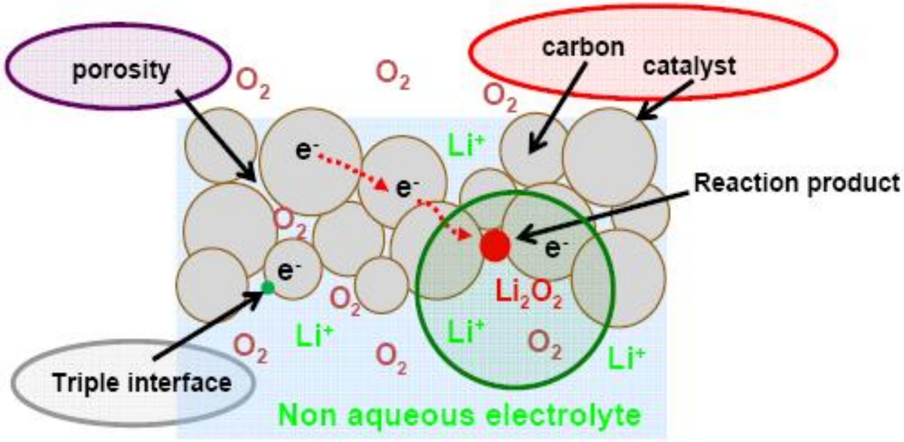


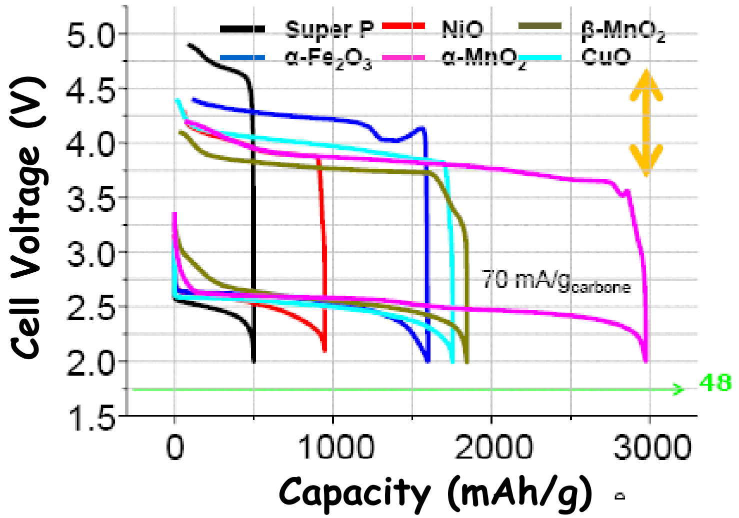


Li Air: Oxygen Cathode



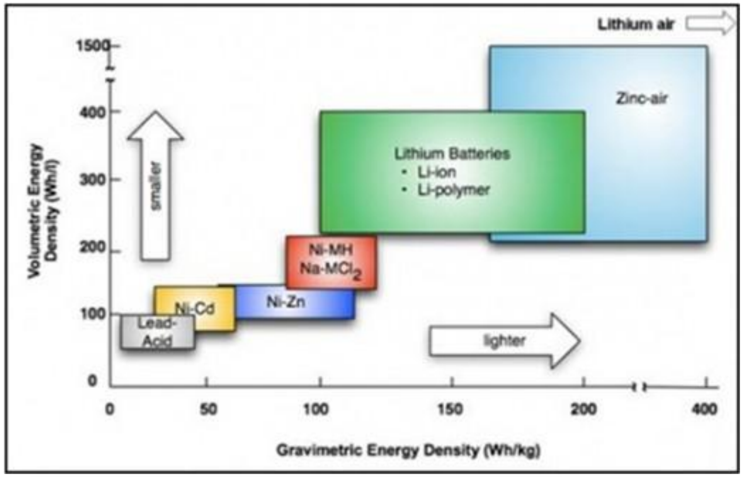


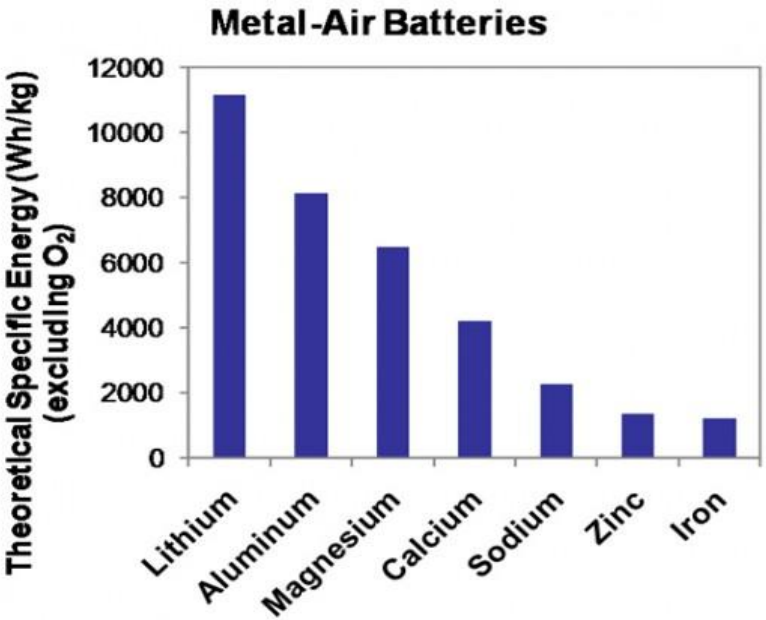


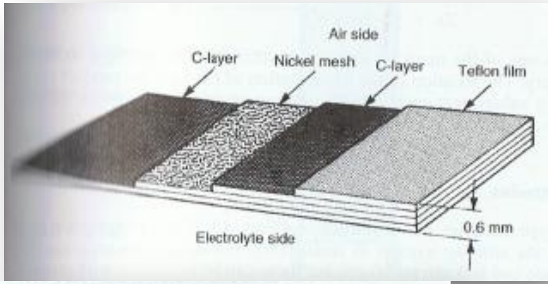


Three-phase boundary is critical!

Metal Air Batteries





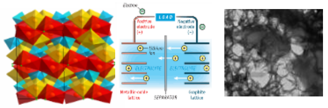


Advantages:

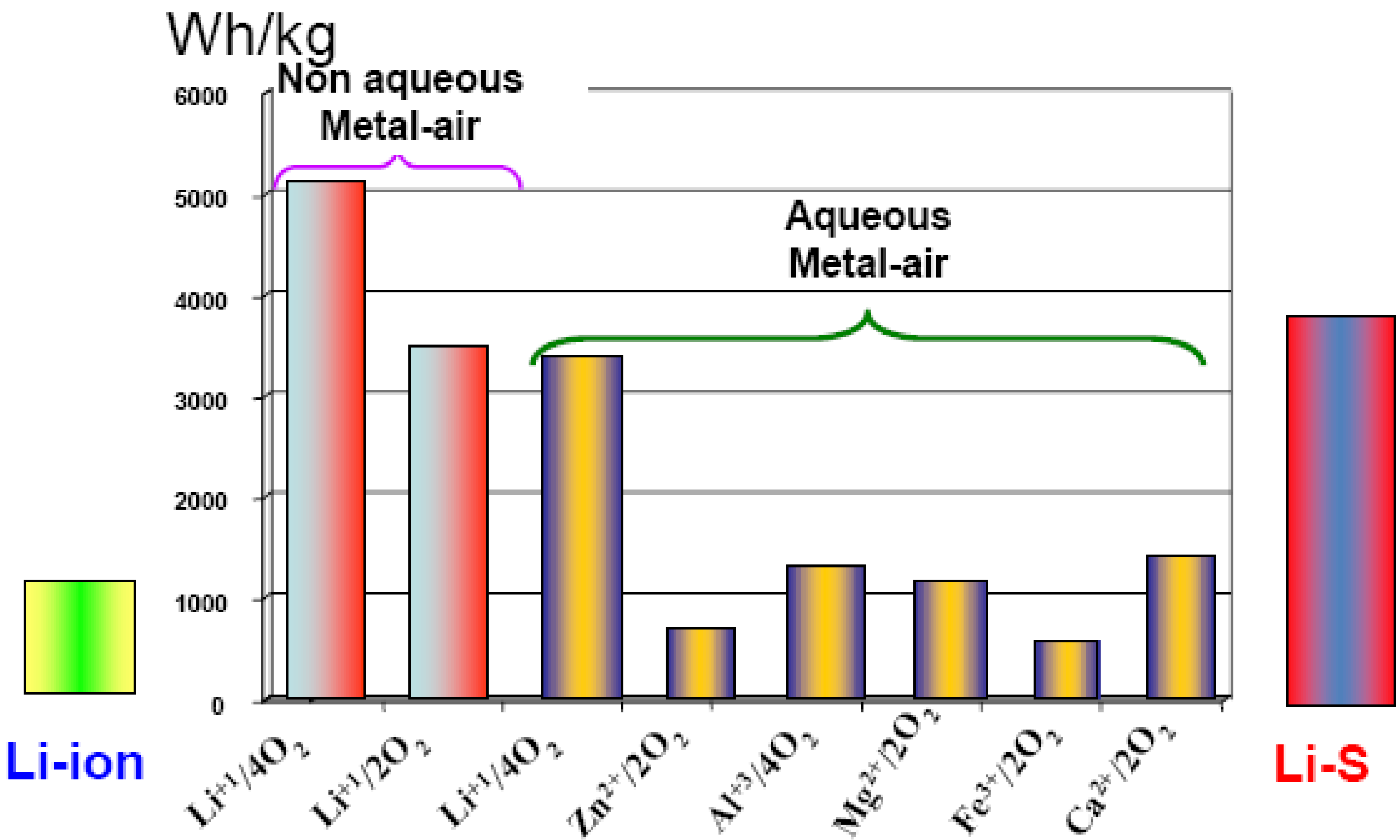
- Inexpensive
- High energy density

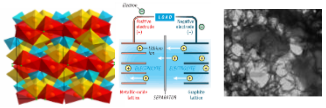
Disadvantages

- High internal resistance – low currents
- High self-discharge
- Carbonate formation



Metal Air Batteries





Sodium Sulfur Battery

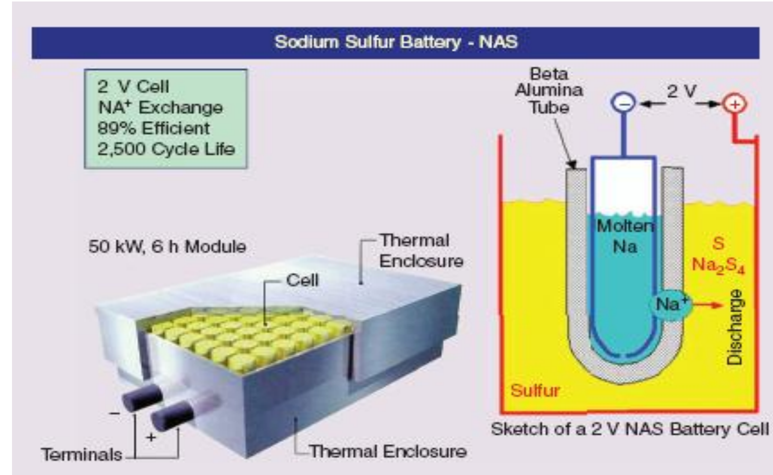
Reactions:

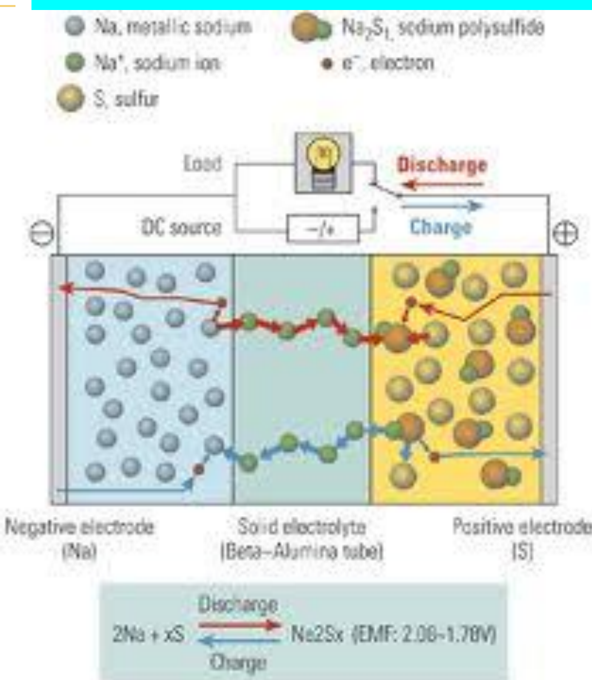
$2Na \leftrightarrows 2Na^{+} + 2e^{-}$

$xS + 2e^{-} \leftrightarrows S_x^{-2}$

$2Na + xS \leftrightarrows Na_2S_5$ (x = 5 – 3)

E^{o} = 2.076 – 1.78 V



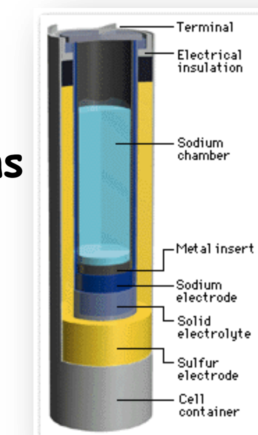


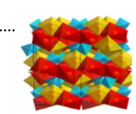
ADVANTAGES:

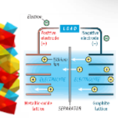
- Low cost
- High cycle life
- High energy density
- High energy efficiency
- Insensitivity to ambient conditions

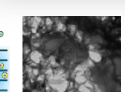
DISADVANTAGES:

- Thermal management
- Safety
- Durable seals
- Mechanical stress





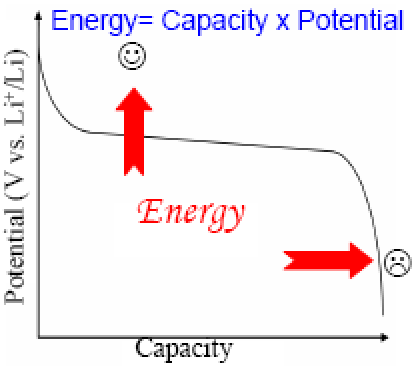


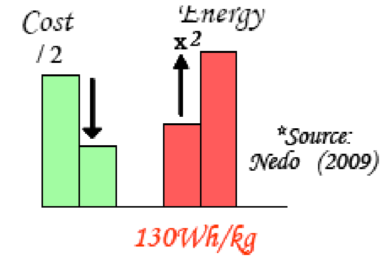


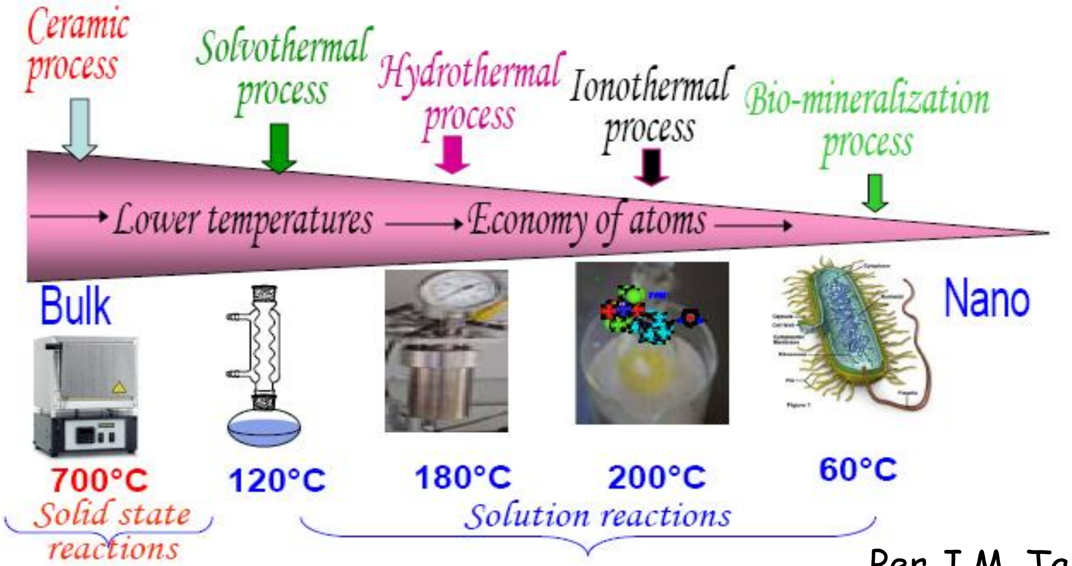
Development Principles

Goals driving new developments:

- Higher energy (e.g., x 2)
- Lower cost (e.g., ½)
- Higher rate
- Higher number of cycles
- Good durability
- Enhanced safety
- Sustainability

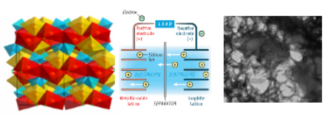




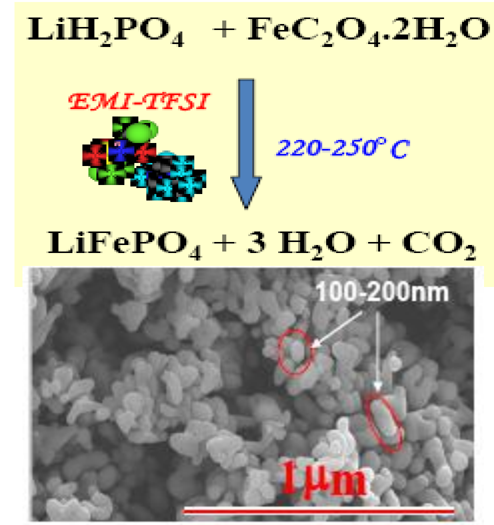


Novel production methods – battery manufacturing has not evolved much in the last 40 years

Per J.M. Tarascon, 2011



Promising Developments



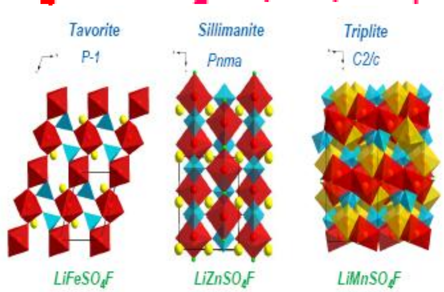
Ionic Liquids:

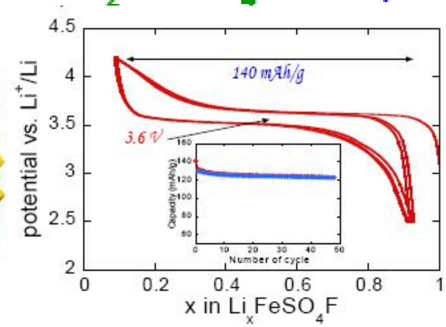
- No vapour tension
- Thermal stability > 300°C
- Non flammable
- Good solvent for numerous salts and polymers
- Cations-anions combinations (estimated at 15000, 1000 realized)

New family of Fluorosulfates $AMSO_4F$, A= Li, Na; M =Fe, Ni, Co

$$MSO_4 \cdot H_2O + LiF \rightarrow LiMSO_4F$$

$LiFePO_4$ $Na_2Fe(Mn)PO_4F$ Li_2FeSiO_4 $LiFe(Mn)PO_4F$

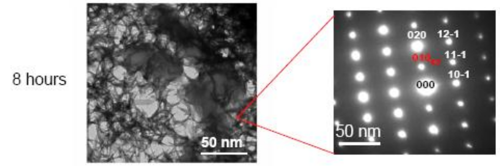


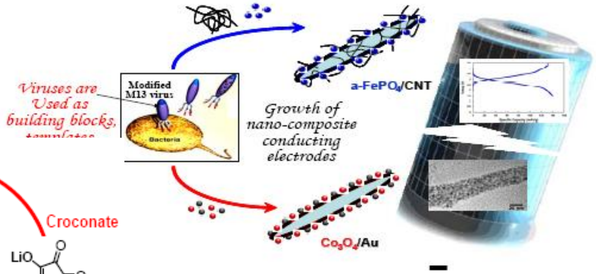


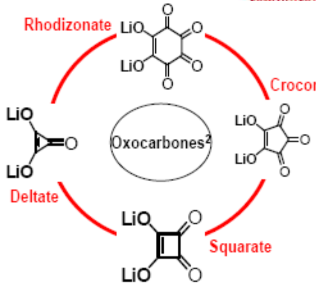
N. Recham, L. Dupont, D. Larcher, M. Armand, and J-M. Tarascon Chemistry of Materials 21(6), (2009), 1096-1107.

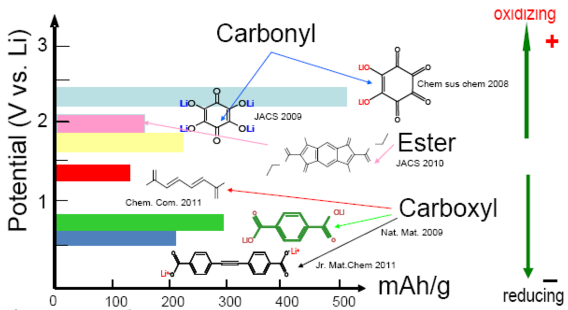
Promising Developments, cont.

- Room temperature synthesis
- Bio-mimetic synthesis
  - $LiFePO_4$ synthesis
- Electrodes from genetically modified viruses
- Organic electrodes
- Sustainable electrodes



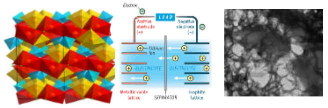




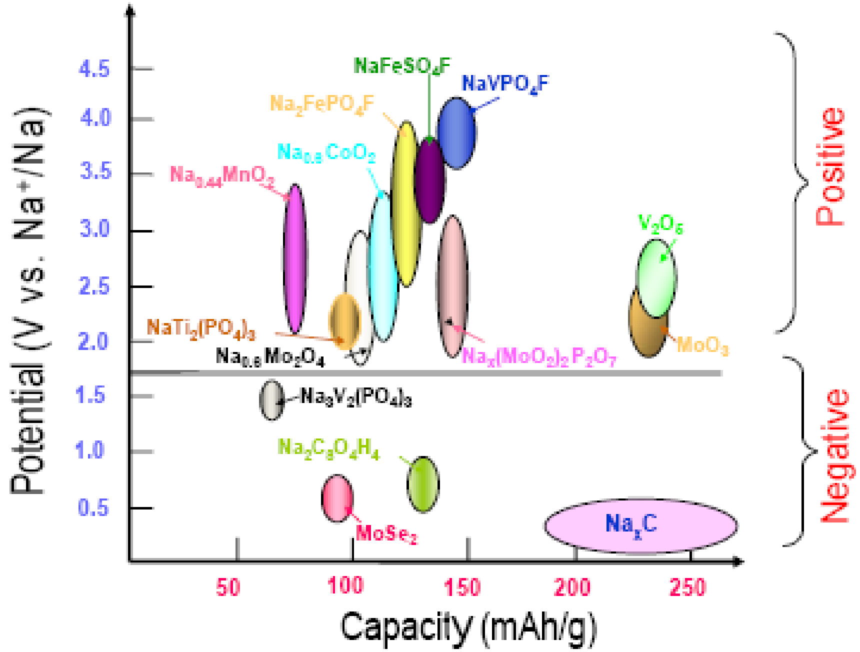


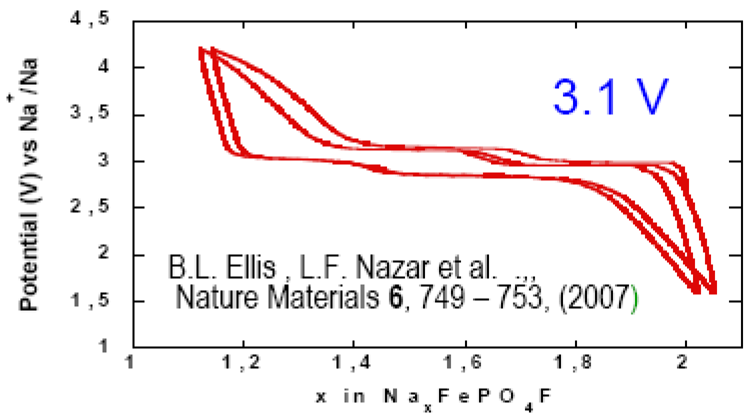
1. N. Ravet, C. Michot, M. Armand, *Mater. Res. Soc. Symp. Proc.*, 496, 263-
2. West, R. & Powell, D. L. New aromatic anions. III. Molecular orbital calculations on oxygenated anions. *J. Am. Chem. Soc.*, 85, 2577-2579 (1963).

Nam, K.T. *et al. Science*. 312, 885-888 (2009)



Sodium Ion Battery?





Higher availability:

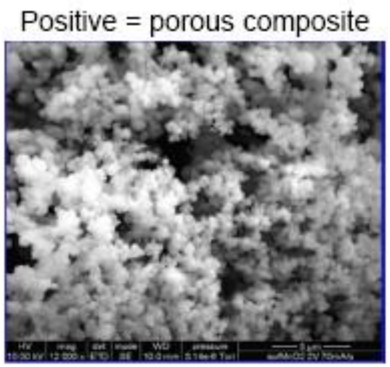
- Na in Earth: 10^3 ppm
- Na in Sea: 10^5 ppm

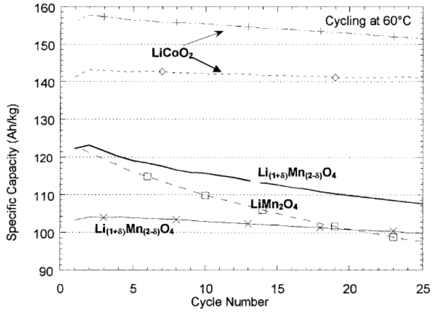
Lower performance than Li Ion:

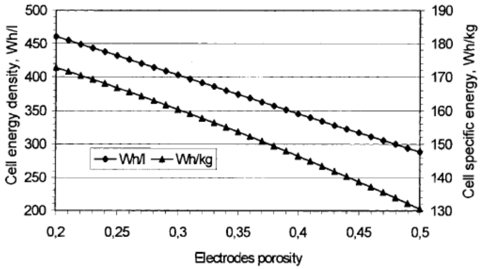
- Electrode potentials: Li (-3.04V), Na (-2.71V)
- Capacity (mAh/g: Li (3860), Na (1166)

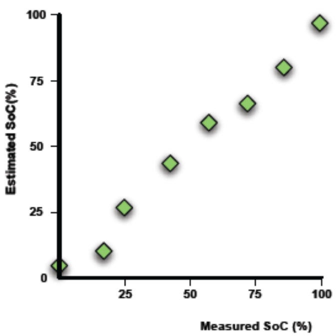
What else is needed?

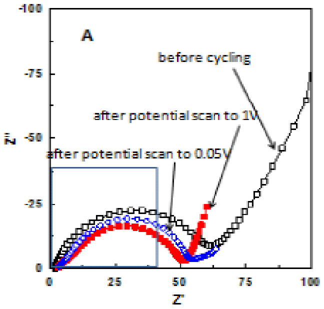
- Understanding reaction mechanisms
- Characterization
- Bringing promising developments to commercialization

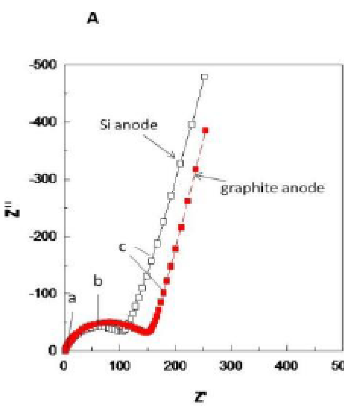


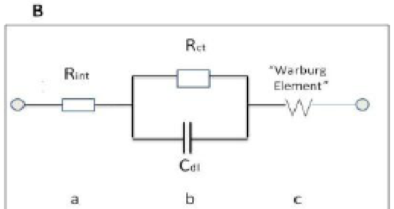




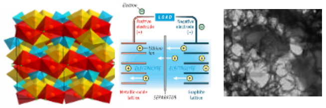








Fitting data / Anode type	Rint (Ω)	Rct (Ω)	Cdl (F)
Si-anode	1.62	94.12	6.34x10-6
C-anode	1.43	125.44	5.02x10-6



Developing Battery Chemistry

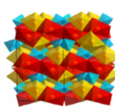
Component Selection

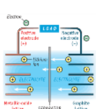
Testing and Modeling

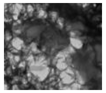
Production Equipment and Facilities

Application Engineering, Qualification

It can take 10 years to get to production!







From Electrode to Commercial Battery

R&D Stage

- Proof of Concept
- Initial Sampling
- Seed funding

~$1M

- Funding ; time consuming
- Multiple iterations needed to optimize materials and document benefits

- **Timeframe: 1-2 years**

DESIGN GAP

Pilot Phase

- Advanced Testing Customer Samples
- A Funding

~$10 M

- Funding ; Difficult
- Customers engaged and want samples
- Enhanced lab required
- Material selection
- Test challenges
- **Timeframe: 2-4 years**

MFG GAP

Mass Production

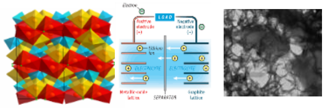
- Final Product Design
- UN/UL Tests
- B Funding to Profitability

~$100 M

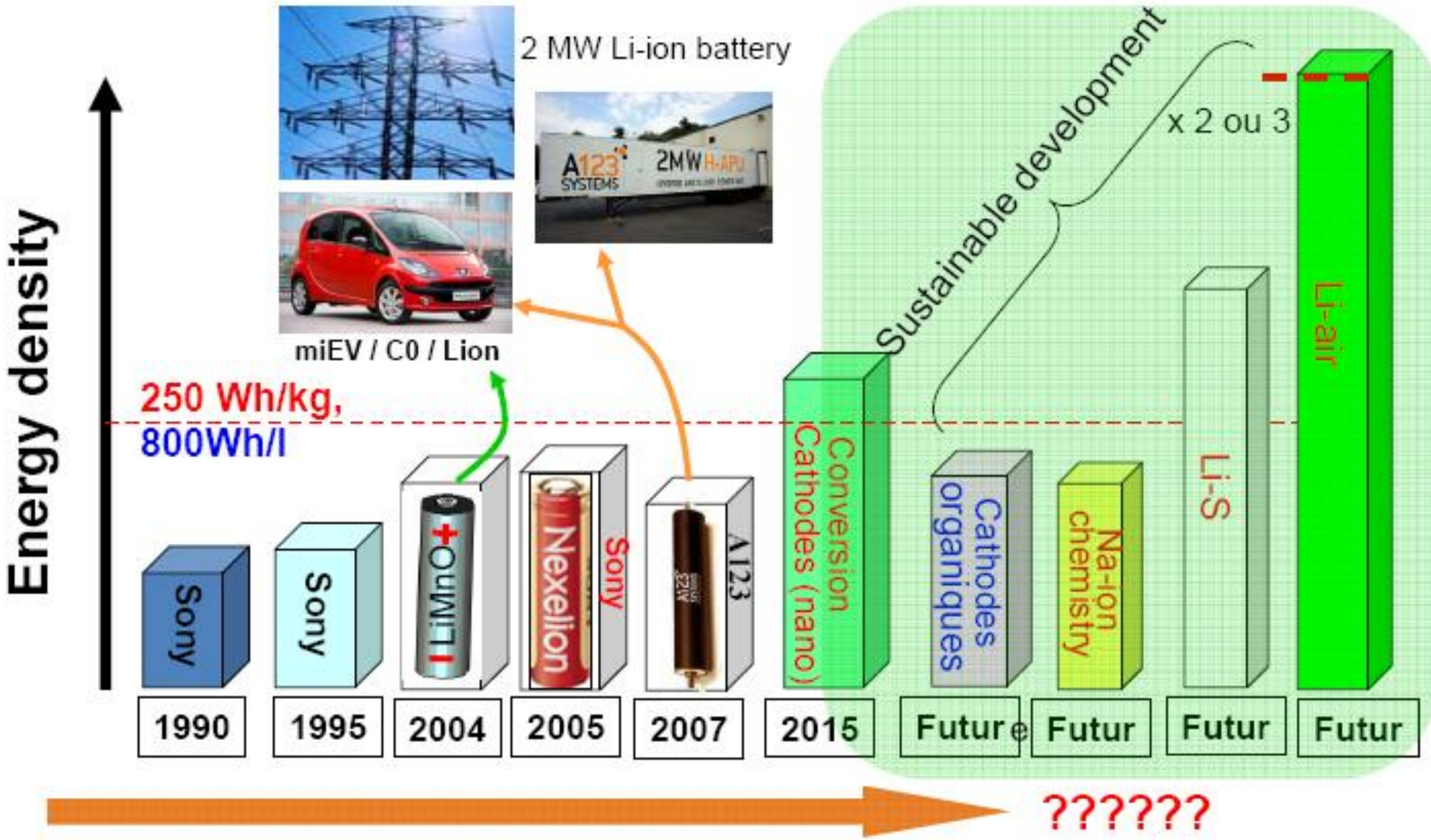
- Funding ; Difficult
- Customer commitment to a product
- Capital, facility, quality, staffing plans required
- Qualification and supplier audit

Timeframe: 3-4 years

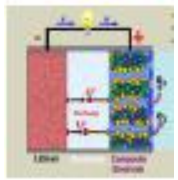
Courtesy of Polaris Battery Labs



Battery Outlook

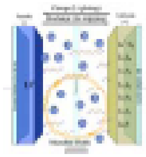


Conclusion: Future Directions



Li Air

Li-S



Li S

Organic electrodes

Cathodes: Solid State Li Ion
$LiCo(Mn, Ni)O_2/C$,
Na_2FePO_4F, $LiVOPO_4$

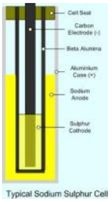
Anodes: Titanates, Si, etc.

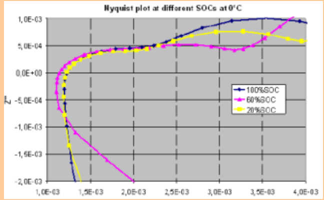
Li Ion

Na Air

Na Ion

Na S



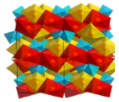


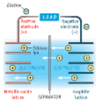
Characterization is critical

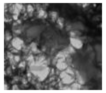
Path to production challenging

Present

Metal Air Batteries	LA and Ni-based Batteries	Flow Batteries







Batteries: The Search for a Perfect Chemistry

Thank you for your attention!

The search for a perfect chemistry is not over. The convergence between new material technologies and batteries brings promise and it is clear that great advances will be made and numerous technologies will be competing in the battery field in the next several years. One day, when the search is over, the battery technology will reach its maturity.