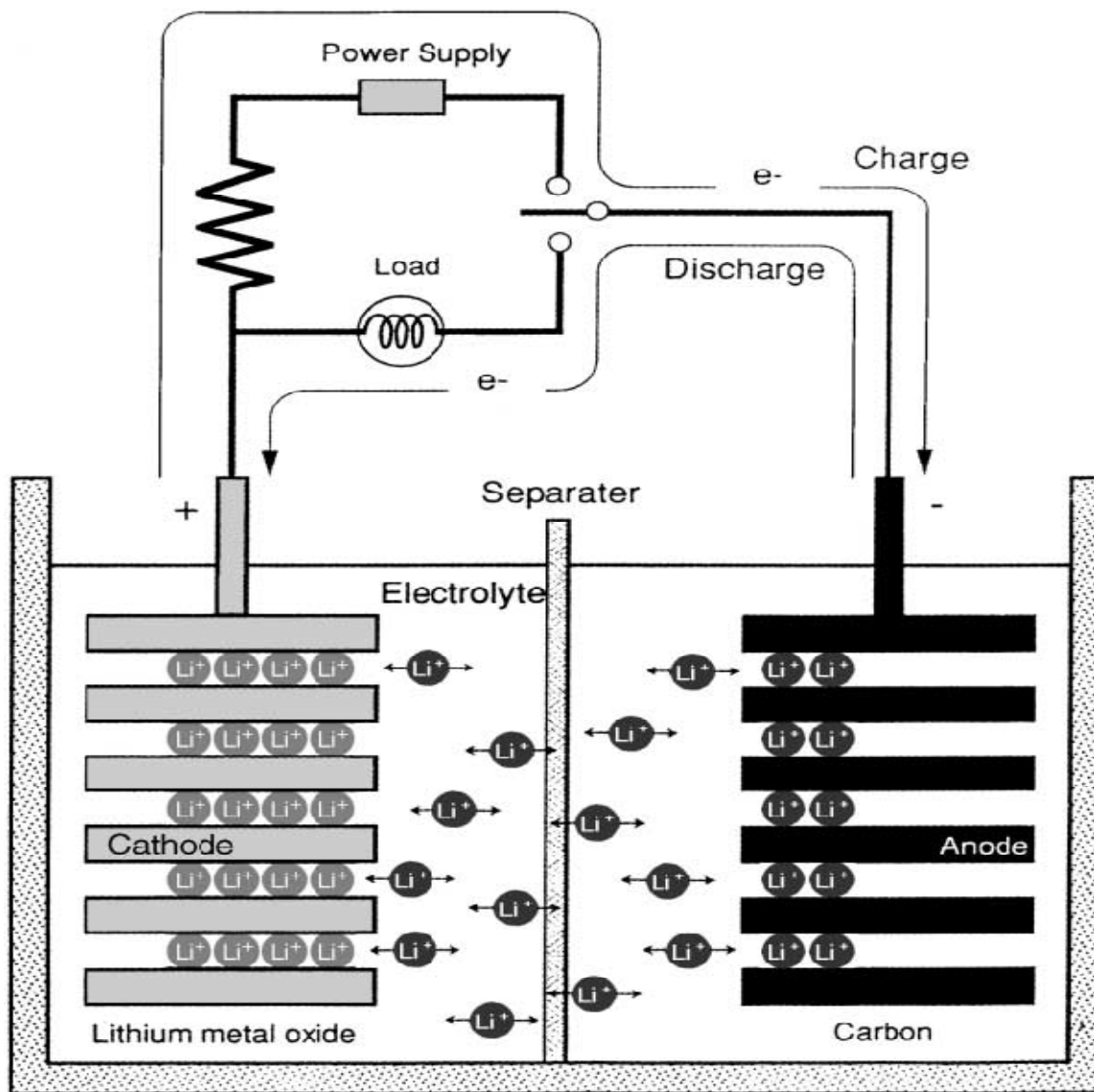


Lithium Ion Batteries –

Can they be the energy conversion devices in the near future?



Outline of the Presentation

- Introduction some concepts of batteries
- Lithium ion battery (LIB)
- Science of LIB
- Concepts on LIB
- Preliminary Proposals

BATTERIES

- Primary batteries not rechargeable
 - Lithium battery and a host of other systems
- Secondary Batteries rechargeable
 - LIB and many others
- In the 1970's, Lithium metal was used but its instability rendered it unsafe and impractical.
Lithium-cobalt oxide and **graphite** are now used as the lithium-Ion-moving electrodes. (Whittingham)
- The Lithium-Ion battery has a slightly lower energy density than Lithium metal, but is much safer.
Introduced by Sony in 1991

Some Typical Secondary Batteries

Zinc-Carbon: used in all inexpensive AA, C and D dry-cell batteries. The electrodes are zinc and carbon, with an acidic paste between them that serves as the electrolyte. (disposable)

Alkaline: used in common Duracell and Energizer batteries, the electrodes are zinc and manganese-oxide, with an alkaline electrolyte. (disposable)

Lead-Acid: used in cars, the electrodes are lead and lead-oxide, with an acidic electrolyte. (rechargeable)

Some modern secondary batteries

Nickel-cadmium: (NiCd); rechargeable, “memory effect”

Nickel-metal hydride: (NiMH) : rechargeable, *no* “memory effect”

Lithium-Ion: (Li-Ion) : rechargeable, *no* “memory effect”

Remarks on Recharge-ability and memory Effect

Recharge-ability: basically, when the direction of electron discharge (negative to positive) is reversed, restoring power.

Memory Effect: (generally) When a battery is repeatedly recharged before it has discharged more than half of its power, it will “forget” its original power capacity.

Cadmium crystals are the culprit! (NiCd)

There are many type of Batteries

Batteries:

**Alkaline, Zinc Chloride, silver oxide
zinc-carbon Lithium etc**

**Lead acid, Li-ion, Ni-Fe, NiMH, NiCd,
NaMCl**



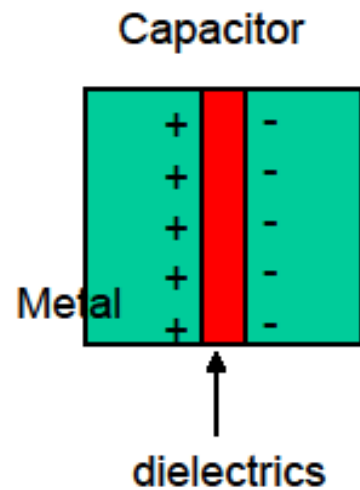
Brief history of Lithium ion Battery

- 1970- M.S. Whittingham of Binghamton Univ Exxon titanium sulphide and lithium metal anode
- 1982-83 Grenoble Inst Tech (INPG) and Natl Cen. Sci Res (CNRS) intercalation in graphite lithium polymer electrolyte/graphite
- 1980s Goodenough various spinel and LiFePO_4
- 2002 Yet-Ming Chiang of MIT performance improvement
- Patent infringement battle between Chiang and Goodenough

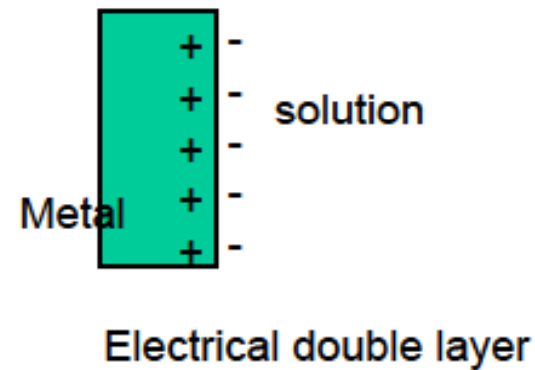
Scope of this presentation

Presenting the state of art of the Lithium ion battery technology, current research into the materials electrodes and electrolytes and the problems on their development, advantages and drawbacks are analyzed. Polymer electrolytes as well as conventional organic liquids are electrolytes are considered

Energy Storage Technologies

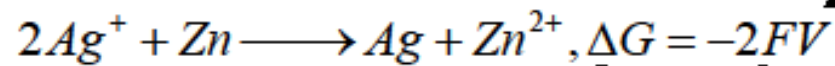
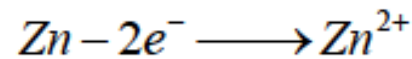
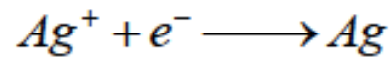
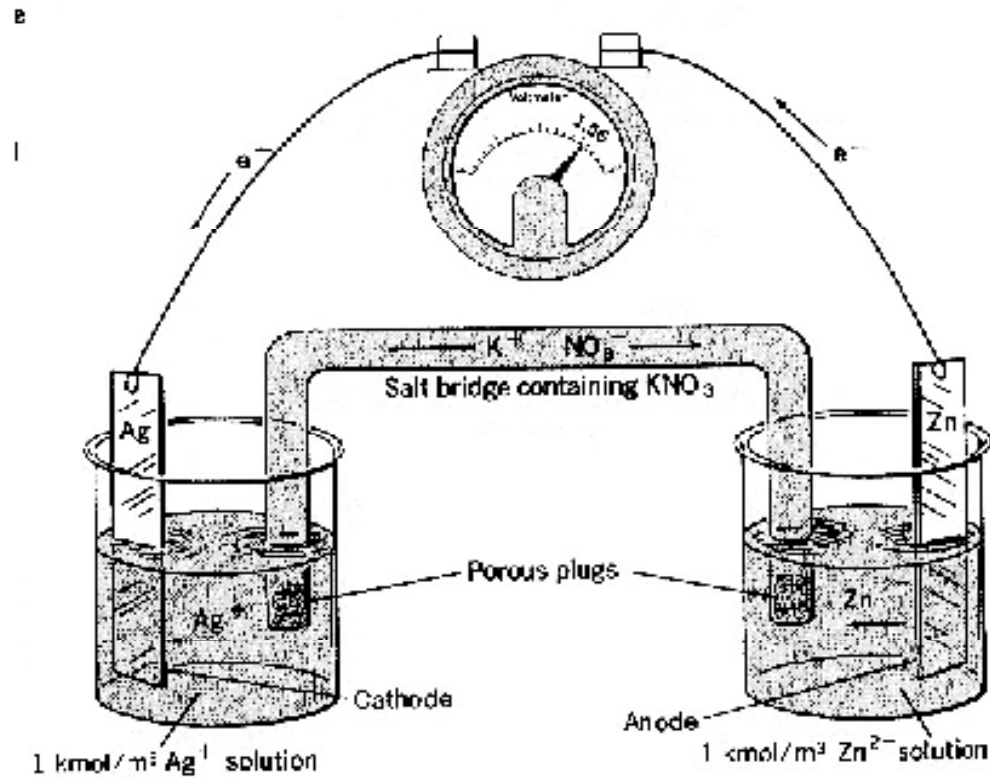


Supercapacitor (Electrochemical capacitor)



$$E = \frac{1}{2} CV^2$$

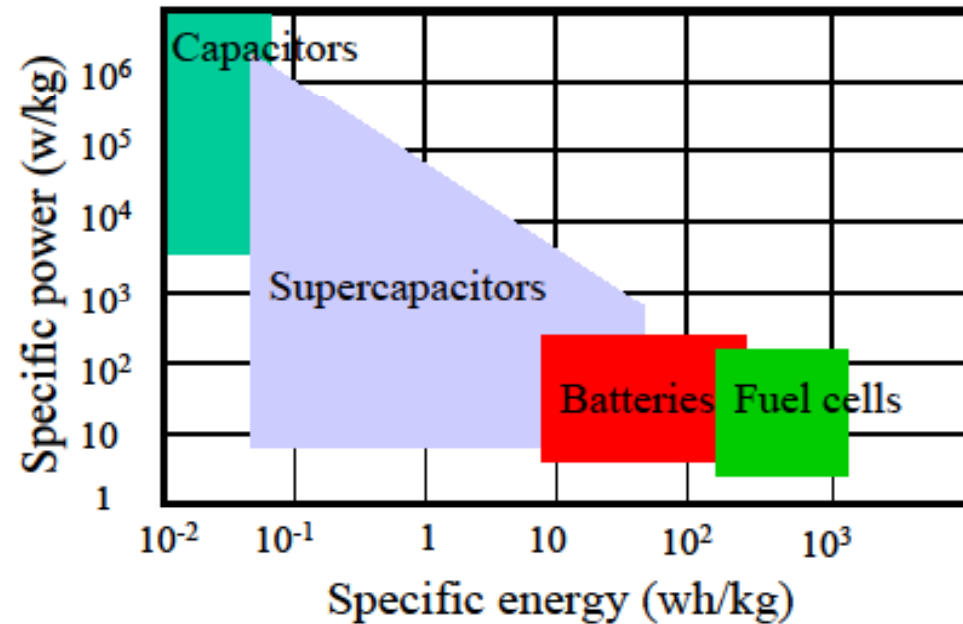
Batteries (Ag-Zn)



Reaction free energy Faraday constant

Battery voltage

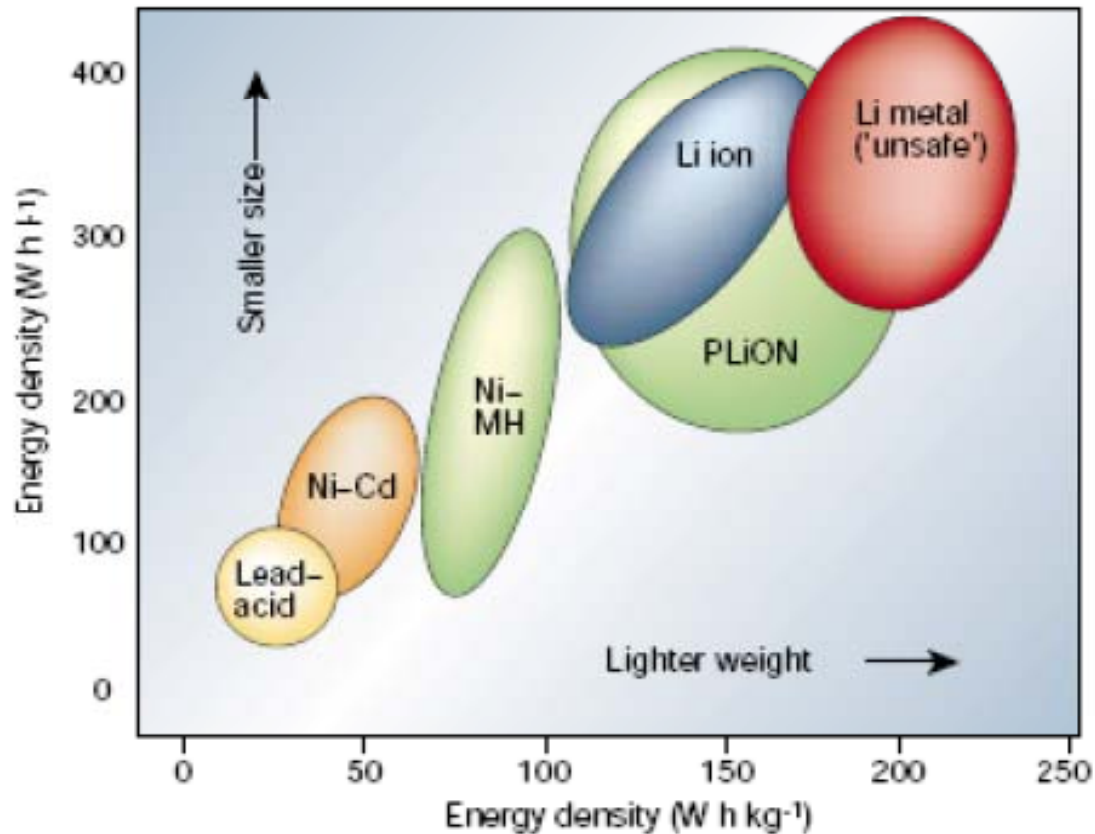
Comparison of Energy Storage Technologies



Important parameters:

- Energy density (Energy per weight or volume)
- Power density (Power per weight or volume)
- Cycle life and safety
- Cost

Why Li Ion Batteries?



Li-related batteries have larger energy density than other batteries.

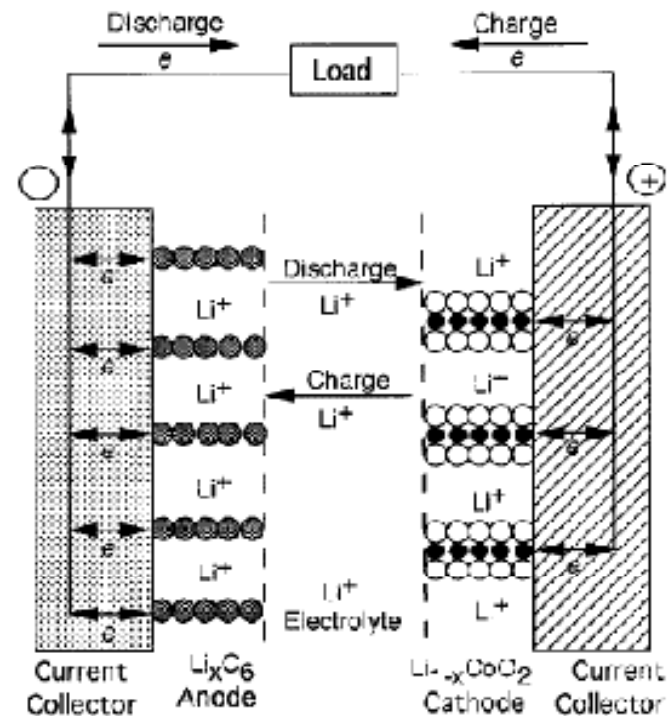
J.-M. Tarascon & M. Armand. *Nature* 414, 359 (2001).

Existing Li Ion Battery Technology

Graphite: 370 mAh/g

LiCoO_2 : 140 mAh/g

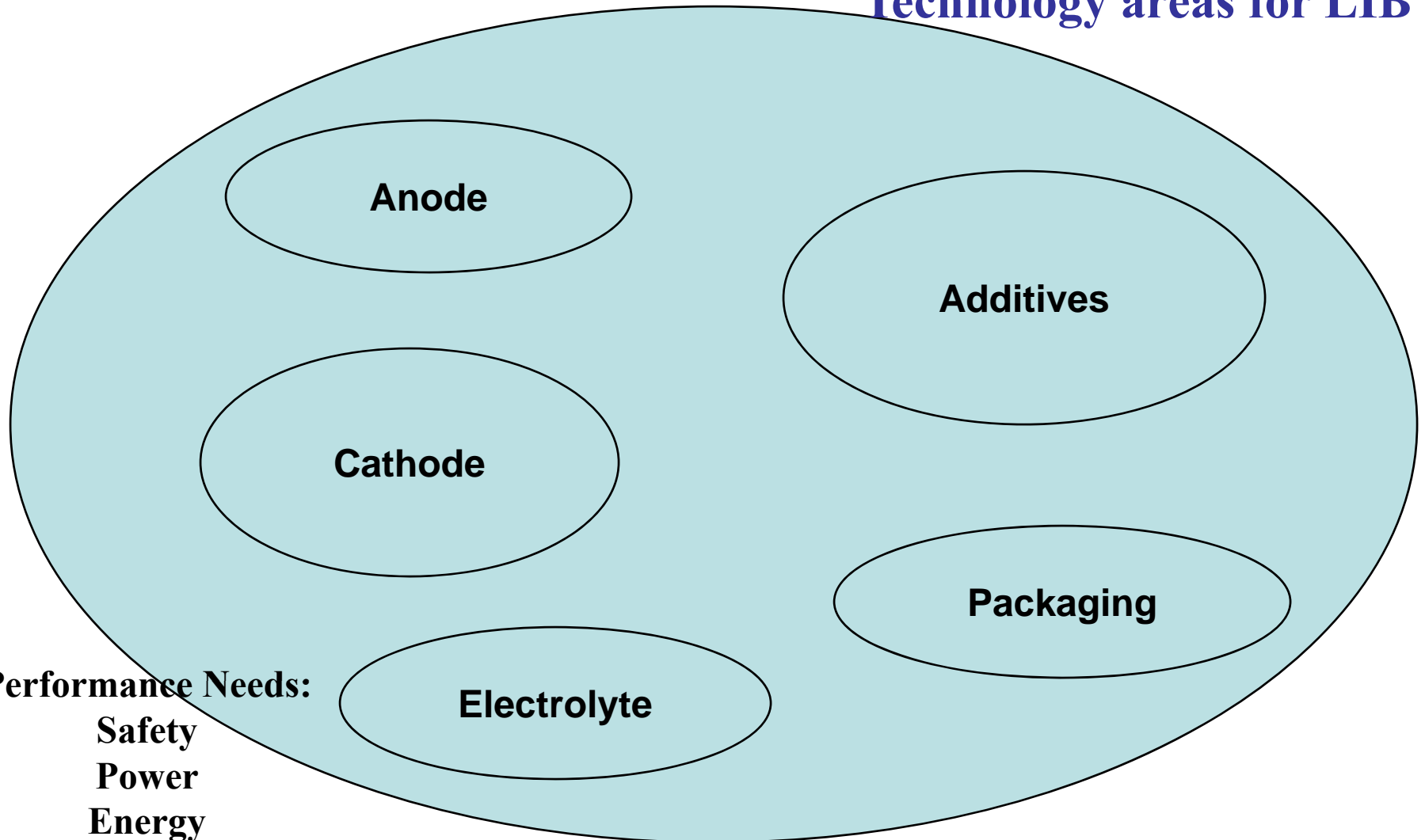
The energy density can not meet the application needs.



1. **Energy density:** - Anode and cathode Li storage capacity
- Voltage
2. **Power density:** - Li ion moving rate
- Electron transport
3. **Cycle, calendar life and safety:** strain relaxation and chemical stability.
4. **Cost:** Abundant and cheap materials

Technology Developments for improved Performance

Technology areas for LIB



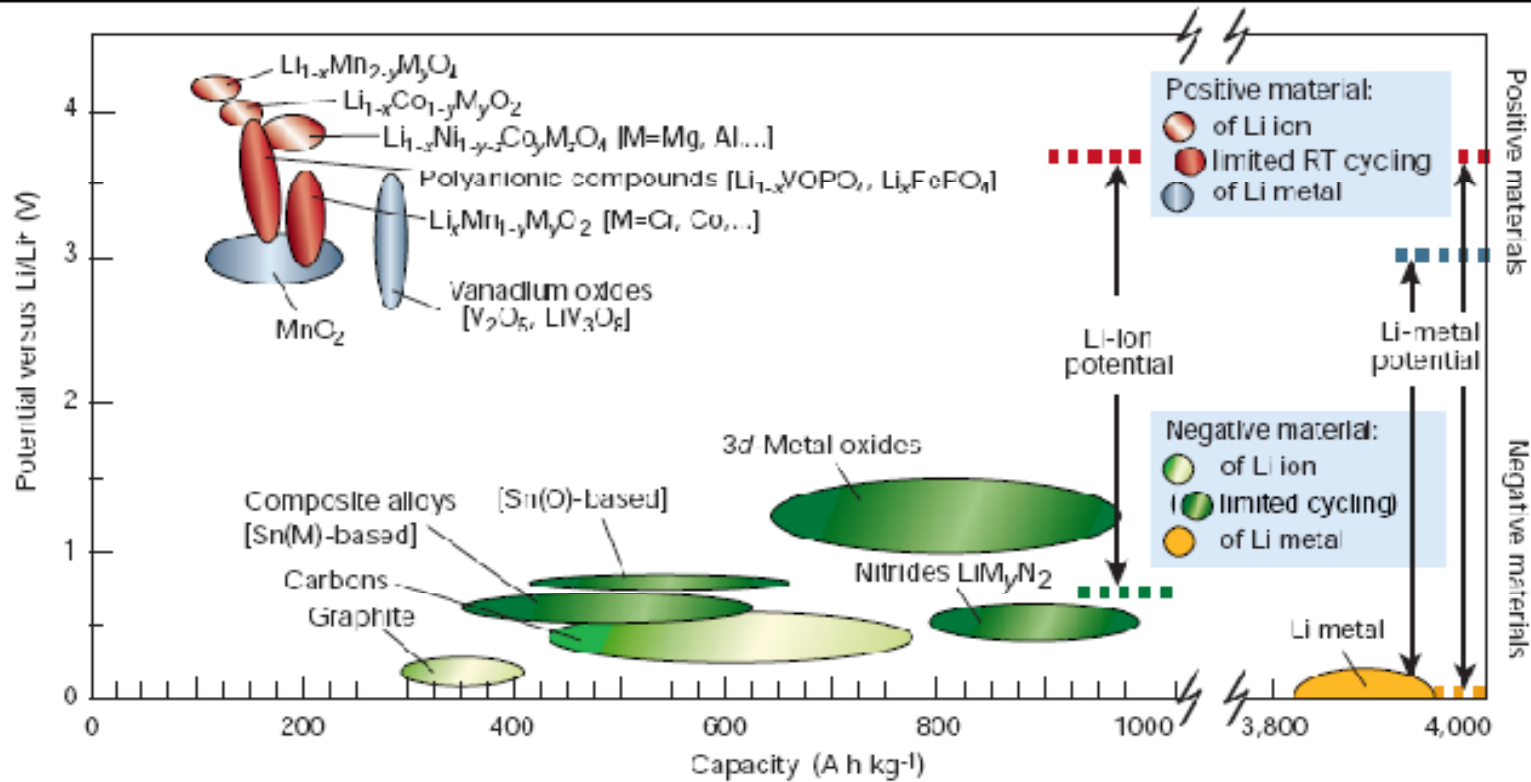
Performance Needs:

- Safety
- Power
- Energy
- Life

Cycle Time

7/31/2010

Electrode Materials



Anode: low potential
Cathode: high potential

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

Two Types of Electrode Materials



	Existing Tech.	Future Tech. New Materials
Mechanism	Intercalation	Displacement/alloy
Volume change	Small	Large
Li diffusion rate	Fast	Slow
Specific capacity	Low	High

CATHODE

Cathode Material	Average voltage	Gravimetric capacity in mA.h/g	Gravimetric energy in kW.h/kg
LiCoO_3	3.7 V	140	0.518
LiMn_2O_4	4.0 V	100	0.400
LiNiO_2	3.5 V	180	0.630
LiFePO_4	3.3 V	150	0.495
$\text{Li}_2\text{FePO}_4\text{F}$	3.6 V	115	0.414
$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$	3.6 V	160	0.576
$\text{Li}(\text{Li}_a\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$	4.2 V	220	0.920

ANODE

Anode	Average voltage (V)	Gravimetric Capacity (mA.h/g)	Gravimetric Energy kW.h/kg
Graphite(LiC ₆)	0.1-0.2	372	0.372-0.0744
Hard carbon (LiC ₆)	?	?	?
Titanate (Li ₄ Ti ₅ O ₁₂)	1-2	160	0.16-0.32
Si(Li _{4.4} Si)	0.5-1	4212	2.106-4.212
Li 4.4 Ge	0.7-1.2	1624	1.137-1.949

What electrolyte?

- Potentials are beyond water potential window and hence non aqueous solutions
- Lithium salts LiPF_6 , LiBF_4 , LiClO_4 in organic solvent ethylene carbonate
- Li ion conduction typical conduction 10 mS/m and temperature coefficient around 30-40%.
- Organic solvents decompose under potential.
- Solid electrolyte interface (SEI) formed by the application of potential are electrically insulating yet sufficiently conducting.
- The interface prevents the decomposition of the electrolyte in the second charge (ethylene carbonate decomposed at a relatively high voltage 0.7 V versus lithium and forms a dense and stable interface.

Advantages

- Shape and size variation
- Lighter than others
- High open circuit voltage
- No memory effect
- Low (?) discharge rate 5-10% compared to 30% of common nickel metal hydride battery
- Smart batteries do self discharge due to built in voltage monitoring circuit.

Disadvantages

- Charging gives rise to deposits – cells capacity diminishes- time dependent charging behaviour
- High charge levels and temperature hasten capacity loss – charging heat
- Loss rates vary with temperature full charge level capacity loss is high
- Internal resistance of lithium ion battery is high as compared to other batteries

Current Market for LIB

First introduced in 1991

Now preferred power source for consumer Electronics

Estimated over 2 billion cells are manufactured since 2006

Major applications for small LIBs	Approximate share (%)
Mobile Phones	~ 55
Note book PCs	~ 25
Cameras, MP3, PDAs	~ 20

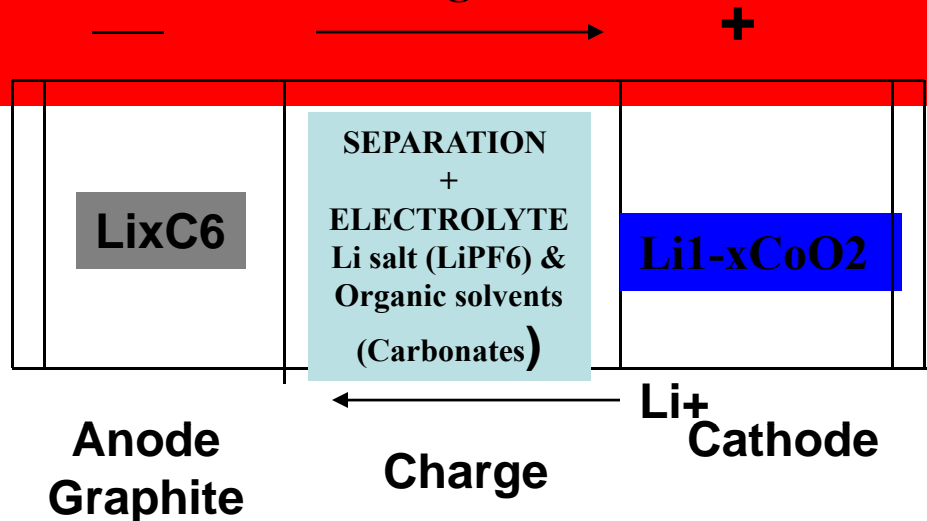
Supply Chain

Mobile phones: Mainly Asia, Japan, Korea and China

Pack manufactures: worldwide but mainly Asia

Final packing with Host device – world wide

Basic Chemistry



Discharged ↔ Charged

Anode
 $\text{Li}^+ + \text{C}_6 + e \leftrightarrow \text{Li}_x\text{C}_6 \ (x < 1)$
 1. $V < E^0 < 0.5 \text{ V vs Li}$

Cathode
 $\text{LiCoO}_2 \leftrightarrow x\text{Li}^+ + \text{Li}_x\text{CoO}_2 + e$
 $x < 0.5$
 $3.5 < E^0 < -4.25 \text{ vs Li}$

Lithiated metal oxide cathode (usually cobalt based)

Graphite anode

Organic solvent electrolyte with Lithium salt

No Lithium metal

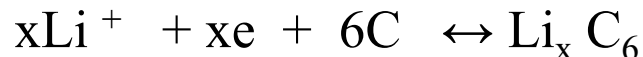
Both the anode and cathode are materials into which, and from which, lithium can migrate. During *insertion* (or intercalation) lithium moves into the electrode. During the reverse process, *extraction* (or *deintercalation*) lithium moves back out. When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode. When the cell is Charging, the reverse occurs.

Useful work can only be extracted if electrons flow through a closed external circuit.

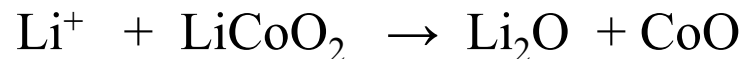
The following equations are in units of moles, making it possible to use the coefficient x . The cathode half reaction (with charging being forwards) is:



The anode half reaction is:



The overall reaction has its limits. Overdischarge supersaturates Lithium cobalt oxide, leading to the production of lithium oxide possibly by the following irreversible reaction:



Overcharge up to 5.2 Volts leads to the synthesis of cobalt(IV) oxide, as evidenced by X-ray diffraction



In a lithium-ion battery the lithium ions are transported to and from the cathode or anode, with the transition metal, cobalt (Co), in Li_xCoO_2 being oxidized from Co^{3+} to Co^{4+} during charging, and reduced from Co^{4+} to Co^{3+} during discharge.

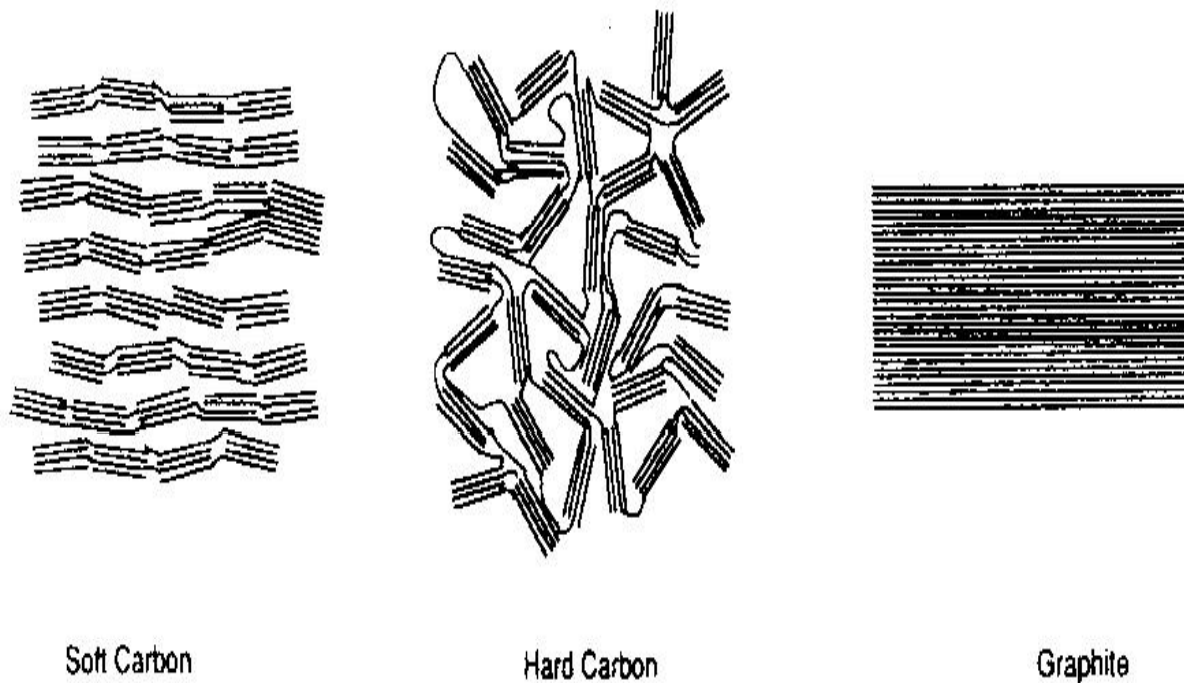
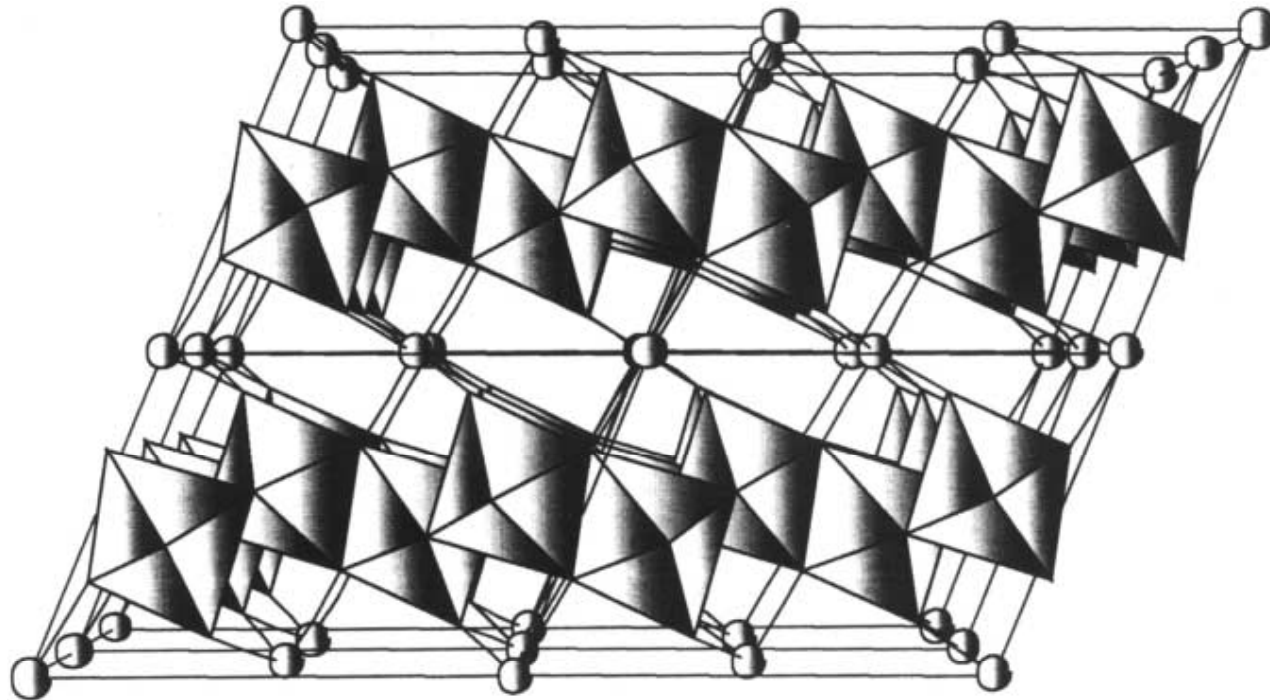


Fig. 4. Three types of carbon.

TYPES OF CARBON MATERIALS EMPLOYED AS ANODES IN LIB



Structure of Brannerite. Mn is represented by the circles and Vanadium is located in the center of each octahedron

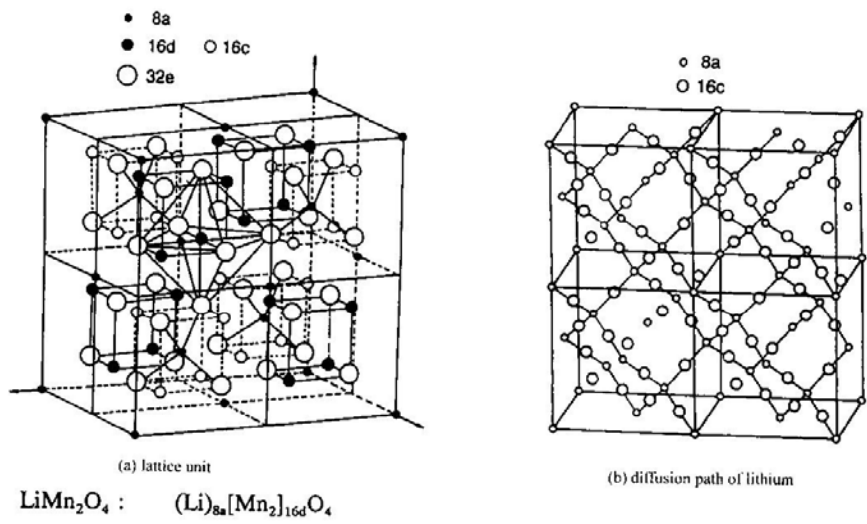


Fig. 21. Structure of spinel (a) unit cell and (b) diffusion path of lithium.

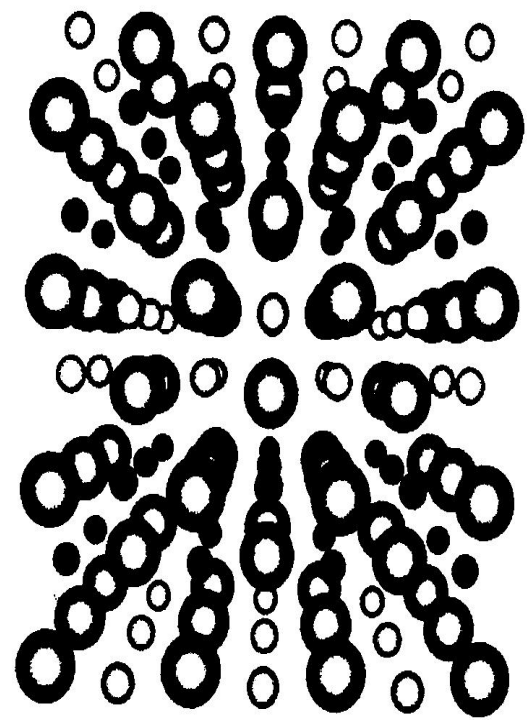


Fig. 19. Zigzag layered structure of LiMnO_2 . (Large circle) oxygen; (small open circle) manganese; (small solid circle) lithium.

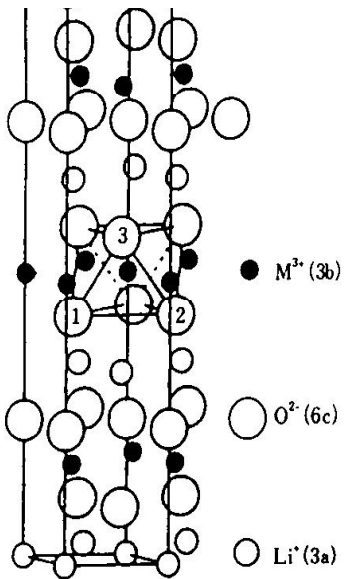


Fig. 16. Structure of $\alpha\text{-NaFeO}_2$.

STRUCTURES OF SOME OF THE CATHODE MATERIALS IN LIB

Principle Characteristics required for cathode materials

- The discharge reaction should have large negative Gibbs free energy (high discharge voltage)
- The host structure must have low molecular weight and the ability to intercalate large amounts of lithium (high energy capacity)
- The host structure must have high lithium chemical diffusion coefficient (high power density)
- The structural modifications during intercalation and de-intercalation should be as small as possible (long cycle life)
- The materials should be chemically stable, non-toxic and inexpensive
- The handling of the materials should be easy

One has to introduce some concepts on intercalation itself – in terms of energetics, space filling and reactivity

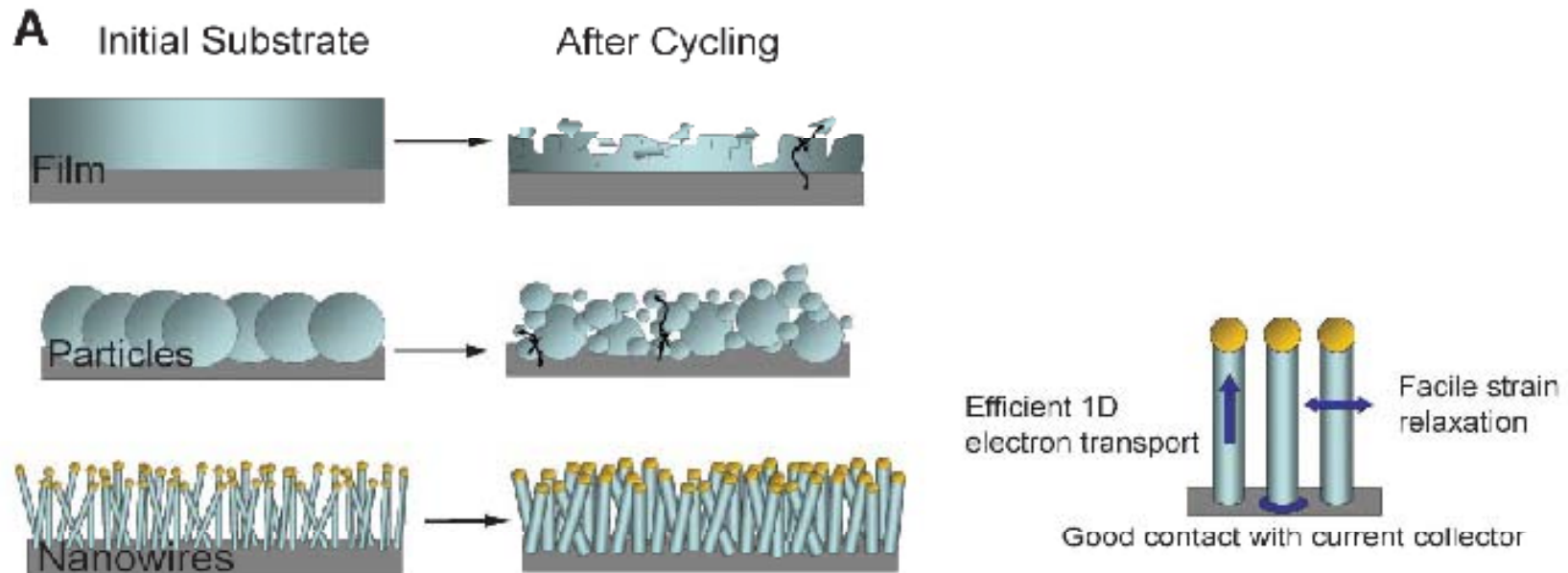
Conductivity of EC-based electrolytes(EC:co-solvent 1:1 by vol at 298 K

Electrolyte salt (1mol/dm ³)	Co-solvent	Specific conductivity (mS/cm)
Li(CF ₃ SO ₂) ₂ N	DME	13.3
	DMC	9.2
	DEC	6.5
	MP	10.8
LiCF ₃ SO ₃	DME	8.3
	DMC	3.1
	DEC	2.1
	MP	3.7
LiPF ₆	DME	16.6
	DMC	11.2
	DEC	7.8
	MP	13.3
7/31/2010	NCCR annual day 2010	30

Physical properties of solvents at 298 K
(^a Donicity; ^b acceptor number; ^c at 303 K; ^d at 313; ^e at 293 K)

solvent	Mp (°C)	Bp(^o C)	Rel Permittivity	Viscosity (CP)	Dipole moment (D)	DN ^a	AN ^b
Acetonitrile(AN)	-45.7	81.8	38	0.435	3.94	14.1	18.9
Gamma Butyrolactone (BL)	-42	206	39.1	1.751	4.12	-	-
Diethyl ether (DEE)	-116.2	34.6	4.27	0.224	1.18	19.2	3.9
1,2-Dimethoxyethane(DME)	-58	84.7	7.20	0.455	1.07	24	-
Dimethylsulfoxide (DMSO)	18.4	189	46.45	1.991	3.96	29.8	19.3
1,2-Dioxolane(DOL)	-95	78	6.79 ^c	0.58	-	-	-
Ethylene carbonate(EC)	39-40	248	89.6 ^d	1.86 ^c	4.80	16.4	-
Methylformate (MF)	-99	31.5	8.5 ^e	0.330	1.77	-	-
2-Methyltetrahydrofuran(MeTHF)	-	80	6.24	0.457	-	-	-
3-Methylazolidin-2-one(MO)	15.9	-	77.5	2.450	-	-	-
Propylene carbonate (PC)	-49.2	241.7	64.6	2.530	5.21	15.1	18.3
Sulfolane (S)	28.9	287.3	42.5 ^c	9.87 ^c	4.7	14.8	19.3
Tetrahydrofuran(THF)	-108.5	65.0	7.25 ^c	0.46 ^c	1.71	20.0	8.0

Nanowires as Li Battery Electrodes



What nanowires can offer:

- Good strain relaxation: new materials possible
- Large surface area and shorter distance for Li diffusion
- Interface control: (better cycle life).
- Continuous electron transport pathway.

Example: Si as Anode Materials

C anode: the existing anode technology.



Theoretical capacity: 372 mA h/g

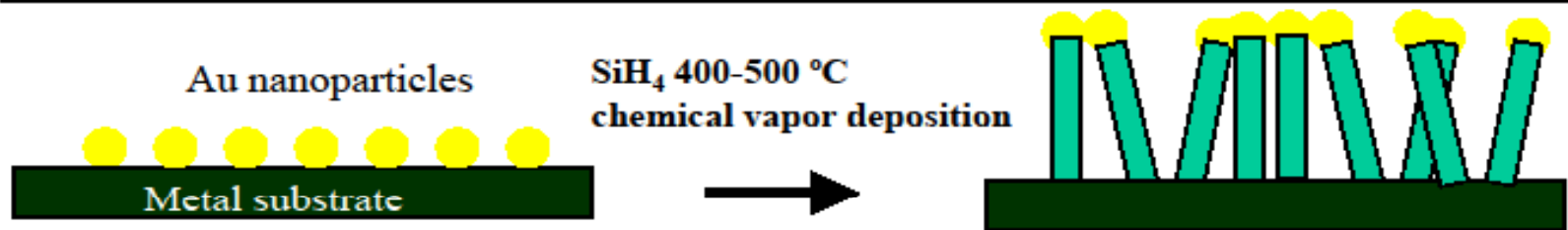
Si anode



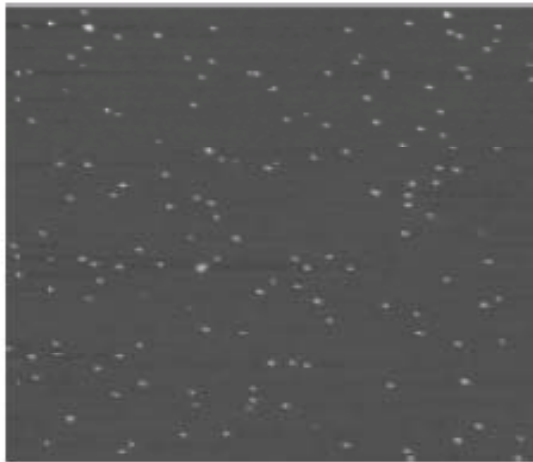
Theoretical capacity: 4200 mA h/g

Problem for Si: 400% volume expansion.

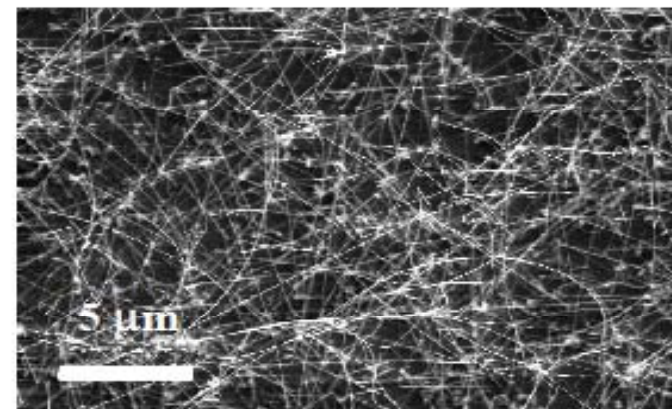
Vapor-Liquid-Solid (VLS) Growth of Si Nanowires



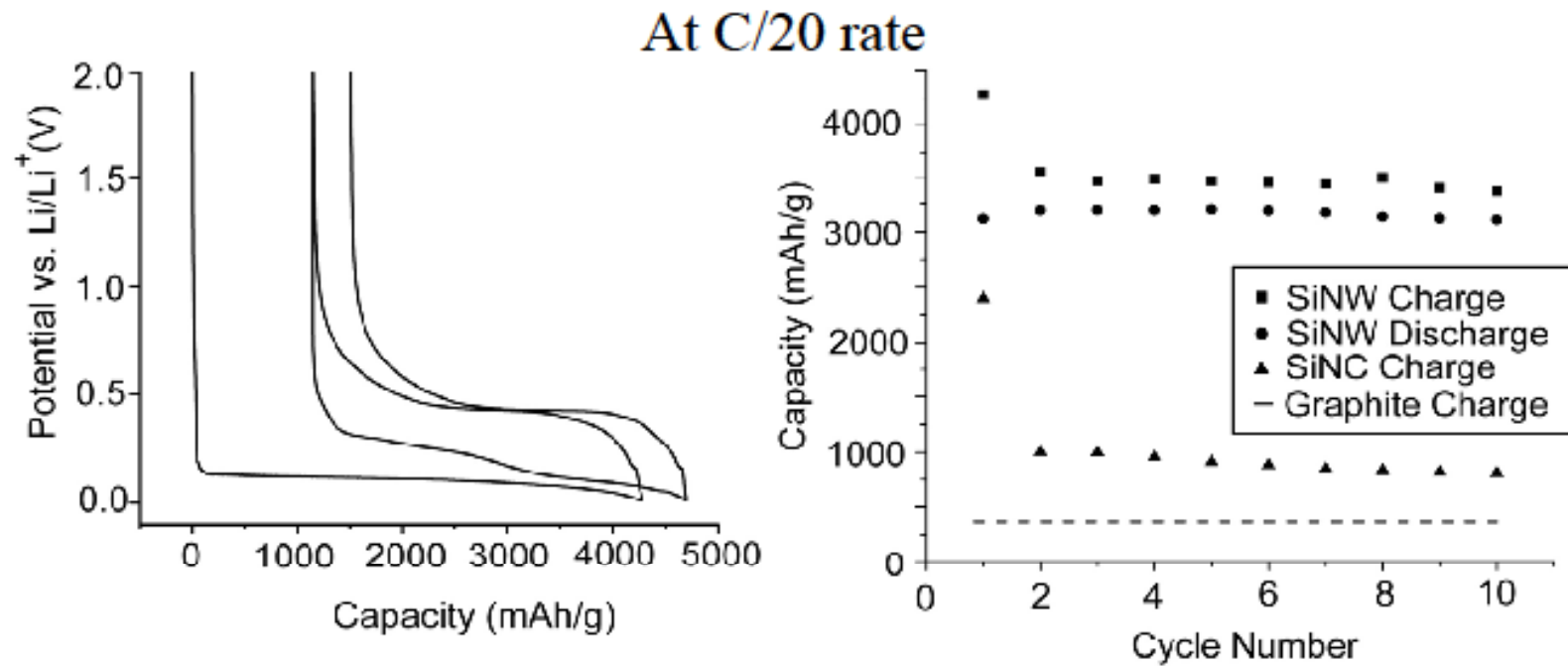
Au Nanoparticles:
Scanning Electron Micrograph



Si Nanowires
Scanning Electron Micrograph

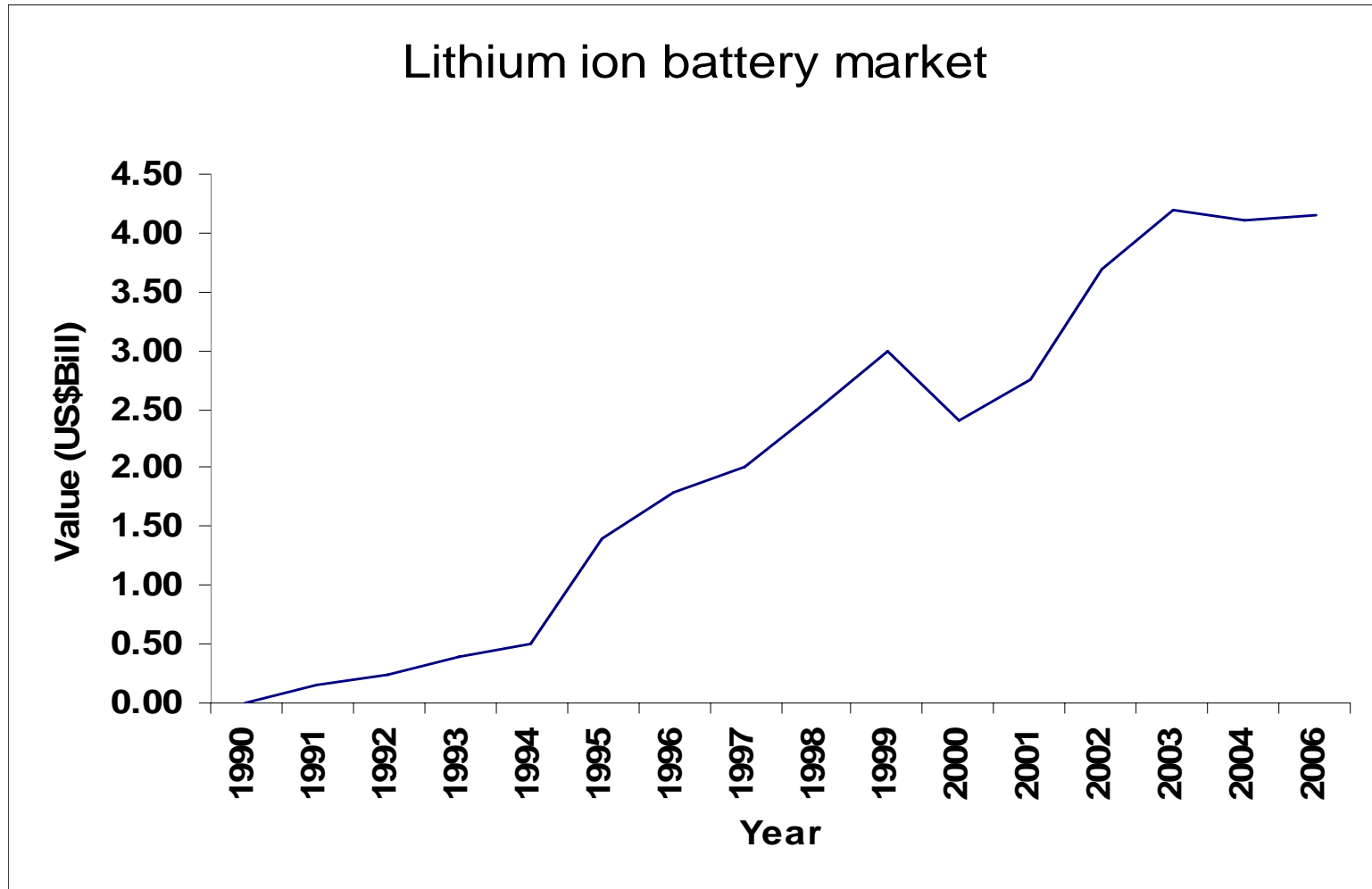


Ultrahigh Capacity Si Nanowire Anodes



- Si nanowires show 10 times higher capacity than the existing carbon anodes.
- Si nanowires show much better cycle life than the bulk, particle and thin film.

C. K. Chan, R. Huggins, Y. Cui and co-workers *Nature Nanotechnology* 3, 31 (2008)



The development of materials for LIB centres around “intercalation” and suitable electrolyte with appropriate “potential window”

INTERCALATION

- Intercalation is an equilibrium process and governed by the free energy considerations.
- Entropy factor may predominate over the enthalpy factor; the translational partition function of the intercalating species is the contributing parameter.
- The lattice in which intercalation takes place should be capable of interacting electronically without affecting the translational entropy of the intercalant.
- The value of the equilibrium constant of the intercalation deintercalation reaction should be near 1.

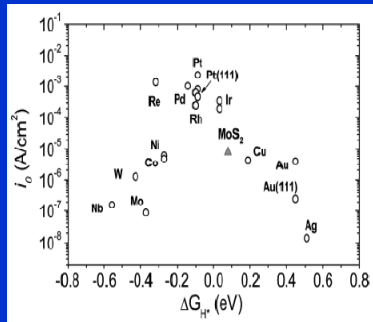
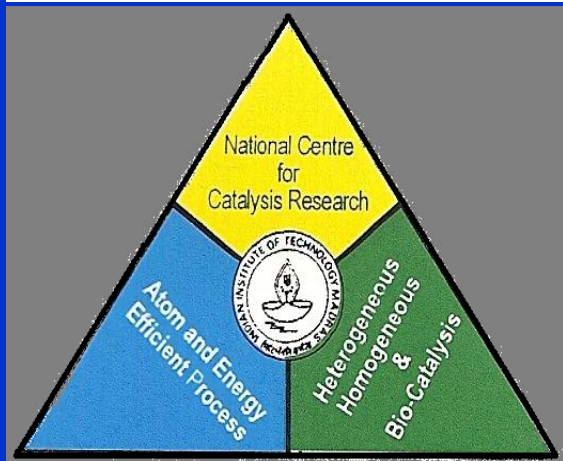
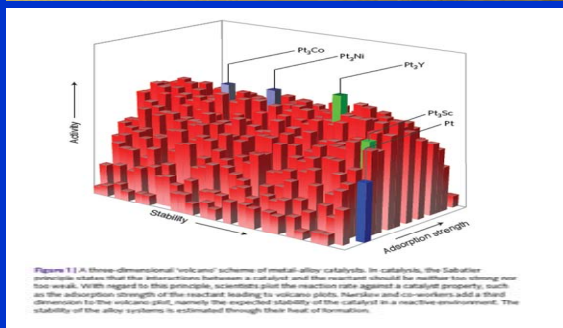
Electrolyte

- The selection of the electrolyte should take into:
- Obviously the **potential window**
- It should not be reactive with Li^+ ions, since it will decide the transport of the Li^+ ions for the intercalation reaction.
- some of the quaternary salts have been employed as supporting electrolytes but they are not considered for LIB - probably for transport control reasons; however, the choice has to be made with due considerations for the ion transport considerations as well as the necessary potential expected of the LIB. **The value should not be considered only on the basis of the Li/Li^+ couple alone.**

INTERCALATION

- Should be completely reversible
- Should be geometrically and electronically fitting to the inter planar spacing
- should be capable of electron exchange
- Other substrates like meso-porous carbons, and other pillared materials can also be thought of.

R & D CHALLENGES continues.....



THANK YOU ALL
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