Università degli Studi di Pavia
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General introduction on lithium batteries

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(pos-doc)

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General introduction on lithium batteries

- Battery: definition
- Some historical aspects
- Batteries types
- Lithium batteries
- Research activity in lithium batteries

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Batteries

Definition: devices that transform chemical energy into electricity

Every battery has two terminals: the positive **cathode** (+) and the negative **anode** (-)

Functioning

Device switched on → chemical reaction started →

→ electrons produced → electrons travel from (-) to (+)

→ **electrical work is produced**

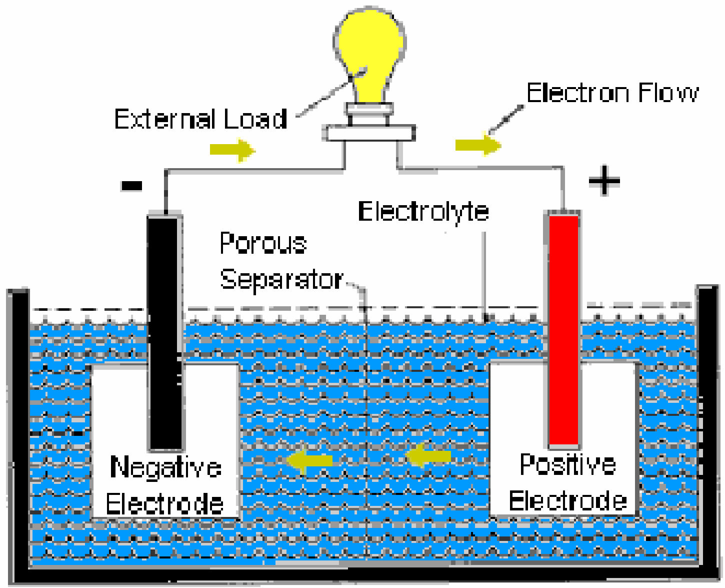
Source:http://chemistry.hull.ac.uk/lectures/mgf/Lithium-Ion%20Batteries.ppt#256,1,Lithium-Ion Batteries

Electrochemical Cell

Batteries consist of electrochemical cells that are electrically connected

An **electrochemical cell** comprises:

1. **a negative electrode to which anions (negatively-charged ions) migrate, i.e. the anode - donates electrons to the external circuit as the cell discharges;**
2. **a positive electrode to which cations (positively-charged ions) migrate, i.e. the cathode.**
3. **electrolyte solution containing dissociated salts, which enable ion transfer between the two electrodes, providing a mechanism for charge to flow between positive and negative electrodes;**
4. **a separator which electrically isolates the positive and negative electrodes.**



Source:http://chemistry.hull.ac.uk/lectures/mgf/Lithium-Ion%20Batteries.ppt#256,1,Lithium-Ion Batteries

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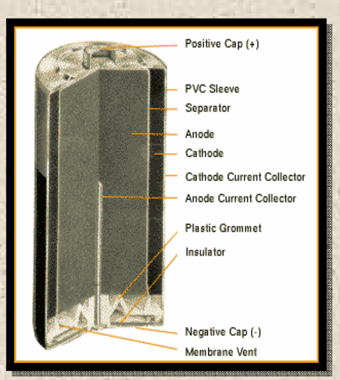
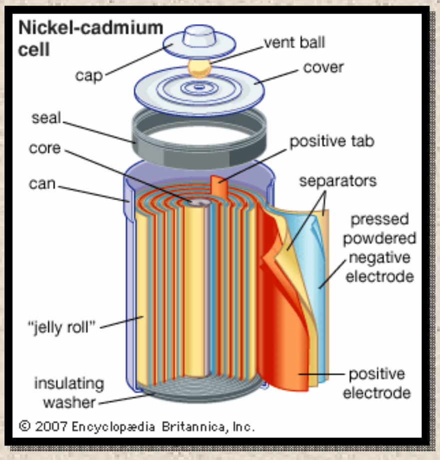
Battery History



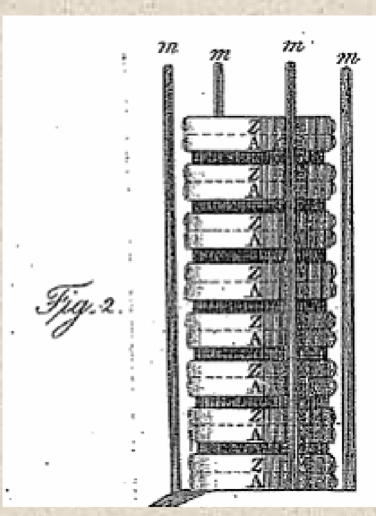


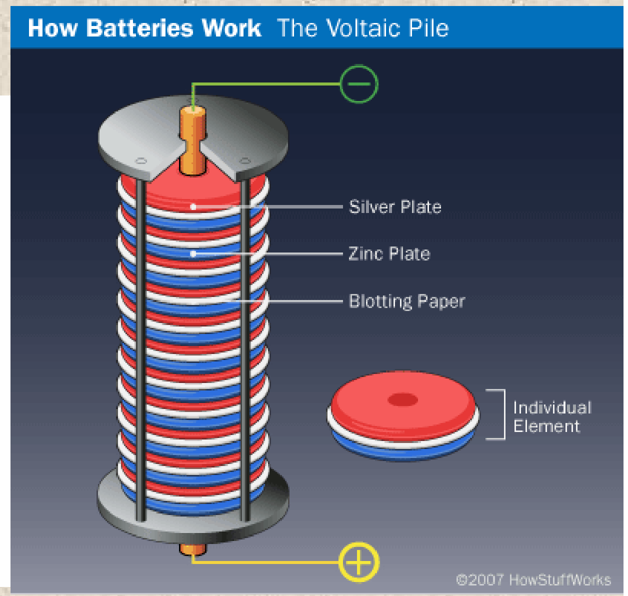
Time	Event	Name
200 B.C.	Baghdad battery	??
1791	Frog leg experiment	Galvani
1800	Voltaic piles	Volta
1802	Mass produced battery	Cruickshank
18[illegible]	Giant battery (2,000 cells)	Davy
1820	Electricity from magnetism	Ampere
1827	Ohm's law	Ohm
1833	Ionic mobility in Ag_2S	Faraday
1836	$Cu/CuSO_4$, $ZnSO_4/Zn$	Daniell
1839	Principle of the air cell	Grove
1859	Lead acid battery	Planté
1868	$Zn/NH_4Cl/C$ wet battery	Leclanché
1874	Telegraph	Edison
1878	Air Cell	Maiche
1880	High capacity lead/acid	Faure
1881	$Zn/NH_4Cl/C$ encapsulated	Thiebault
1885	Zinc-bromine	Bradley
1887	$Zn/NH_4Cl/C$ dry battery	Gassner
1891	Thermodynamics of dry cells	Nernst
1899	Nickel cadmium battery	Jungner
1900	Ni Storage batteries	Edison
1905	Ni iron batteries	Edison
1911	Automobile self-starter	Kettering
1927	Silver zinc	Andre
1930	Nickel-zinc battery	Drumm
1943	Cuprous chloride battery	Adams
1945	Mercury cell	Ruben
1950	Sealed mercury Cell	Ruben
1956	Alkaline fuel cell	Bacon
1959	Alkaline primary cell	Urry
1983	Lithium metal rechargeable	Moli
1991	Commercial lithium ion	Sony
1992	Reusable alkaline	Kordesch
1995+	Recent developments	..

Source:www.physics.nus.edu.sg/solidstateionics/LIB%20JULY2008.ppt

Battery History

- The modern battery was developed by Alessandro Volta in 1800.
  - ✓ Ingredients: Zinc, Saltwater paper, and Silver
  - ✓ An electrochemical reaction.
  - ✓ The “Voltaic Pile”





Source:http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/PowerPoints/BryanLamble.ppt

Battery History

- Shortly after Volta Leclanche´ introduced the zinc–carbon cell;
- 1859: Gaston Plante´ the lead-acid battery;
- 1899 by Waldemar Jungner with the nickel–cadmium battery.

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Primary vs. Secondary Batteries

- ✓ Primary batteries are disposable because their electrochemical reaction cannot be reversed.
- ✓ Secondary batteries are rechargeable, because their electrochemical reaction can be reversed by applying a certain voltage to the battery in the opposite direction of the discharge.

Source:http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/PowerPoints/BryanLamble.ppt

Standard Modern 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).

Battery types (cont'd)

- Nickel-cadmium: (NiCd)
  - ✓ rechargeable,
  - ✓ "memory effect"
- Nickel-metal hydride: (NiMH)
  - ✓ rechargeable
  - ✓ "memory effect" (*less susceptible than NiCd)*
- Lithium-Ion: (Li-Ion)
  - ✓ rechargeable
  - ✓ *no* "memory effect"

High energy density, power rate, cycle life, costly

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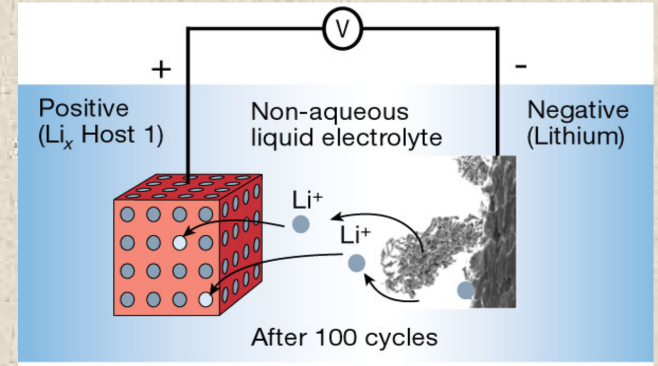
Lithium Battery Development

- Pioneering work for the lithium battery began in 1912 by G. N. Lewis but it was not until the early 1970's when the first non-rechargeable lithium batteries became commercially available.

- In the 1970's, Lithium metal was used but its instability rendered it unsafe.

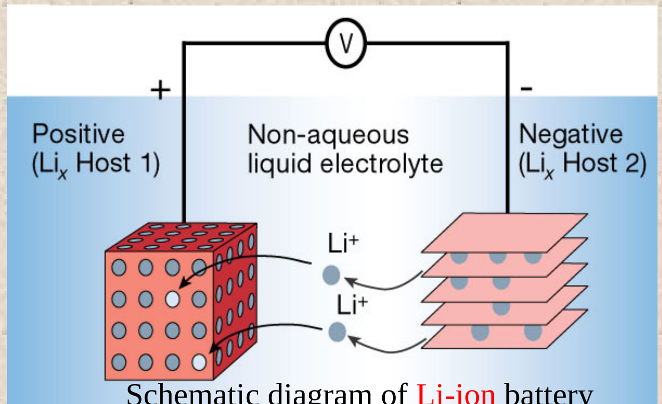


Schematic diagram of Li-metal battery

Lithium Battery Development

- Attempts to develop rechargeable lithium batteries followed in the eighties, but failed due to safety problems.

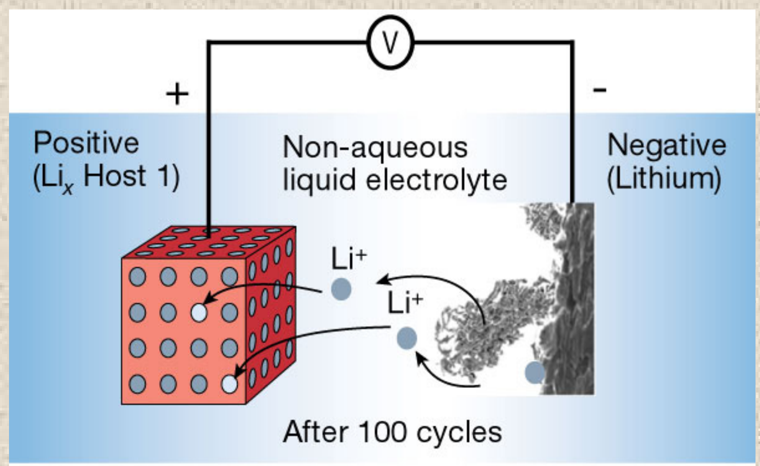
- The Lithium-Ion battery has a slightly lower energy density than Lithium metal, but is much safer. Introduced by Sony in 1991.



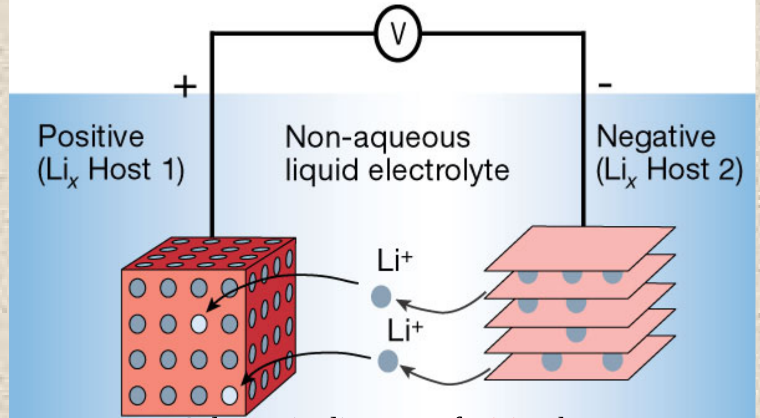
Schematic diagram of Li-ion battery

Lithium secondary battery

1972 Define the concept of chemical intercalation



Schematic diagram of Li-metal battery



Schematic diagram of Li-ion battery

Source:http://diamond.kist.re.kr/DLC/R&D_DB/images/battery/6.ppt#266,1,History of Lithium secondary battery;
J.-M. Tarascon and M. Armand , Nature, 414, 359, 2001.

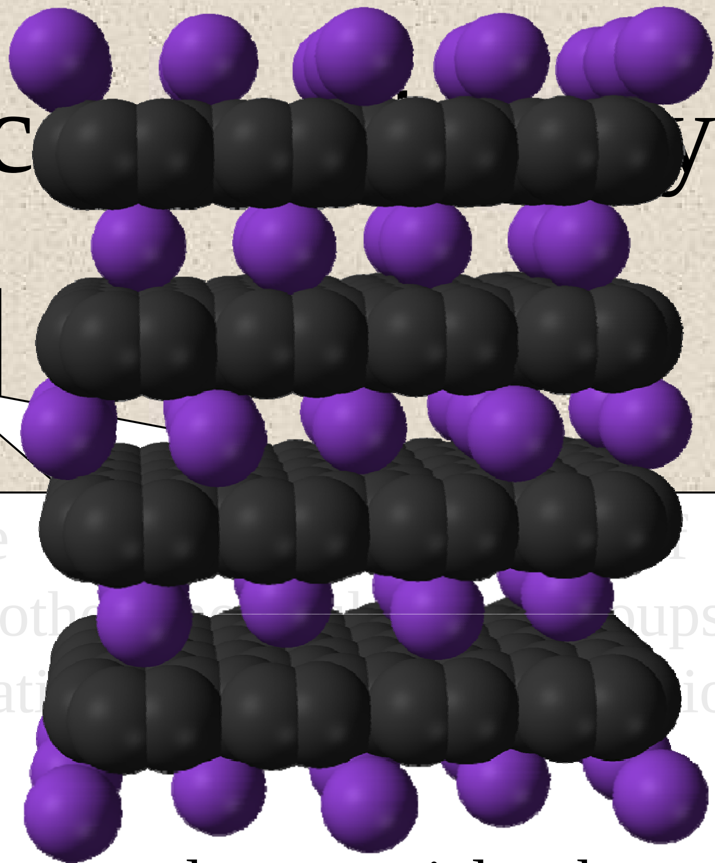
Lithium secondary battery

1972 Define the concept of chemical intercalation

In chemistry, intercalation is the reversible inclusion of a molecule between two other molecules. Ex: graphite intercalation compounds.

Lithium sec... y

1972 Define the concept of chemical intercalation



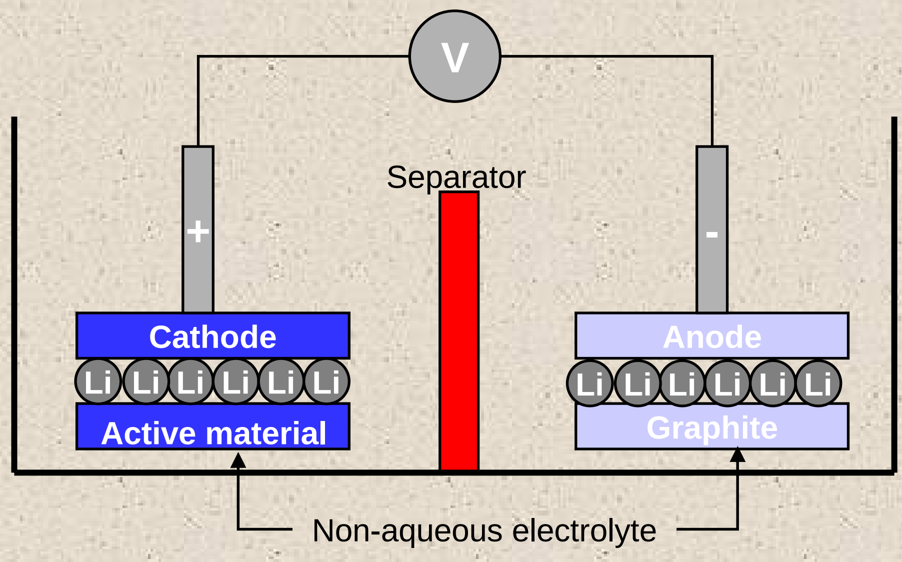
In chemistry, intercalation is the ... a molecule (or group) between two oth... ...ups). Examples include DNA intercalati... ...ion compounds, etc.

Graphite intercalation compounds are complex materials where an atom, ion, or molecule is inserted (intercalated) between the graphite layers. In this type of compound the graphite layers remain largely intact and the guest species are located in between

Figure:Space-filling model of potassium graphite KC8 (side view) from: http://en.wikipedia.org/wiki/Graphite_intercalation_compound

A Li-ion battery is a electrochemical device which converts stored chemical energy directly into electricity.

To a large extent, the cathode material limits the performance of current Li-ion batteries



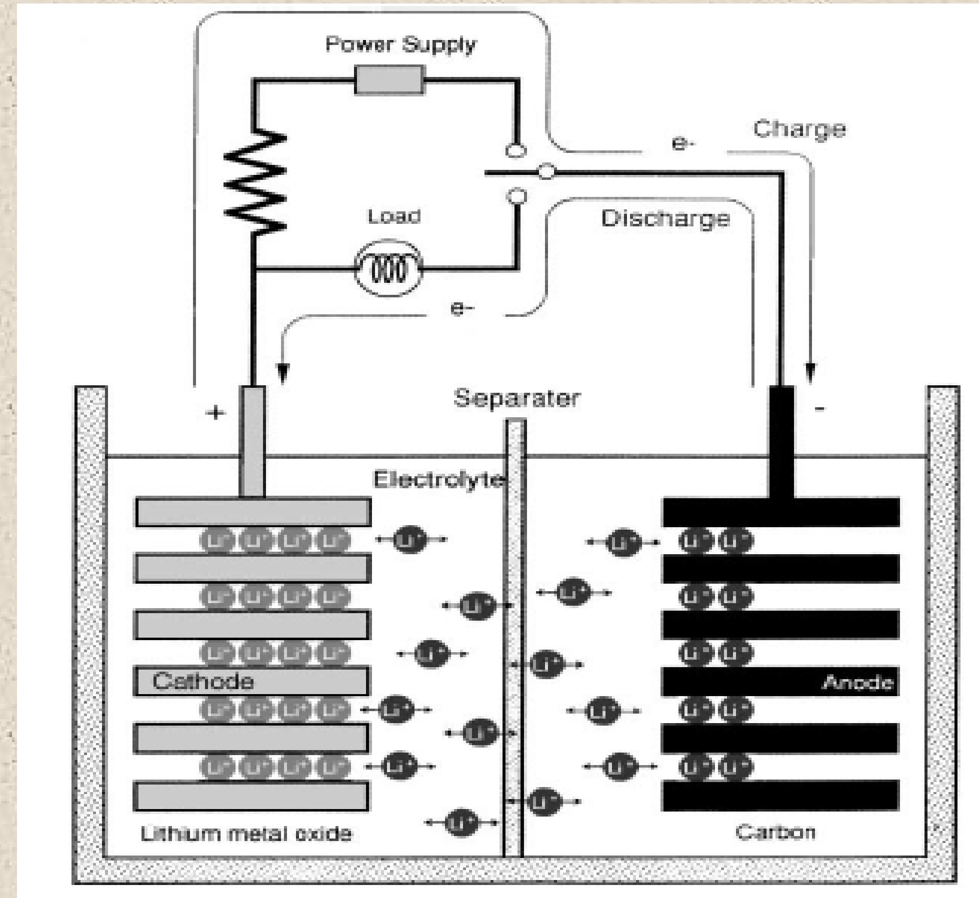
- During charging an external voltage source pulls electrons from the cathode through an external circuit to the anode and causes Li-ions to move from the cathode to the anode by transport through an liquid electrolyte.
- During discharge the processes are reversed. Li-ions move from the anode to the cathode through the electrolyte while electrons flow through the external circuit from the anode to the cathode and produce power.

Source:http://www.math.wpi.edu/MPI2008/TIAX/MPI-web.ppt#256,1,Modeling battery electrode properties

Principle of Operation

Charging

$Co^{3+} \rightarrow Co^{4+}$



Discharging

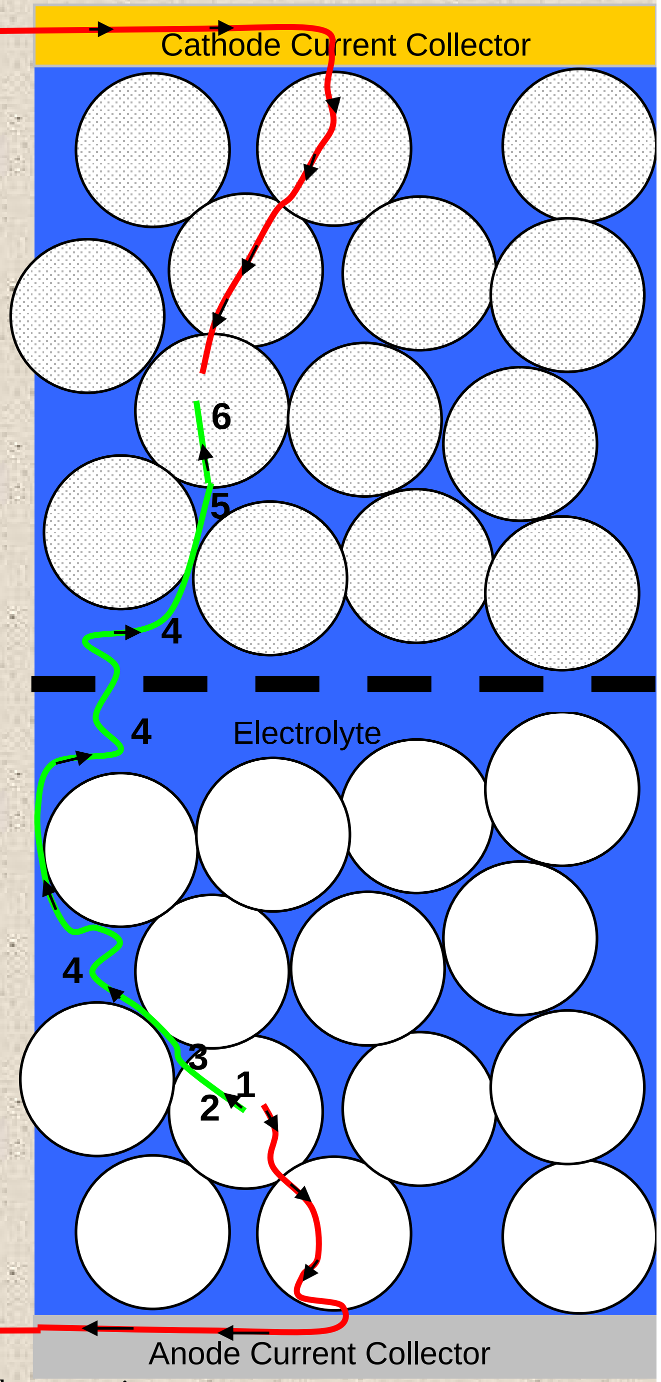
$Co^{4+} \rightarrow Co^{3+}$

$LiCoO_2$

Source: www.physics.nus.edu.sg/solidstateionics/LIB%20JULY2008.ppt

More details on the transport of Li-ions.

- **Both the anode and cathode are made from a collection of powder particles which are bonded together into a 3-D porous body (electrode).**
- **During discharge, ion transport in the electrode occurs as follows (green line)**
  1. **Li-ion starts in the bulk of a anode particle.**
  2. **It undergoes solid state diffusion in the particle.**
  3. **At the surface it disassociates from the e$^-$ and enters the electrolyte which occupies the pores of the electrode.**
  4. **The ion is transported through the electrolyte (liquid phase diffusion) to the cathode.**
  5. **In enters the cathode.**
  6. **It undergoes solid state diffusion in the cathode.**
- **At the same time, the electron must pass through the collection of solid particles to a metal current collector where it can be extracted from the cell and used to power a device (red line). It can not travel in the electrolyte.**



Source:http://www.math.wpi.edu/MPI2008/TIAX/MPI-web.ppt#256,1,Modeling battery electrode properties

Key Battery Attributes

- ✓ **Energy Density:** Total amount of energy that can be stored per unit mass or volume. How long will your laptop run before it must be recharged?
- ✓ **Power Density:** Maximum rate of energy discharge per unit mass or volume. Low power: laptop, i-pod. High power: power tools.
- ✓ **Safety:** At high temperatures, certain battery components will breakdown and can undergo exothermic reactions.
- ✓ **Life:** Stability of energy density and power density with repeated cycling is needed for the long life required in many applications.
- ✓ **Cost:** Must compete with other energy storage technologies.

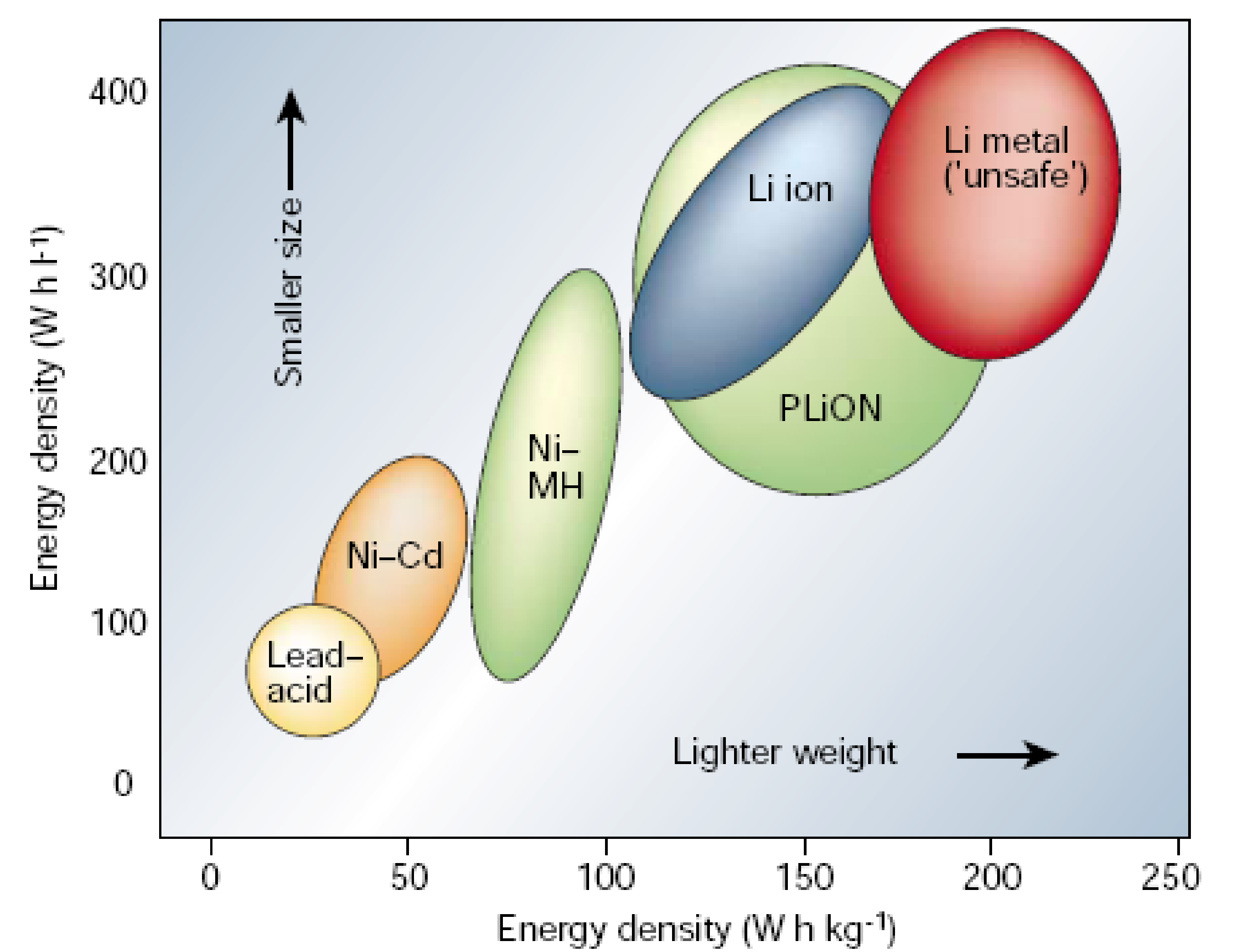
Source: http://www.math.wpi.edu/MPI2008/TIAX/MPI-web.ppt#256,1,Modeling battery electrode properties

Advantages of Using Li-Ion Batteries

- **POWER** – High energy density means greater power in a smaller package.
  - ✓ 160% greater than NiMH
  - ✓ 220% greater than NiCd
- **HIGHER VOLTAGE** – a strong current allows it to power complex mechanical devices.
- **LONG SELF-LIFE** – only 5% discharge loss per month.
  - ✓ 10% for NiMH, 20% for NiCd

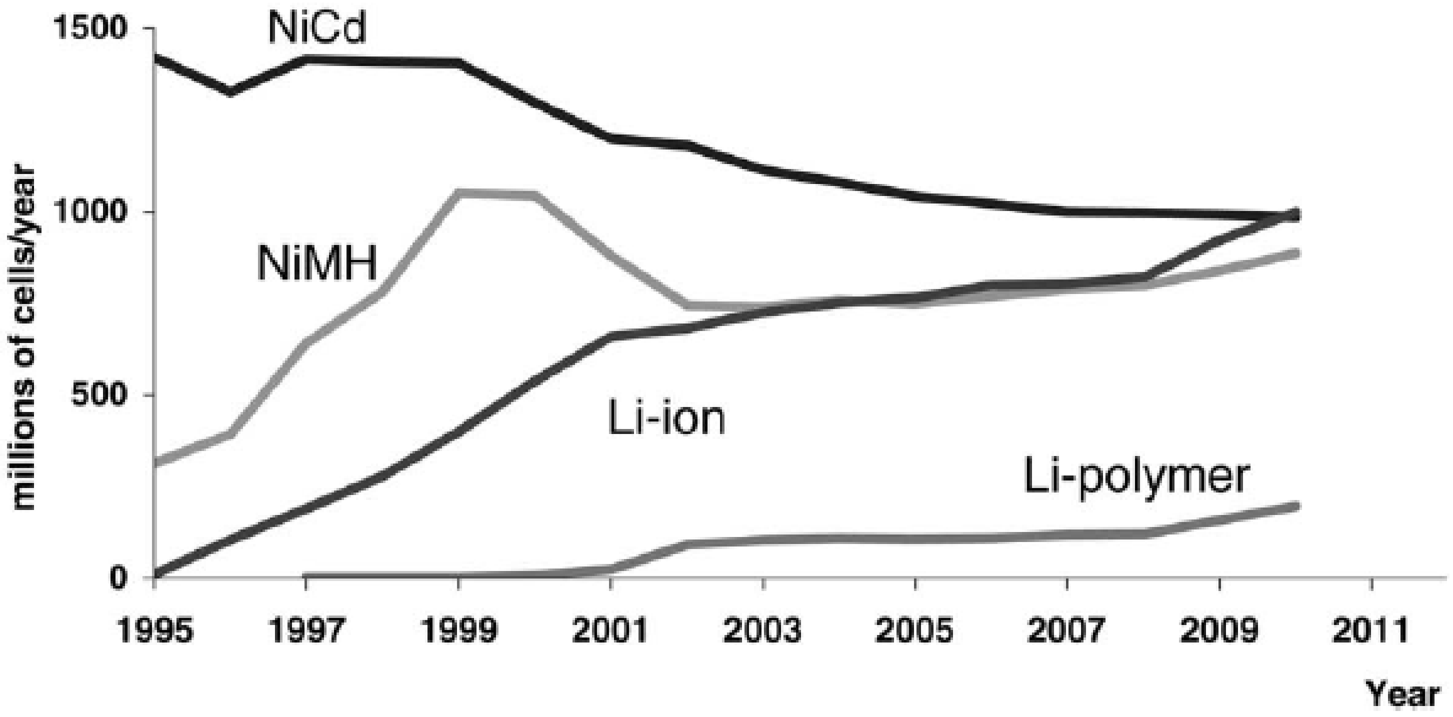
Source: http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/PowerPoints/BryanLamble.ppt

Comparison of the different battery technologies in terms of volumetric and gravimetric energy density.



Source: J.-M. Tarascon and M. Armand , Nature, 414, 359, 2001.

Lithium Battery Evolution



Market forecast for portable batteries.

Source: Scrosati, B. Journal of Power Sources 116 (2003) 4–7

Cathode Materials Challenges:

- The most desirable cathode materials are strong oxidizing agents that can react with and decompose organic electrolytes;

- In extreme cases, problems with internal shorts or improper voltages can trigger exothermic reactions, leading to thermal runaway and catastrophic failure.

Source:http://ecow.engr.wisc.edu/cgi-bin/getbig/interegr/160/johnmurphy/3lectureno/archivedle/lecture15_walz.ppt#299,1,Energy Storage, Lithium Ion Batteries, and Electric Vehicles

Electrolyte Challenges:

❑ Liquid electrolyte

✓ Problems : leakage, sealing, non-flexibility of the cells, side reactions with charged electrodes;

↓

Explosions

Source: www.physics.nus.edu.sg/solidstateionics/LIB%20JULY2008.ppt

Outcome Of Catastrophic Battery Failure

Source: http://www.ostp.gov/galleries/PCAST/zinc_matrix.ppt#295,1,Advanced Battery Technology

The New York Times

Dell Recalls Notebook Batteries

By REUTERS
Published: August 15, 2006

Filed at 10:37 a.m. ET

REUTERS

SAN FRANCISCO/TOKYO (Reuters) - Dell Inc. (DELL.O) said on Monday it will recall 4.1 million notebook computer batteries because they could overheat and catch fire, in the biggest recall in its 22-year history.

wcco.com 4

Laptop Fires Prompt Battery Recalls

May 29, 2006
8:28 am US/central
By David Schechter

Dave Brown

(WCCO) Nick Brown, 11, was playing on his Apple iBook laptop about one month ago when, like most children, he got distracted and left the room.

His mom, Cindy Brown, explains what happened next. "My husband and I were in the other room, heard a popping noise, came out and the room was filled with smoke," she said.

iTWire IT and TELCO news — Australia's #1 Technology website — don't take our word for it >>

HP issues battery fire hazard recall number 3

By Stan Beer
Wednesday, 07 June 2006

Hewlett-Packard, appears to have a serious quality control problem with its battery powered systems. The giant computer maker has just issued its third major global product recall because of potential fire hazards to consumers within just nine months.

In its latest recall, the largest to date, HP has issued a public recall notice for 679,000 model R707 digital cameras sold between August 2004 and April 2006.

Source:http://ecow.engr.wisc.edu/cgi-bin/getbig/interegr/160/johnmurphy/3lectureno/archivedle/lecture15_walz.ppt#299,1,Energy Storage, Lithium Ion Batteries, and Electric Vehicles

- None of the existing electrode materials alone can deliver all the required performance characteristics including high capacity, higher operating voltage, long cycle life and safety.

↓

RESEARCH AND DEVELOPMENT

Source: modified from http://www.kentlaw.iit.edu/faculty/fbosselman/classes/Spring2008/PowerPoints/BryanLamble.ppt

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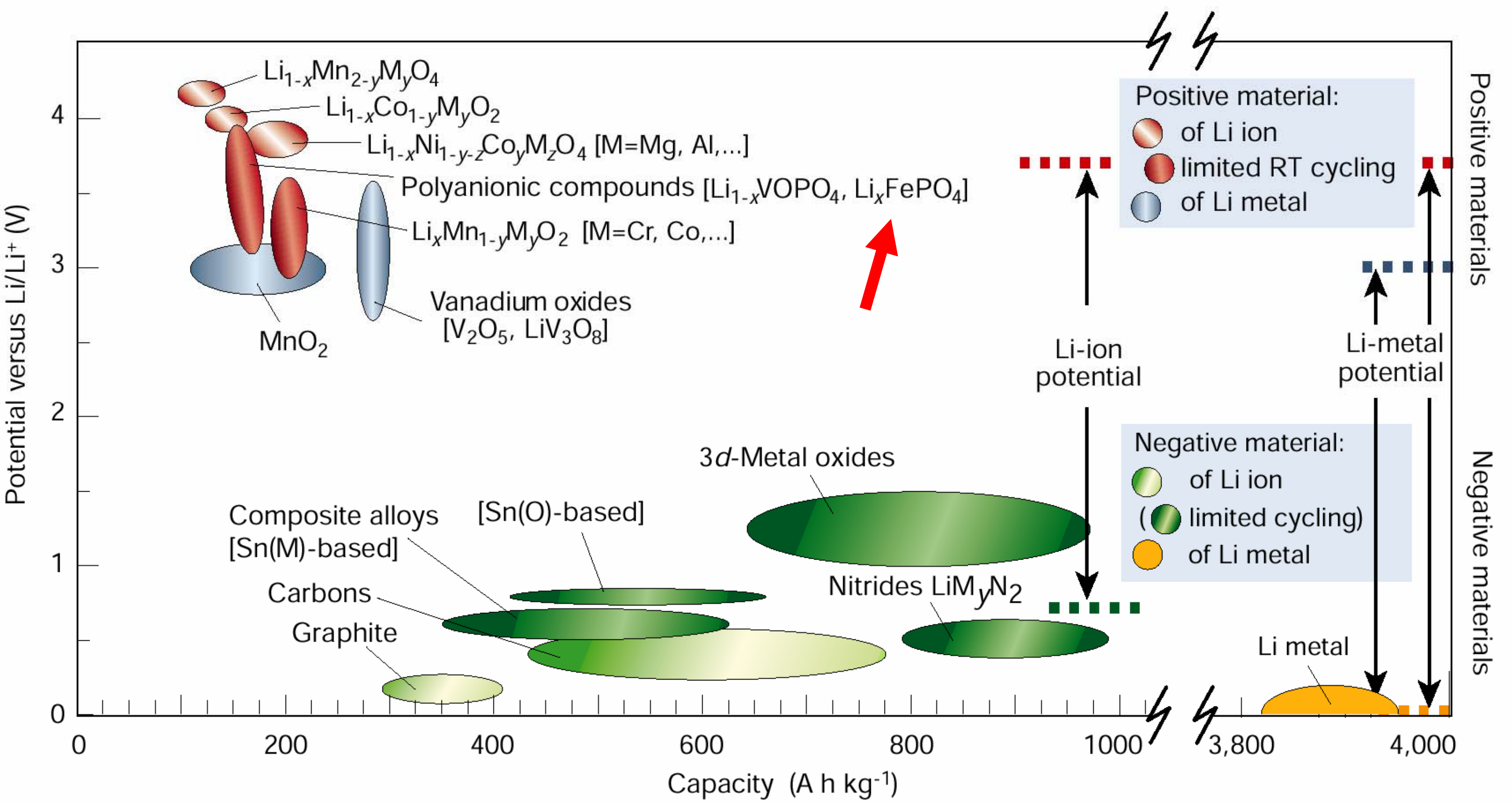
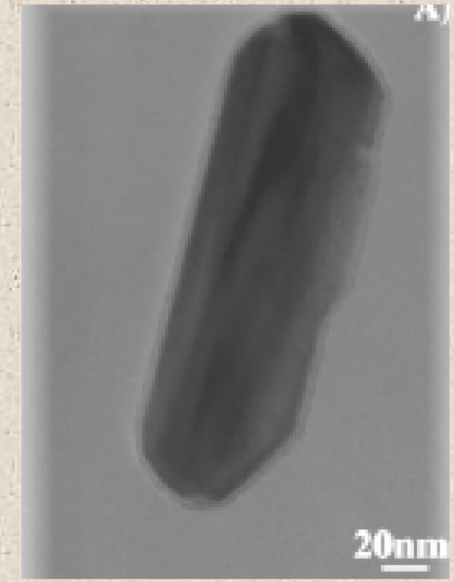
- **Research activity in lithium batteries**

Active materials for rechargeable Li-based cells

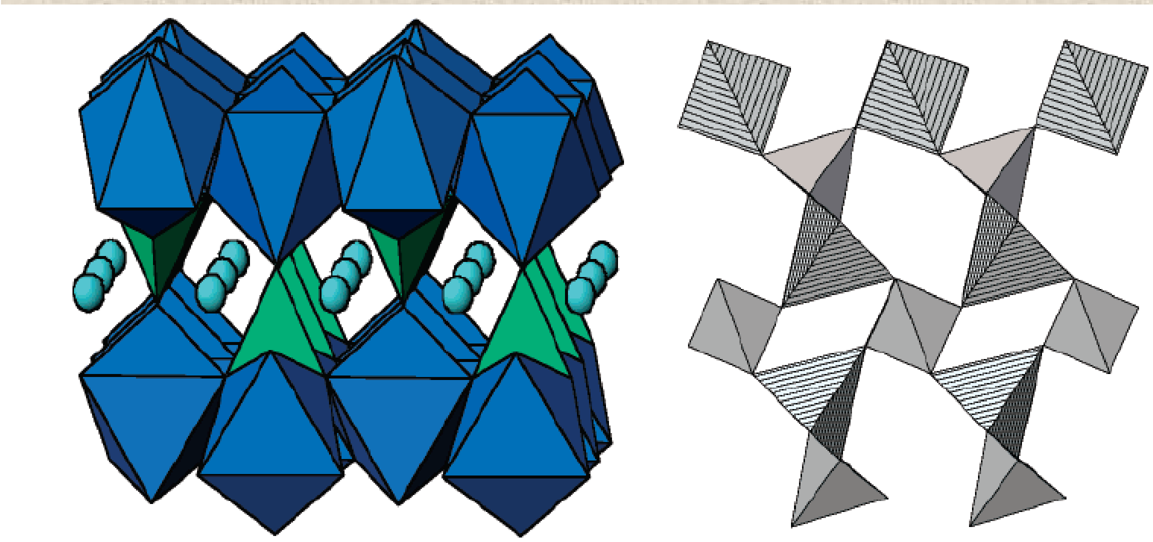


Source: J.-M. Tarascon and M. Armand , Nature, 414, 359, 2001.

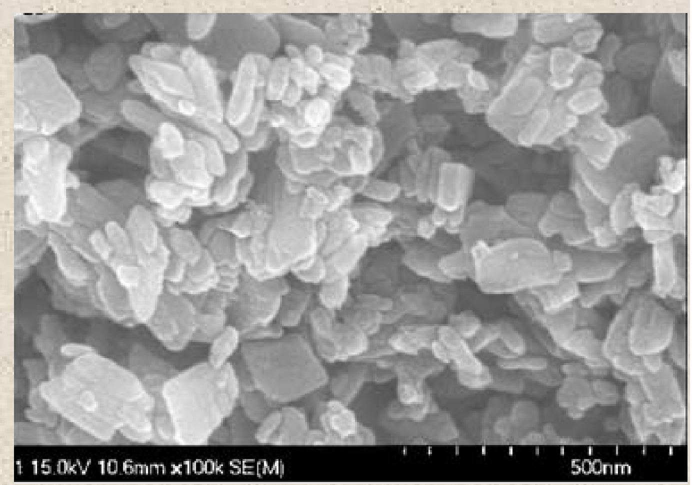
$LiFePO_4$ active material for lithium batteries



- Potentially low cost and plentiful elements;
- Environmentally benign;
- Theoretical capacity = 170 mAh/g
- Different synthetic methods: sol-gel, solid state, hydrothermal...

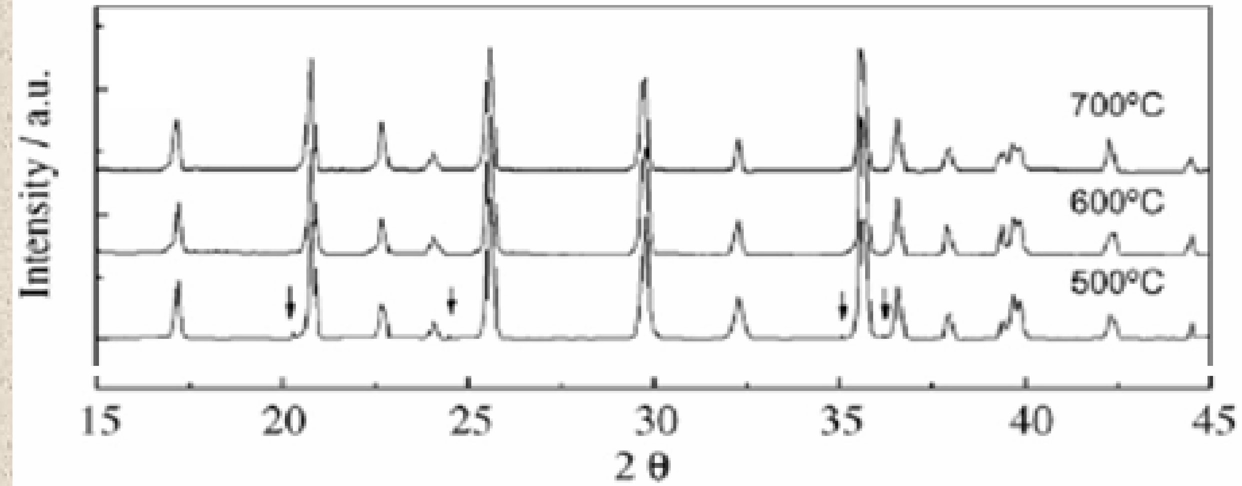


Structures of orthorhombic $LiFePO_4$ and trigonal quartz-like $FePO_4$.

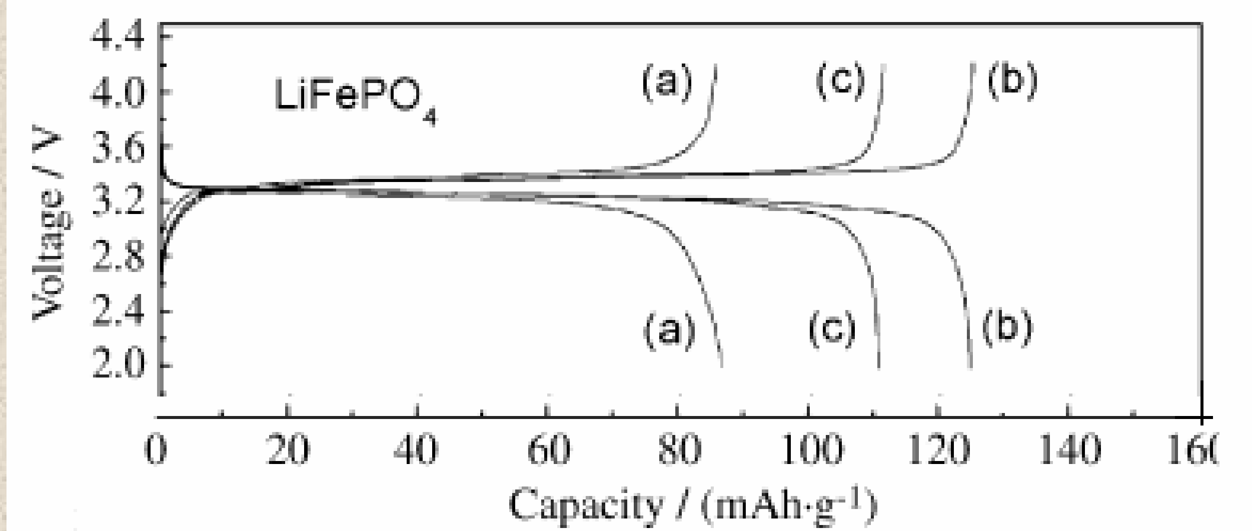


Source: M. Stanley Whittingham. Chemical Reviews, 104 (2004) 4271-4301; R. Dominko,et al. Journal of The Electrochemical Society, 152 (2005) A607-A610; Bo Jin et al. J Solid State Electrochem (2008) 12:1549–1554.

Influence of the synthesis temperature and purity



Samples	Sintering temperature (°C)		The lattice parameters			Crystallite size D_{131} (nm)	Particle size (nm)
			a (nm)	b (nm)	c (nm)		
	500	(a)	1.032	0.5996	0.4689	38	90–230
$LiFePO_4$	600	(b)	1.031	0.5998	0.4687	49	120–350
	700	(c)	1.031	0.6001	0.4686	75	150–800



Source: Modified from F. Gao et al. / Electrochimica Acta 53 (2007) 1939–1944

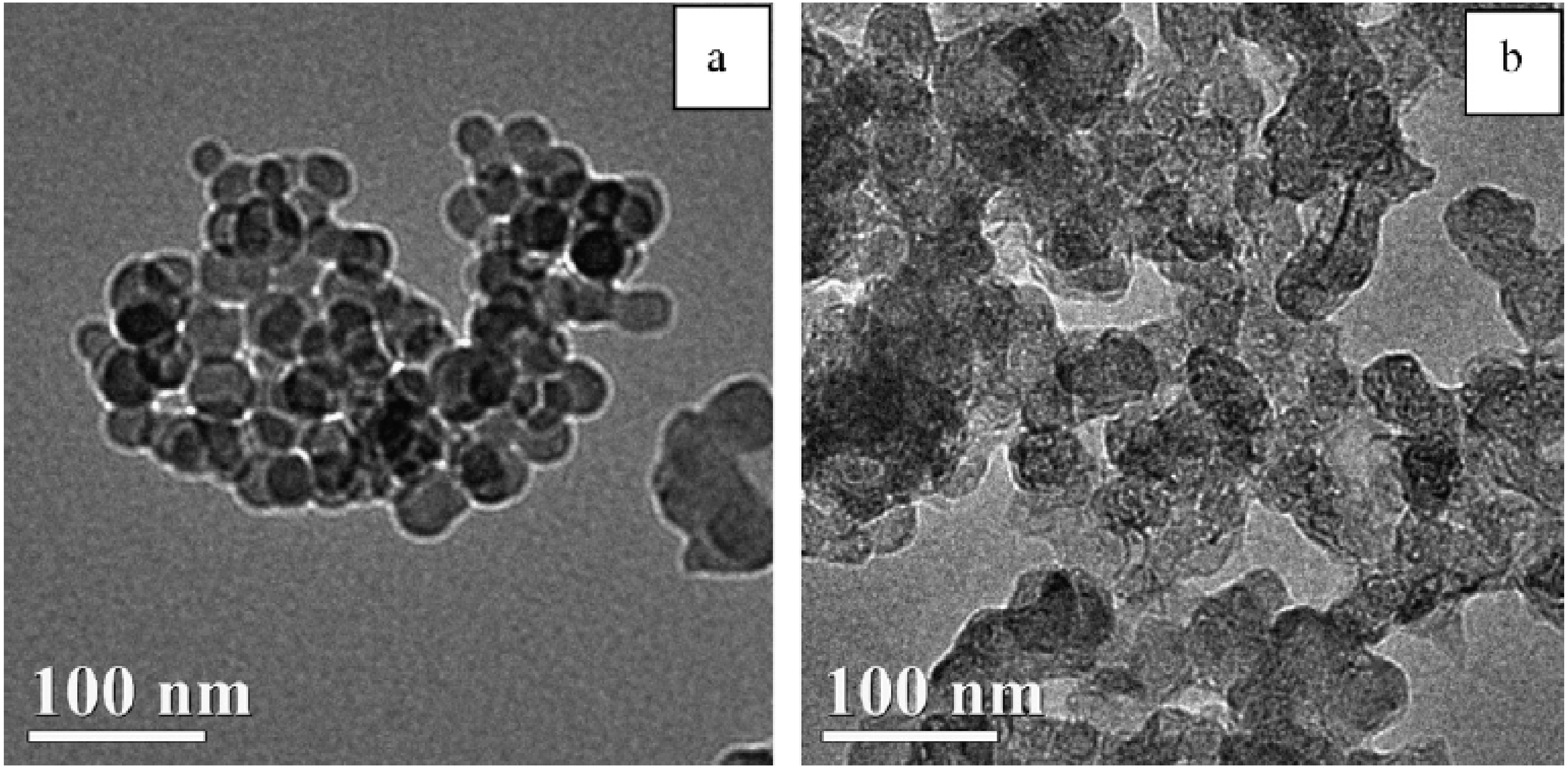


Fig. 4. TEM photograph of samples synthesized at different temperature: (a) 600 °C; (b) 700 °C.

Source:Zhihui Xu et al. Materials Chemistry and Physics 105 (2007) 80–85

Influence of the carbon coating

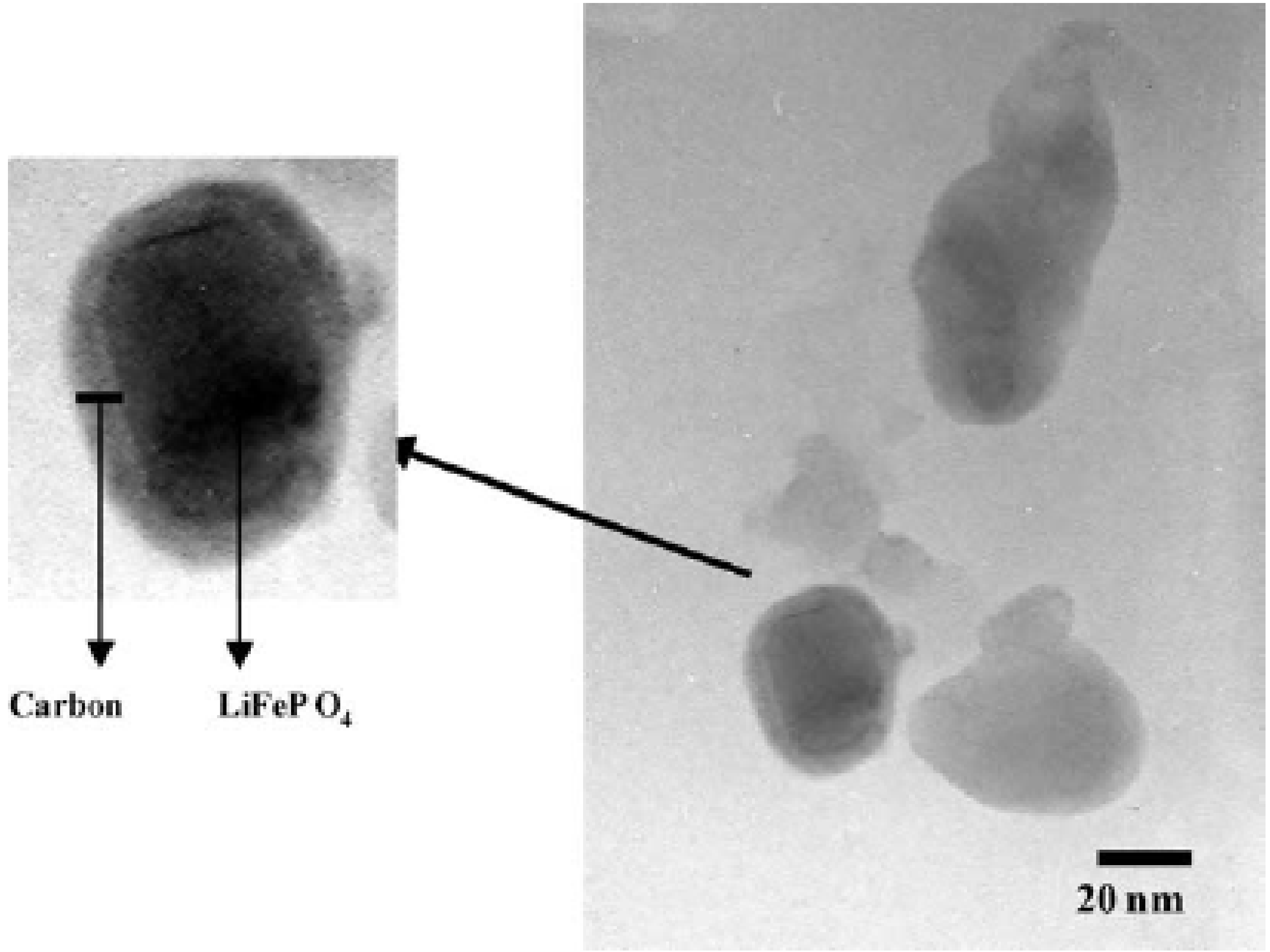


Fig. 8. TEM observation of $LiFePO_4/C$ composite prepared by MA method.

Source: S.J. Kwon et al. / Journal of Power Sources 137 (2004) 93–99

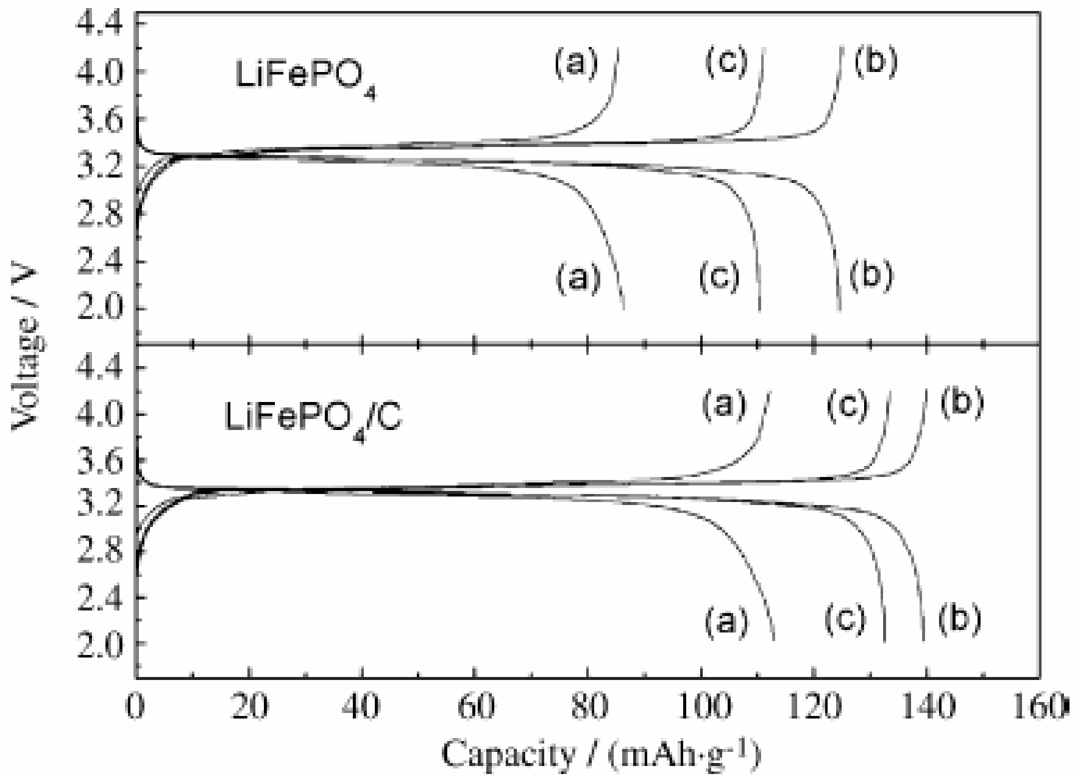
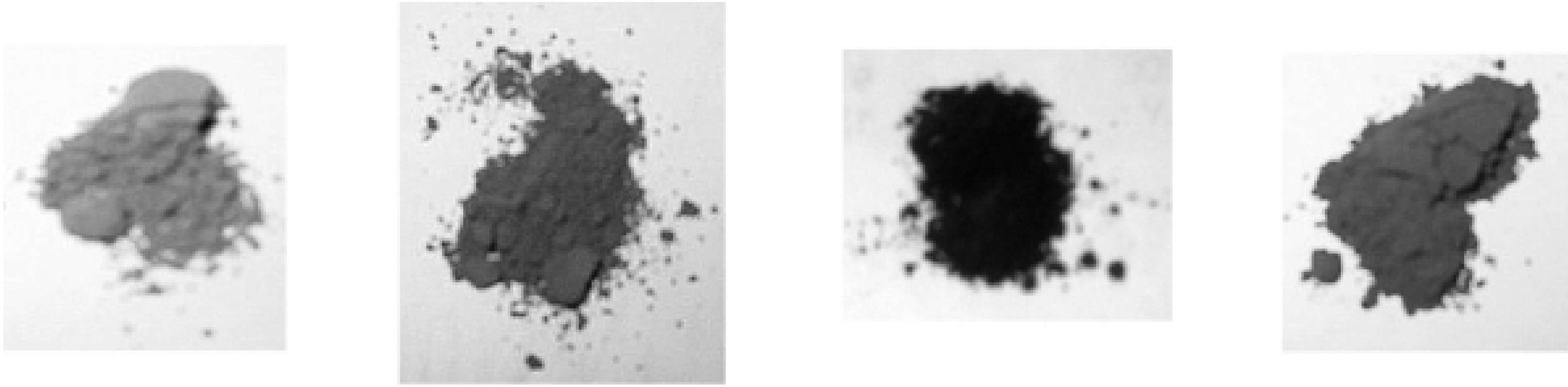


Fig. 3. Initial charge and discharge capacities of $LiFePO_4$ and $LiFePO_4$/C samples prepared at different temperatures (a) 500 °C, (b) 600 °C and (c) 700 °C at *C*/5 rate.

Source: F. Gao et al. / Electrochimica Acta 53 (2007) 1939–1944

Influence of the amount of carbon



0.3%C 0.7%C 1.15%C 1.5%C

Fig. 1. Photographs of $LiFePO_4$ powders containing varying amounts of in situ carbon. The first three samples were prepared by sol–gel synthesis following procedures outlined in Ref. [11], and the rightmost sample was prepared by the solid-state reaction described by Yamada et al. [21].

Source: M. M. Doeff et al. Journal of Power Sources 163 (2006) 180–184

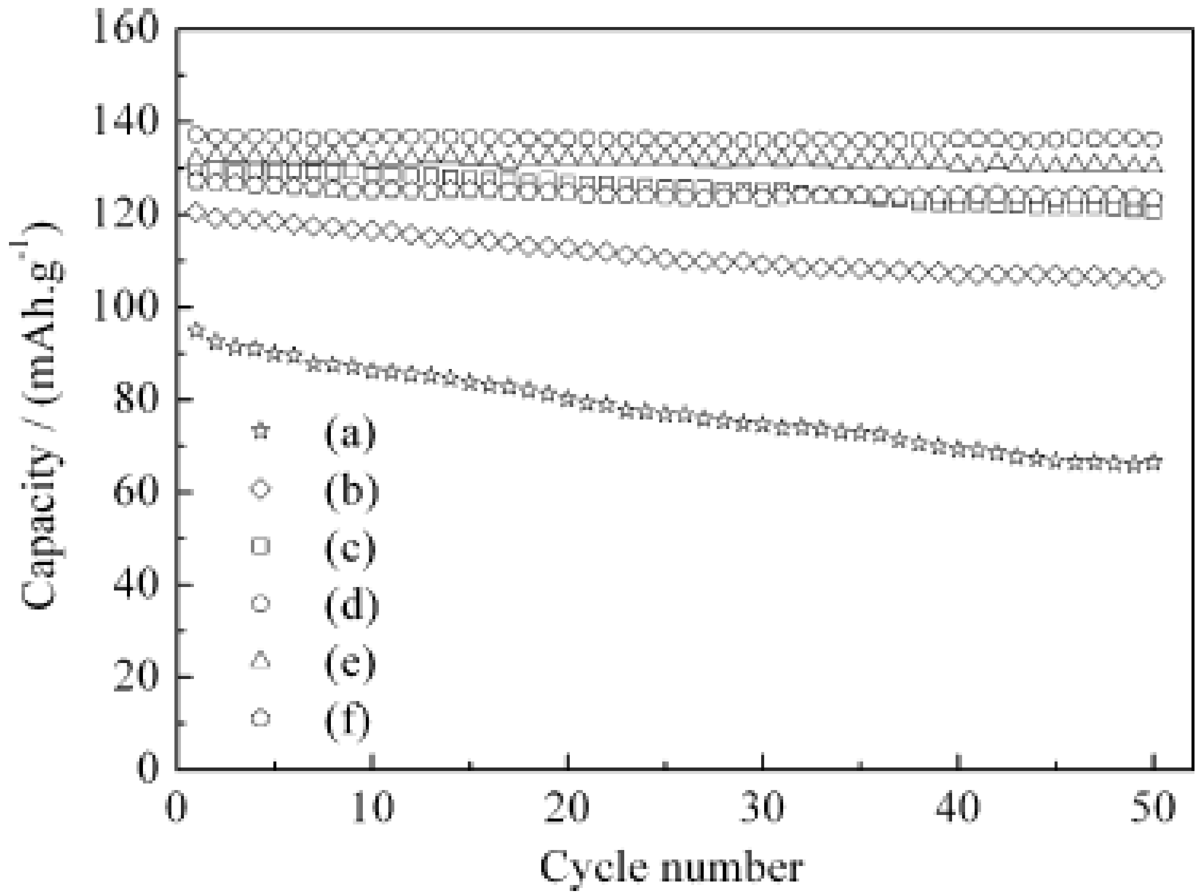
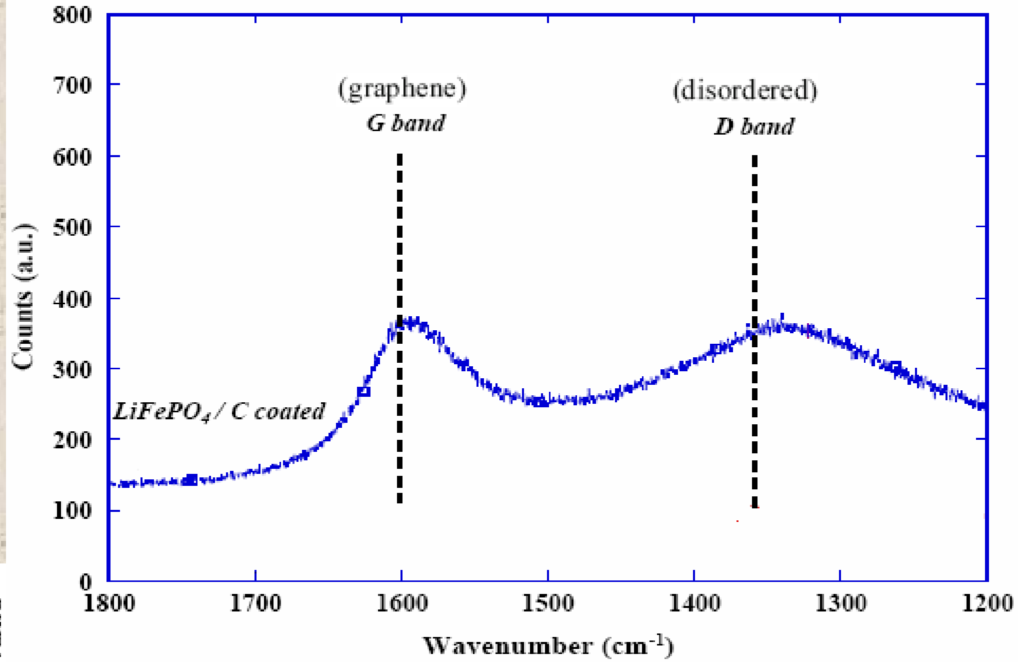


Fig. 5. Cycling performance at 1*C* rate for $LiFePO_4$/MCMB batteries. $LiFePO_4$/C composites as cathode materials are synthesized with: (a) 0 wt.%; (b) 1.7 wt.%; (c) 3.4 wt.%; (d) 5.1 wt.%; (e) 6.8 wt.%; (f) 8.5 wt.% glucose, respectively.

Source: F. Gao et al. / Electrochimica Acta 53 (2007) 1939–1944

Influence of the type of carbon



Micro-Raman spectra of a carbon-coated LiFePO4 powder.

Source: modified from F. Sauvage et al. Solid State Ionics 176 (2005) 1869 – 1876

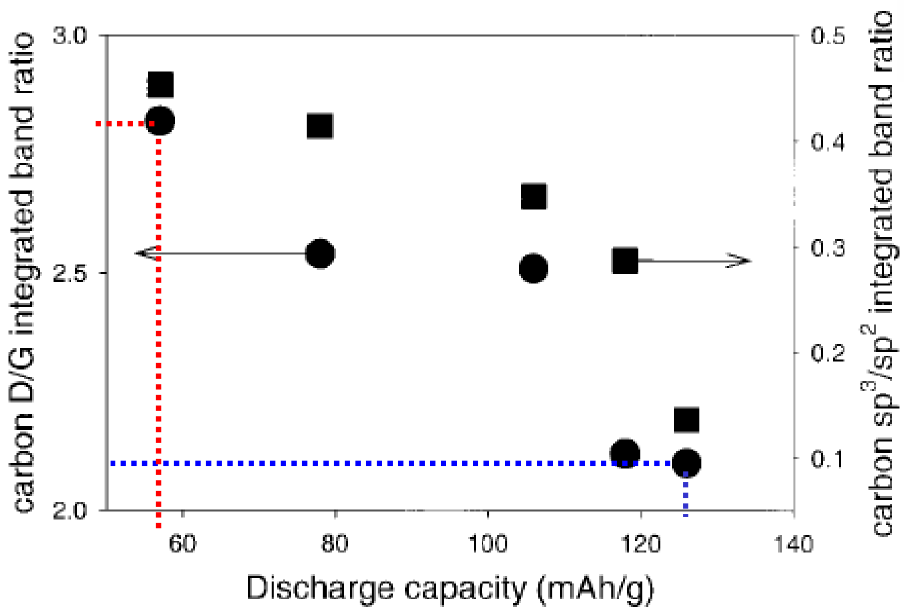


Figure 2. Electrochemical discharge capacity of $LiFePO_4$ electrodes in lithium cells *vs.* structure of residual carbon. Decreasing D/G and sp^3/sp^2 band ratios indicate increased amounts of graphene clusters in the structure.

Source:M. M. Doeff et al. Electrochemical and Solid-State Letters, 6 (2003)A207-A209.

Influence of the cathode thickness

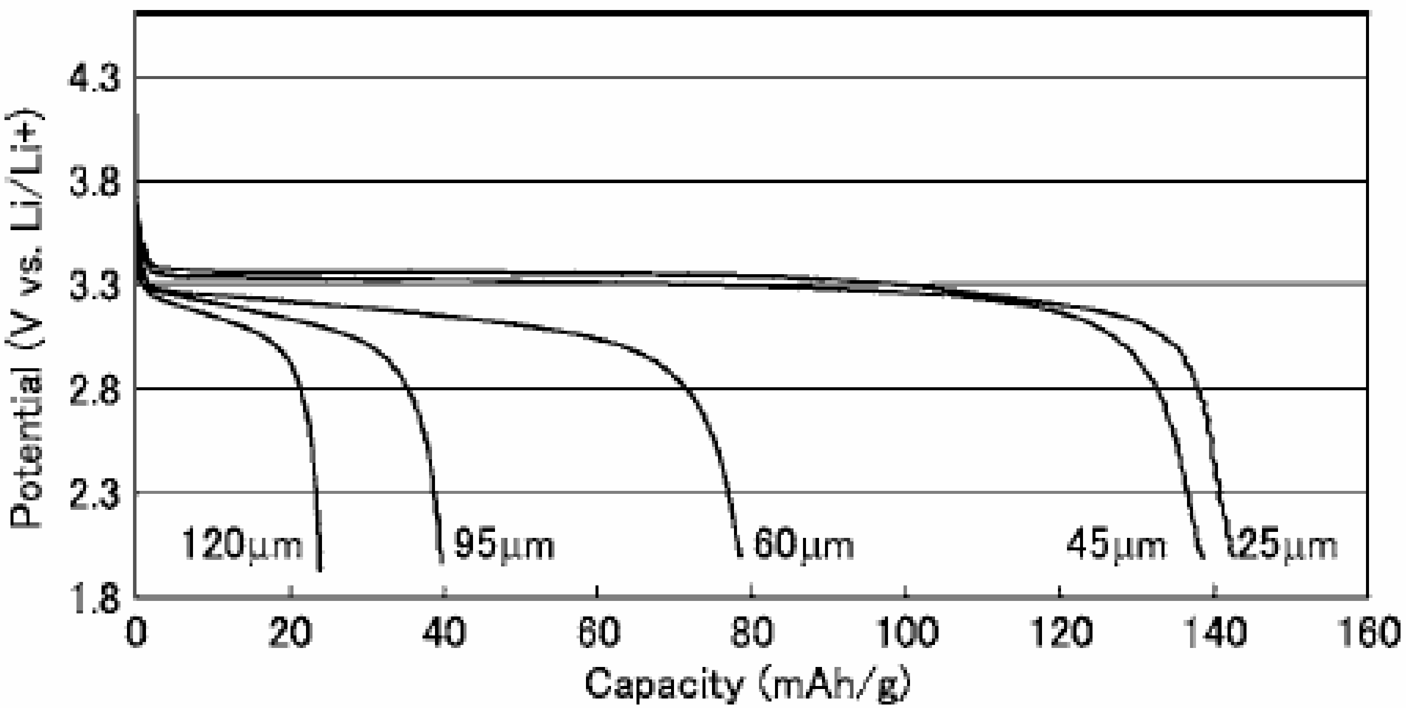


Figure 2. Discharge curves of $LiFePO_4$ electrodes with different thicknesses at a rate of 2 C in 1 M $LiPF_6$ EC/DEC = 3:7 by volume.

Cathode Composition (weight%)

70-80% LiFePO4
10-20% Carbon (carbon black or graphite)
5-10% PVDF

Source: Journal of The Electrochemical Society, 153 (2006) A835-A839.

Electrolytes

- Li salt dissolved in a solvent.
- LIB Operation range : 3.0-4.2 V, Decomposition potential of H_2O = 1.23 V Aqueous electrolyte not used

Source: www.physics.nus.edu.sg/solidstateionics/LIB%20JULY2008.ppt

Electrolytes

Italian groups involved in lithium ion battery R&D

Institution	Topic	Sponsor
Department of Chemistry, University of Rome "La Sapienza"	New cathodes materials: $LiNi_yCo_{1-y}O_2$; iron phosphates; new anode materials: lithium alloys, inter-metallic compounds. Lithium polymer electrolytes; composite lithium conducting membranes	MIUR[a], CNR[b]
Faculty of Pharmacy, University of Bologna	Manganese spinel cathode materials. Active carbon anodes	MIUR[a], CNR[b]
Department of Chemistry, University of Camerino	Large surface area carbon anodes; lithium-rich graphites	MIUR[a], CNR[b]
Department of Chemistry, University of Pavia	Lithium polymer electrolytes	MIUR[a], CNR[b]
Department of Materials Science & Chemical Eng. Polytechnic of Turin	New cathodes materials; substituted iron phosphates	MIUR[a]
Faculty of Pharmacy, University of Chieti	Iron phosphate cathodes; nano-composite polymer electrolytes.	MIUR[a]
Center for Electrochemistry of Interfaces, Rome	Substituted manganese spinel cathodes	CNR[b]
ENEA, Casaccia, Rome	Iron phosphate cathodes; polymer electrolytes; fabrication and test of lithium ion battery prototypes	MIUR[a]

[a] Italian Ministry for University and Research.
[b] Italian National Research Council.

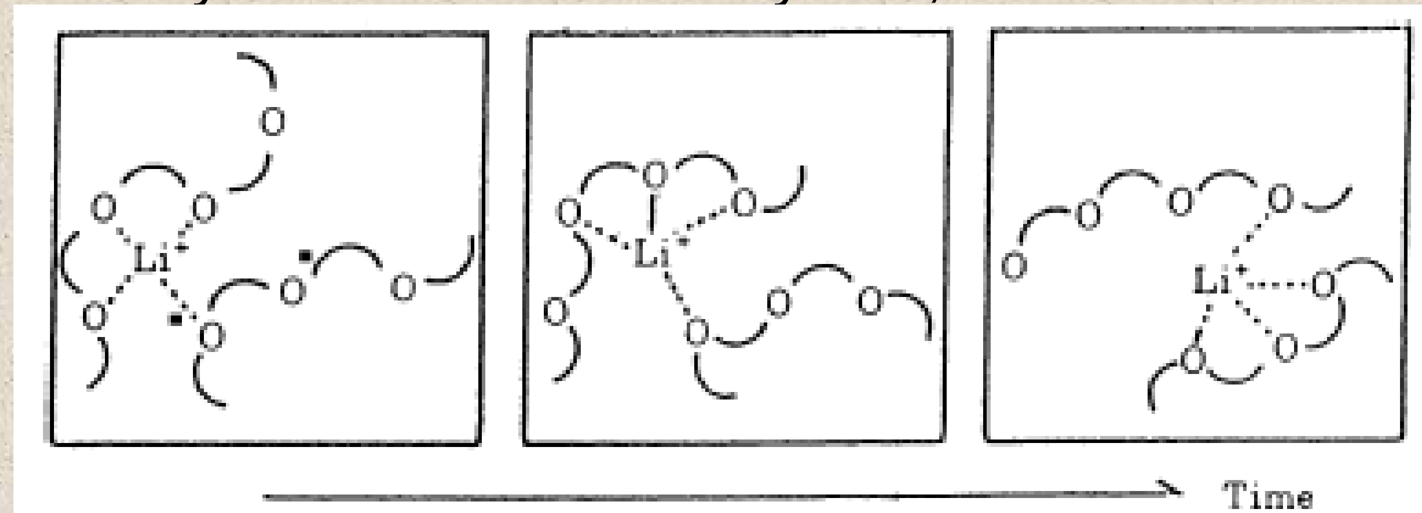
Source: Scrosati, B. Journal of Power Sources 116 (2003) 4–7

- 4 types of non-aqueous electrolytes in use: organic liquid, gel, polymer and ceramic-solid electrolytes.

Source: www.physics.nus.edu.sg/solidstateionics/LIB%20JULY2008.ppt

Polymer Electrolytes

- A salt ($LiPF_6$, $LiClO_4$, etc.) dissolved in a high-molecular-weight polymer matrix (should contain a heteroatom): Poly(ethylene oxide) PEO
- Chemically stable – contains only C-O, C-C and C-H bonds.



- Cation mobility - cation-ether-oxygen co-ordination bonds, regulation - local relaxation and segmental motion of the PEO polymer chains -> ionic conductivity of the electrolyte.

Source: www.physics.nus.edu.sg/solidstateionics/LIB%20JULY2008.ppt

Solid polymer electrolytes: advantages to liquid electrolytes

- High reversibility of the processes (high electrochemical stability);
- Solid => no risk of leakage of electrolyte;
- Can be used in a wider range of temperature;
- Lightweight
- High Flexibility
- Possibility of miniaturization.

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- Problems: low conductivities at or below room temperature (10^{-8} a 10^{-5} S/cm)

1) Preparation of crosslinked polymer networks, random, block or comb-like copolymers, withshort chains of ethylene oxide, in order to minimize crystallization;

Source:E. Quartarone et al. / Solid State Ionics 110 (1998) 1 –14

2) Utilization of doping salts which form low temperature eutectics with pristine PEO phase (plasticizing salts): ex: $LiN(CF_3SO_2)_n$(n = 2–5);

3) Utilization of organic plasticizers to increase the flexibility of the host polymer chains;

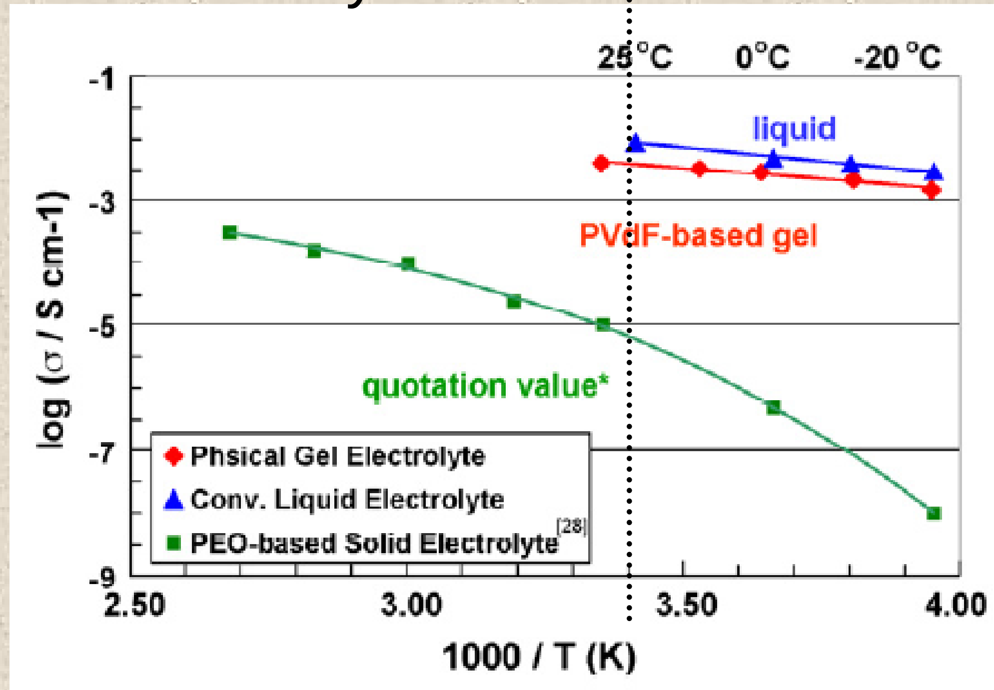
4) The addition of inorganic and/or organic additives, with the aim of reducing the crystallizing ability of the polyether host without reducing the mechanical properties of the system.

Source:E. Quartarone et al. / Solid State Ionics 110 (1998) 1 –14

- ❑ More recently: gel electrolytes: polymer matrix are solvated by a large amount of the trapped solvent;

- ✓ Polymer acts like a support;
- ✓ high value of conductivity at room temperature (10^{-2}–10^{-4} S/cm),
- ✓ ionic liquid ⟶ research activity.

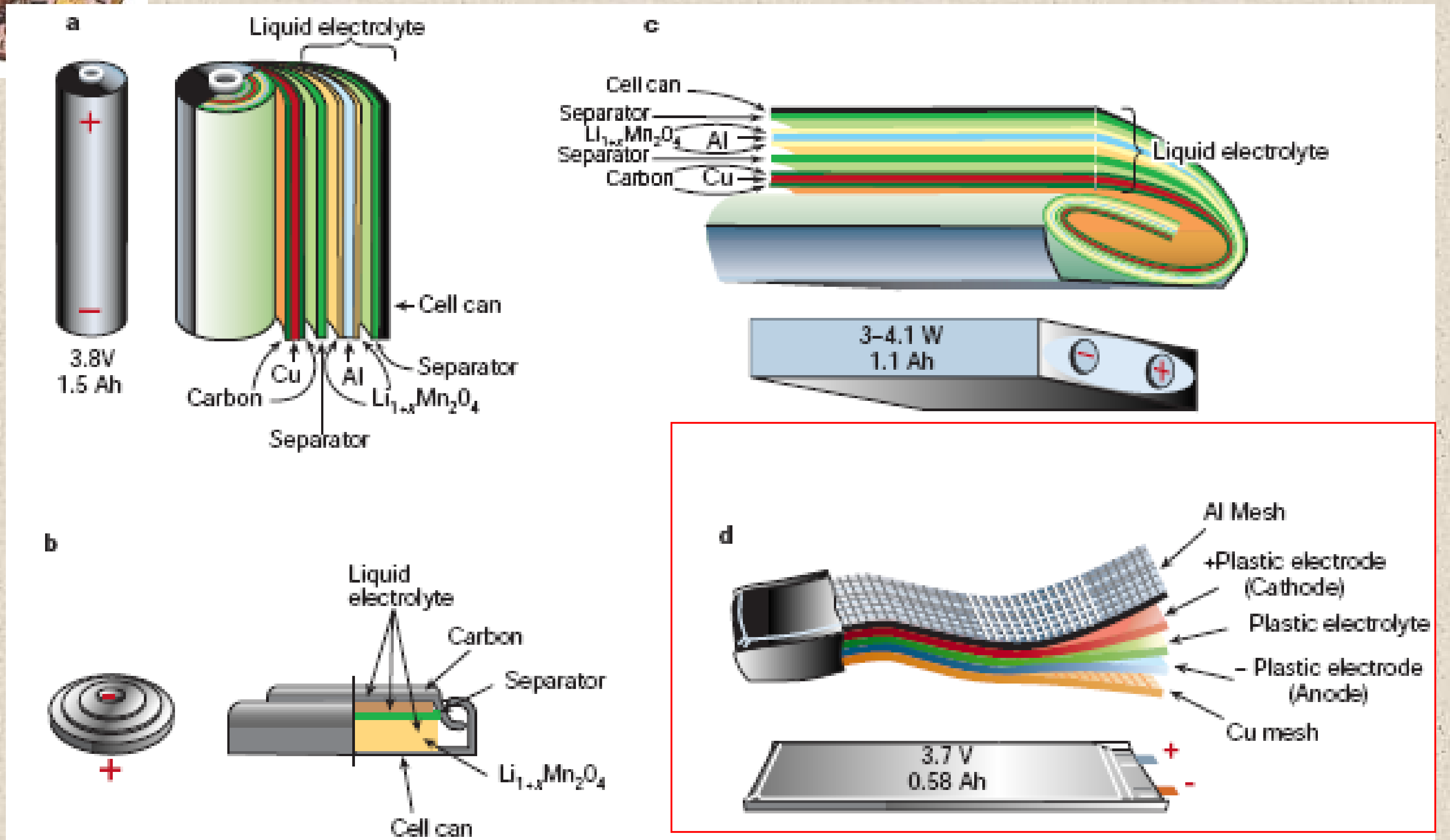
Fig. 1. Picture of PVDF gel electrolyte.



*Y. Kato, M. Watanabe, K. Sanui, N. Ogata, Solid State Ionics 40&41 632 (1990)

Source:T. Yamamoto et al. / Journal of Power Sources 174 (2007) 1036–1040

LIB Technology



Different configurations : a) cylindrical b) coin c) prismatic d) thin and flat (pLiON).

Source: J.-M. Tarascon and M. Armand , Nature, 414, 359, 2001.

Thank you for your attention!!