The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

# Workshop on "Physics for Renewable Energy"
## October 17 - 29, 2005

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# "BATTERIES"

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# ADVANCES IN BATTERY SCIENCE & TECHNOLOGY


*Bruno Scrosati*

Laboratory for Advanced Batteries and Fuel Cell Technology

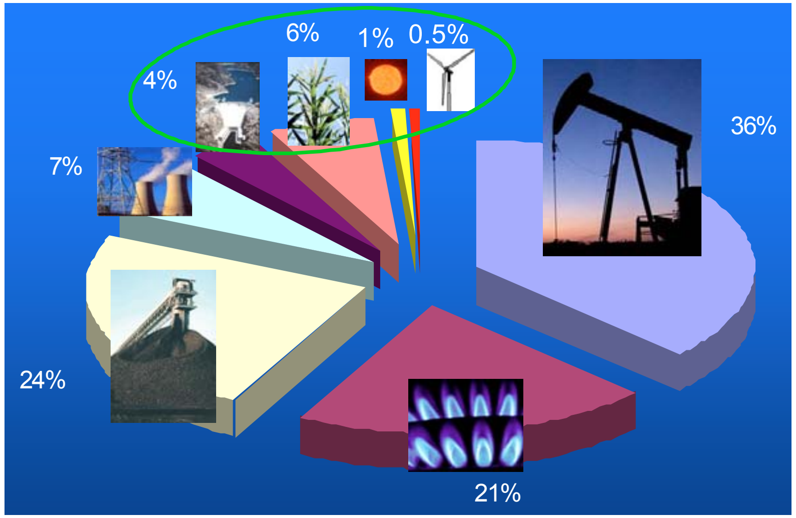
## LAB-FCT

Dipartimento di Chimica,

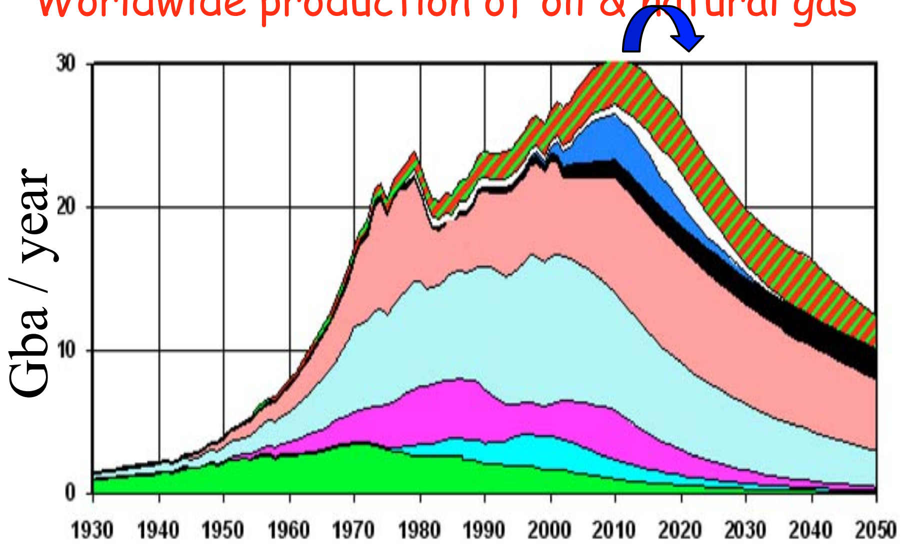
Università "La Sapienza" Rome, Italy


# Oil: social and economic stakes

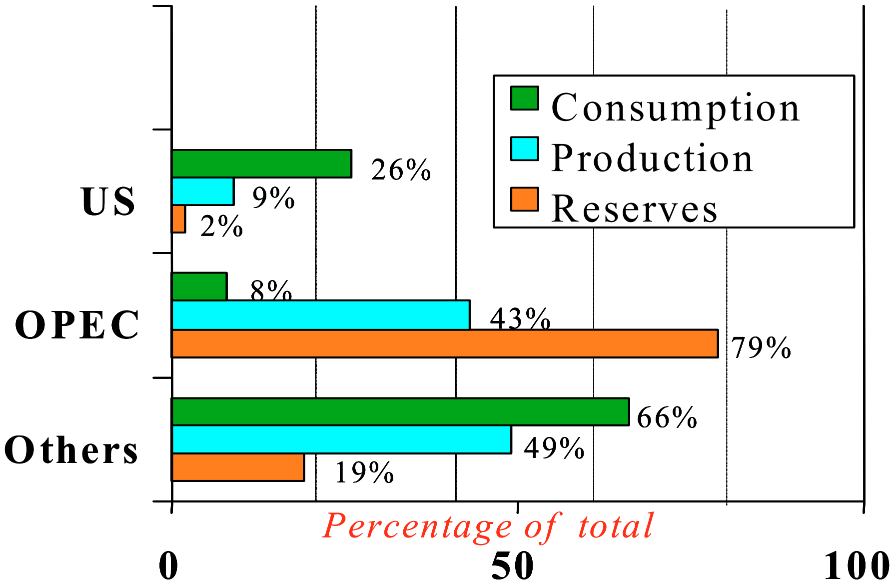
## The energy forms used in the World today?



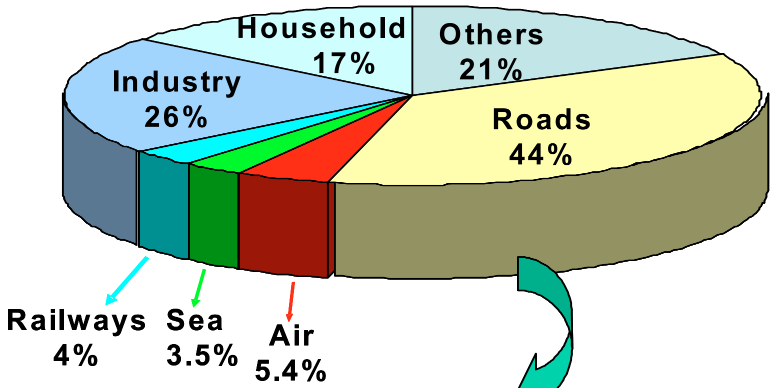

## Worldwide production of oil & natural gas




## World oil reserves/consumption




## Detailed oil consumption



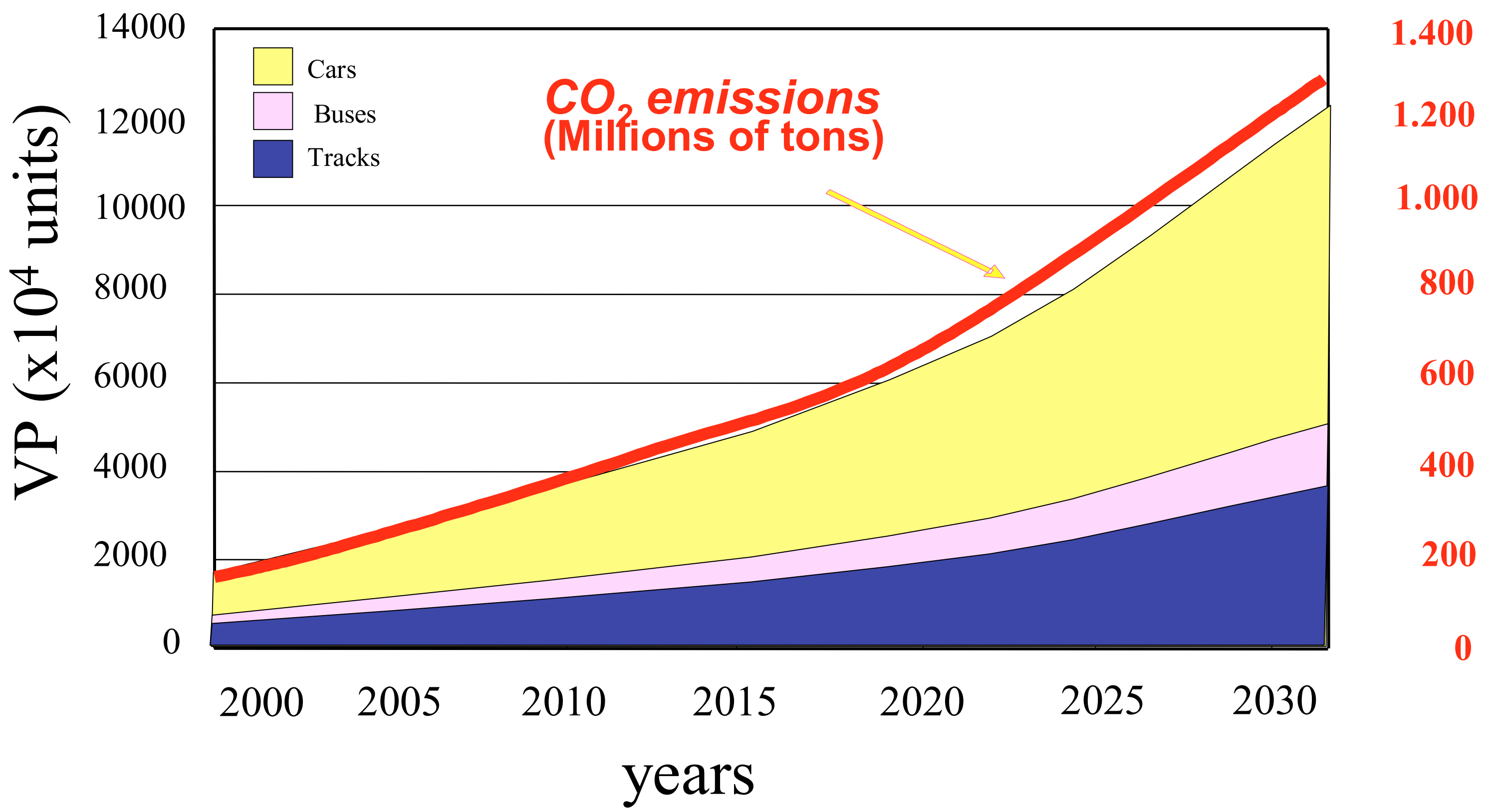

$$C_8H_{18} + 12.5\ O_2 \rightarrow 8CO_2 + 9\ H_20$$

----------- $\rightarrow NO_x$

$\rightarrow$ C.O.V

# *Foreseen evolution of $CO_2$ emissions linked to transportation in the World*

Millions of cars circulating in 2004:
294 in Europe and 307 in the U.S.




Courtesy of Dr. J-M. Tarascon, Amiens


México, D.F.

# The ten most polluted cities in the world!

1. Taiwan
2. Milan
3. Beijing
4. Urumchi
5. Mexico
6. Lanzhou
7. Chonqing
8. Jinan
9. Shijizhuang
10. Teheran

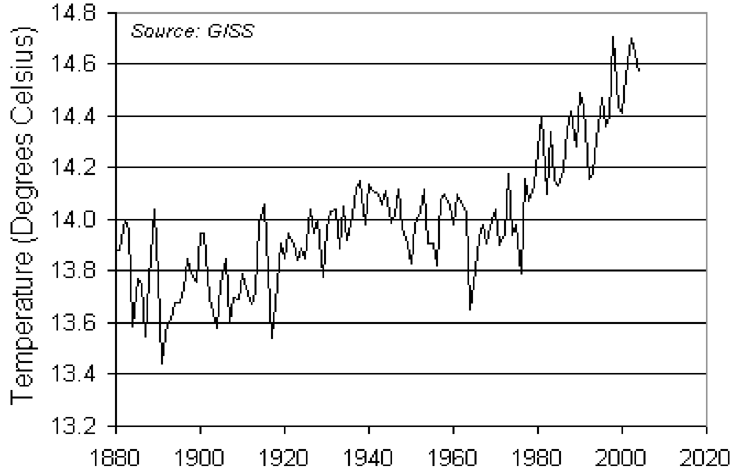
**7 in China!**

Source: J-M. Tarascon, CNRS Amiens

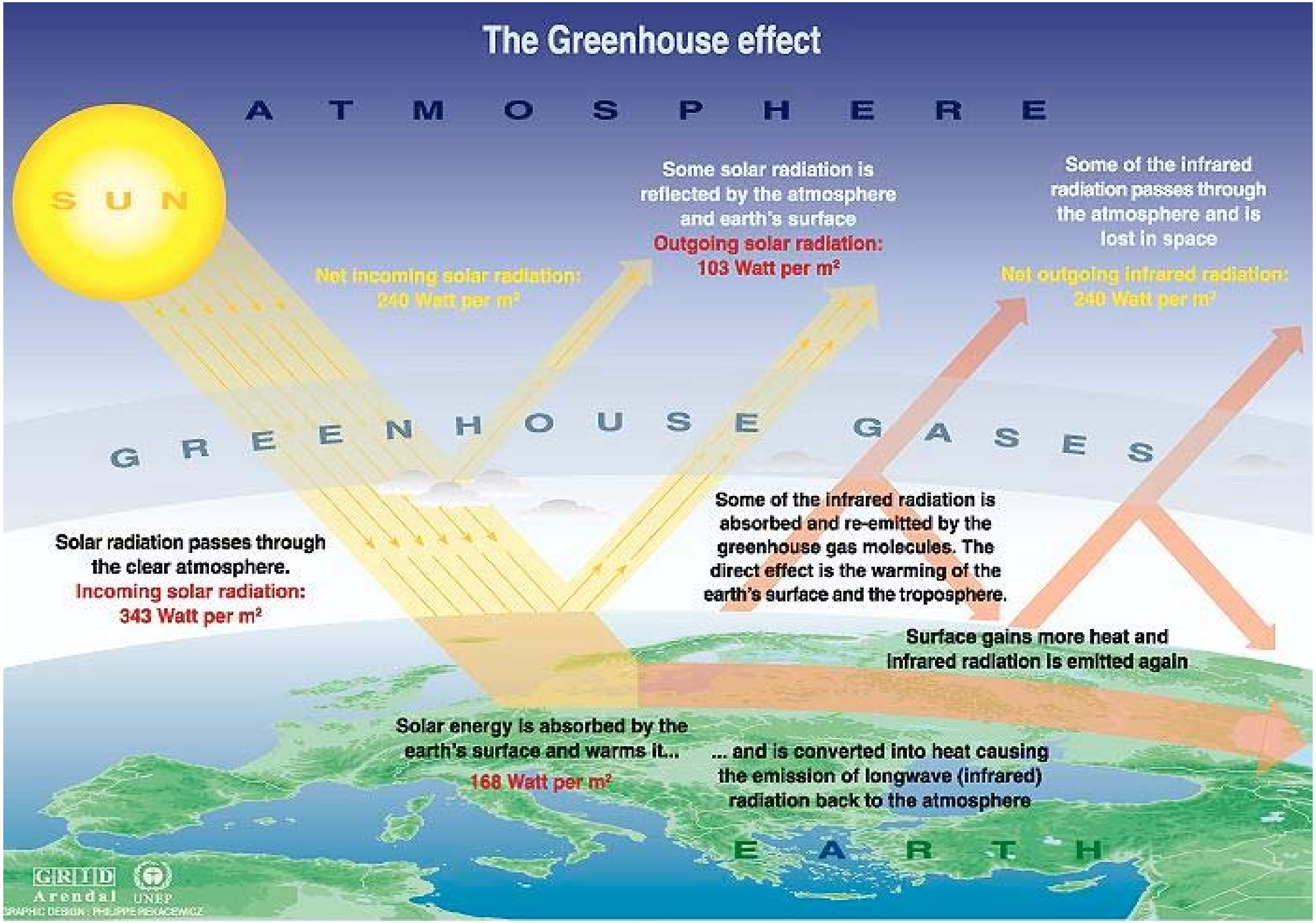
# The $CO_2$ issue

Air pollution in large urban areas

Average Global Temperature, 1880-2004

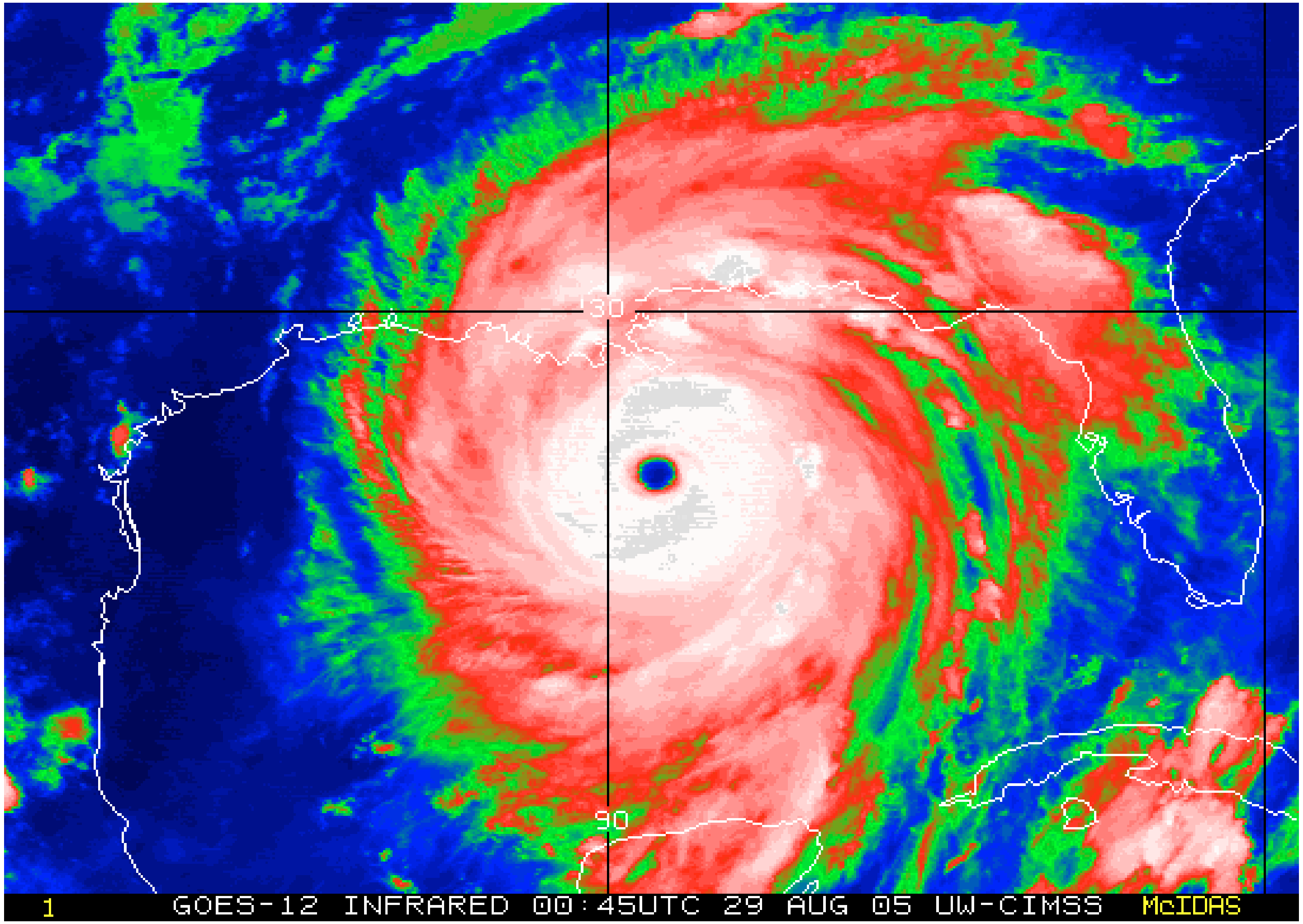



Increase of global warming
(Greenhouse effect)




Sources: Okanagan university college in Canada, Department of geography, University of Oxford, school of geography; United States Environmental Protection Agency (EPA), Washington; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge university press, 1996.

Hurricanes get energy flux from water evaporation from the oceans




Pseudo-color IRF image of Katrina in the Gulf (from NASA)

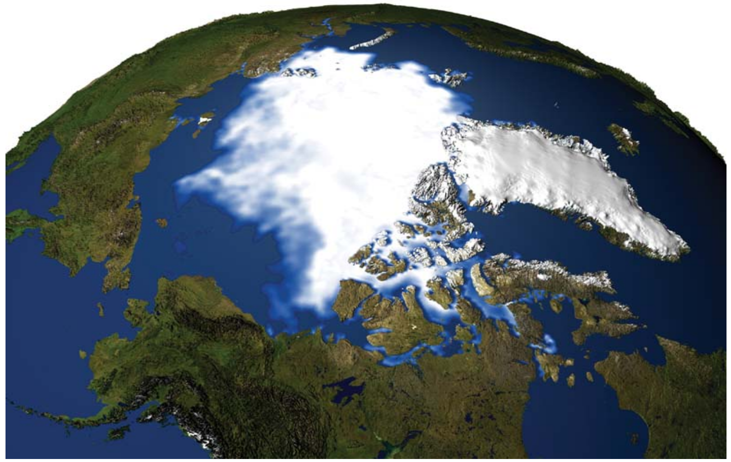
# New Orleans flood

# Hurricane Rita in Cuba

# The $CO_2$ issue

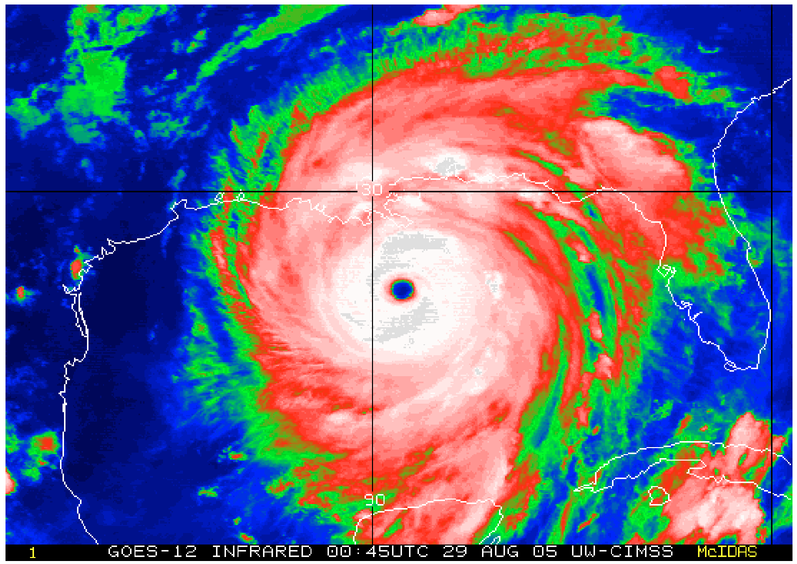
## Unusual natural disasters!

Icecap melt in Artic



Glacier extension in N.P.

Devastating hurricanes



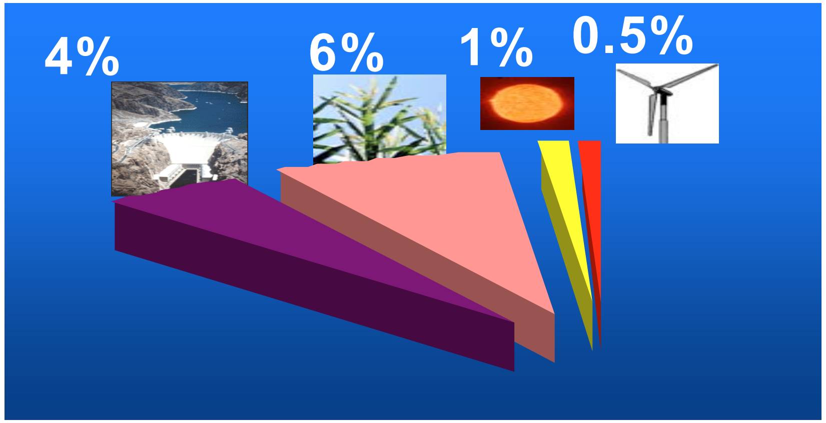

Pseudo-color IRF image of Katrina in the Gulf (from NASA)

Drowning of rivers

Amazon river in Brazil

To control environment pollution and..

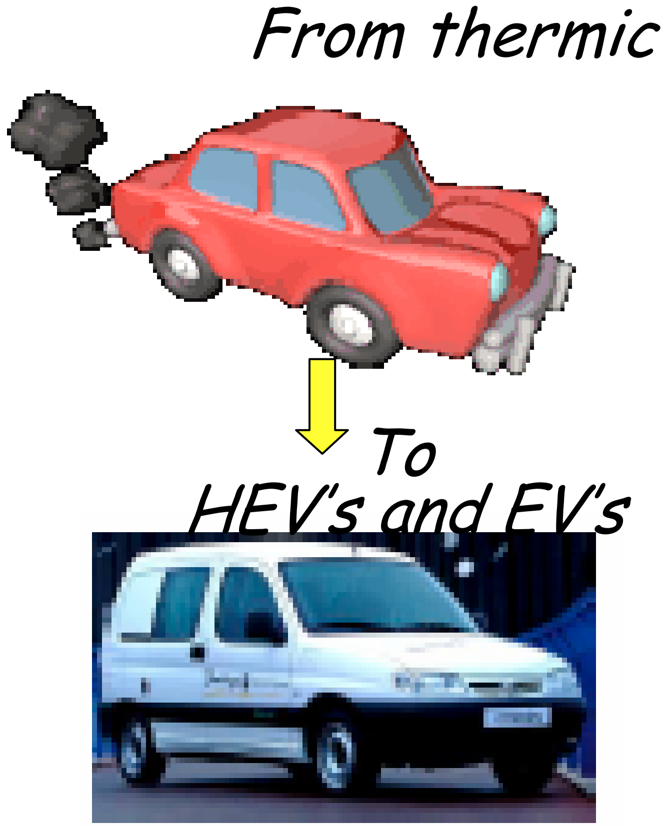
..to better implement renewable energies in our day-to-day lives
Sun doesn't shine on demands…
Wind doesn't blow every days..




Cost-efficient, long-life, high-power energy electrochemical power sources (e.g. batteries or fuel cells) are urgently needed!

How we can we address the $CO_2$ issue and control the pollution in urban area ?

Among other actions, the replacement of a large fraction of internal combustion vehicles with zero or controlled-emission cars, i.e. EVs or HEVs, is urgently needed!




Advanced energy storage systems, i.e. cost-efficient, long-life, high-power energy storage batteries, are requested to power these cars!

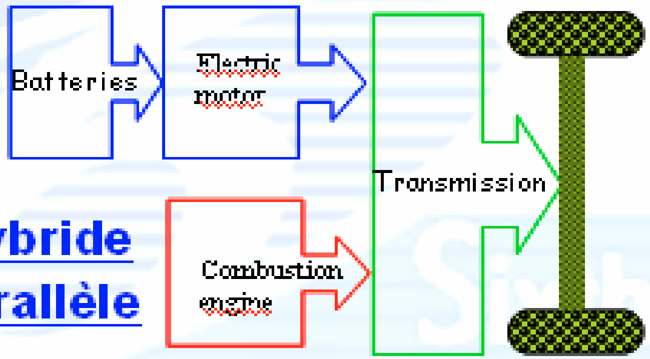
# State-of-the-art in Electric Vehicles: mechanical aspects

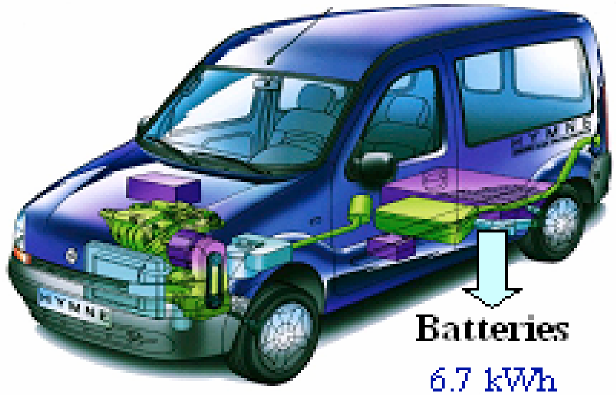
**(1)**

**Hybrid electric vehicle: HEV**

(hybrid motorisation): Long distance

**Hybride parallèle**

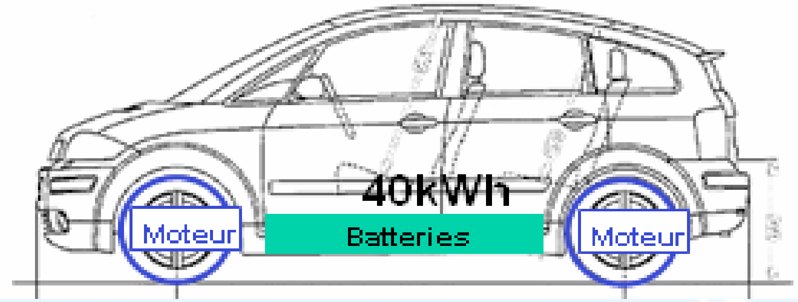



**(2)**

**Electric vehicle : EV**

*In town*

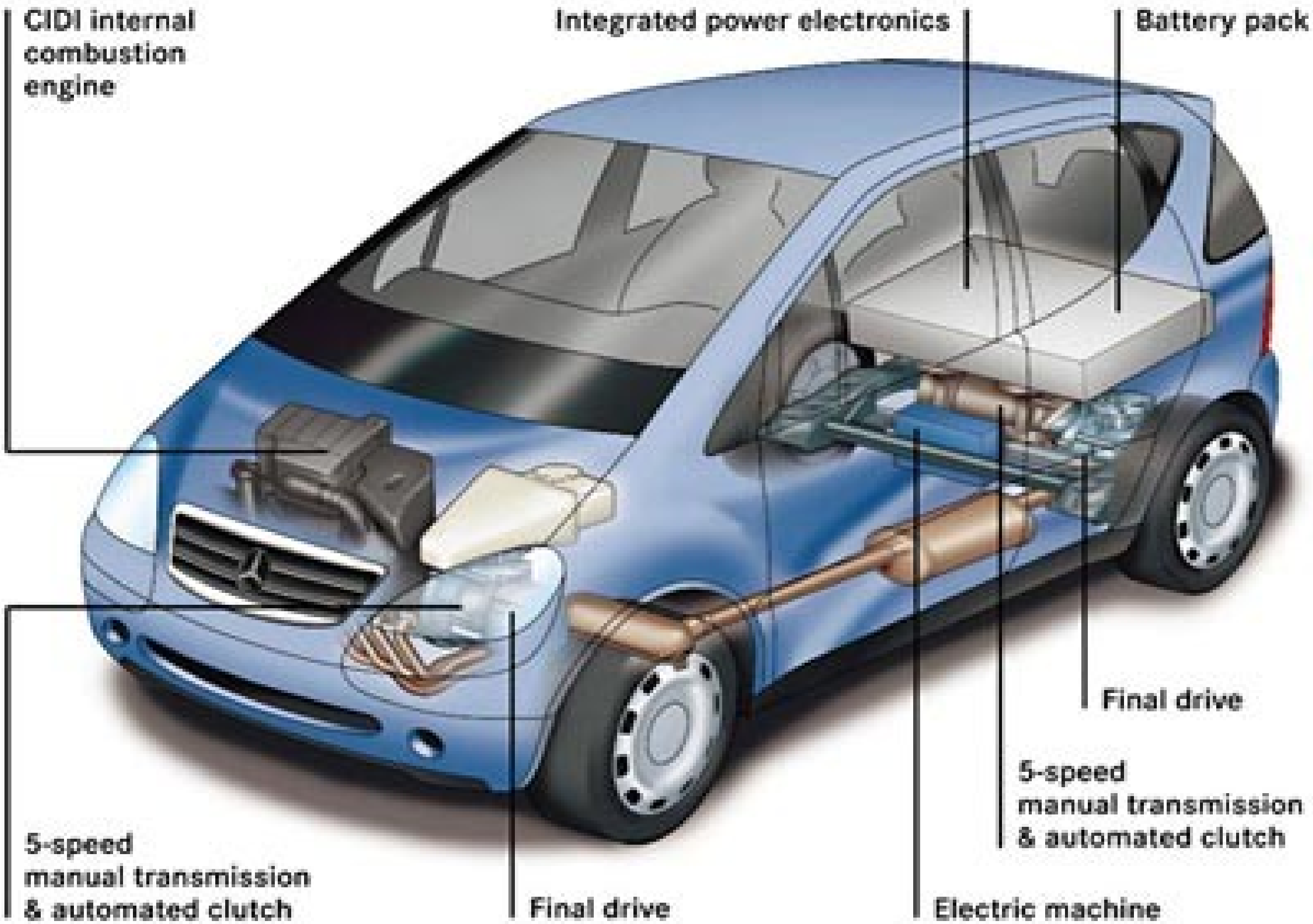



JM Tarascon

## On-board energy storage :

**Cost efficient long-life, high-power energy storage systems, batteries**

# The Hybrid Car (HEV)



| | **Fuel*** (estimated per year) | | **Vehicle emissions** (estimated, per year in pounds) | | | | |
|---|---|---|---|---|---|---|---|
| | **Con-sumption** | **Cost** | **Carbon dioxide** | **Carbon monoxide** | **Nitrogen oxides** | **Hydro-carbons** | **What if...** |
| **1998 MERCEDES-BENZ SL500** (18.0 mpg, Tier 1) 12,500 miles/year | 695 gal | $966 | 13473 lb | 344.5 lb | 31.7 lb | 22.3 lb | not applicable pre 1998 |
| **2002 TOYOTA PRIUS** (48.6 mpg, SULEV) 12,500 miles/year | 258 gal | $358 | 4990 lb | 79.9 lb | 0.8 lb | 0.8 lb | |
| **2002 HONDA CIVIC HYBRID** (47.8 mpg, ULEV) 12,500 miles/year | 262 gal | $364 | 5074 lb | 135.0 lb | 9.4 lb | 3.3 lb | |

* Actual fuel consumption and emissions will vary depending on the specific vehicle configuration, how well the vehicle is maintained, and your driving habits. (See methodology for details.) Fuel cost is based on a national average fuel price of $1.39 (as of June 11, 2002, from the Energy Information Administration).

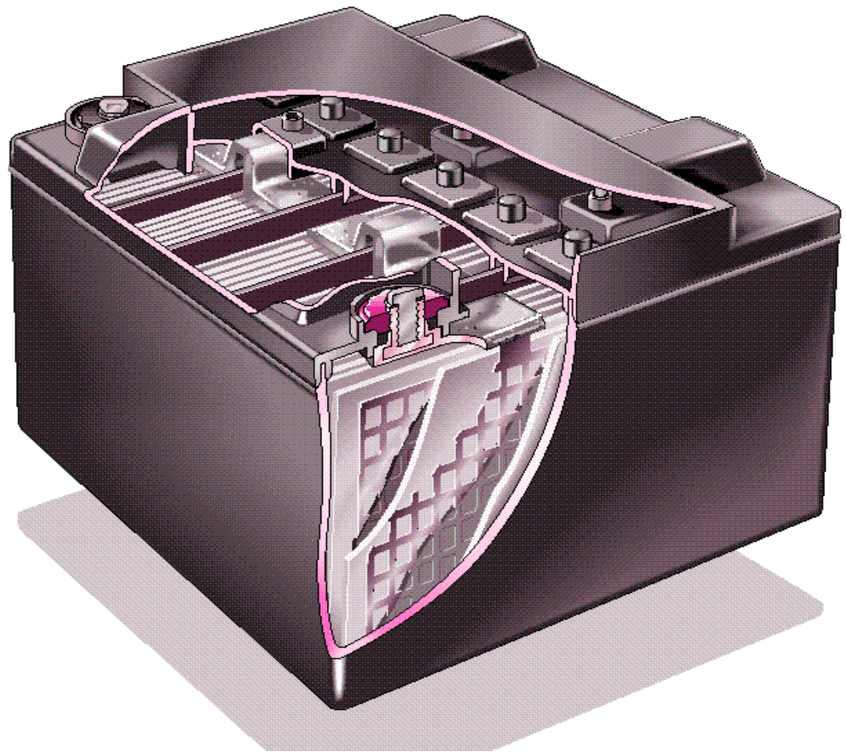
You now have a choice. The Toyota Prius and Honda Civic are hybrid-electric vehicles of similar size to the car(s) you've selected for comparison, and each have superior environmental performance. Both incorporate the best, cutting-edge, mainstream technologies available to automakers. The Prius achieves the highest fuel economy of any compact car sold in America and emits far less pollution than the typical vehicle, making it one of the cleanest vehicles available today. Just behind the Prius in terms of environmental performance is the Civic Hybrid. It also achieves impressive fuel economy and reduced tailpipe emissions, well above the average automobile.

Low cost, high energy batteries are needed for an efficient electric or hybrid car operation.

# BATTERIES

# Conventional batteries

Lead-acid batteries:
$Pb / H_2SO_4 / PbO_2$
Voltage: 2 V
too heavy;
low energy density, ≈
40 Wh/kg



# Conventional batteries

Nickel-Cadmium:
Cd /KOH /NiOOH
Voltage: 1.6V
too heavy, low energy density, ≈ 50 Wh/kg and toxic components (Cd)

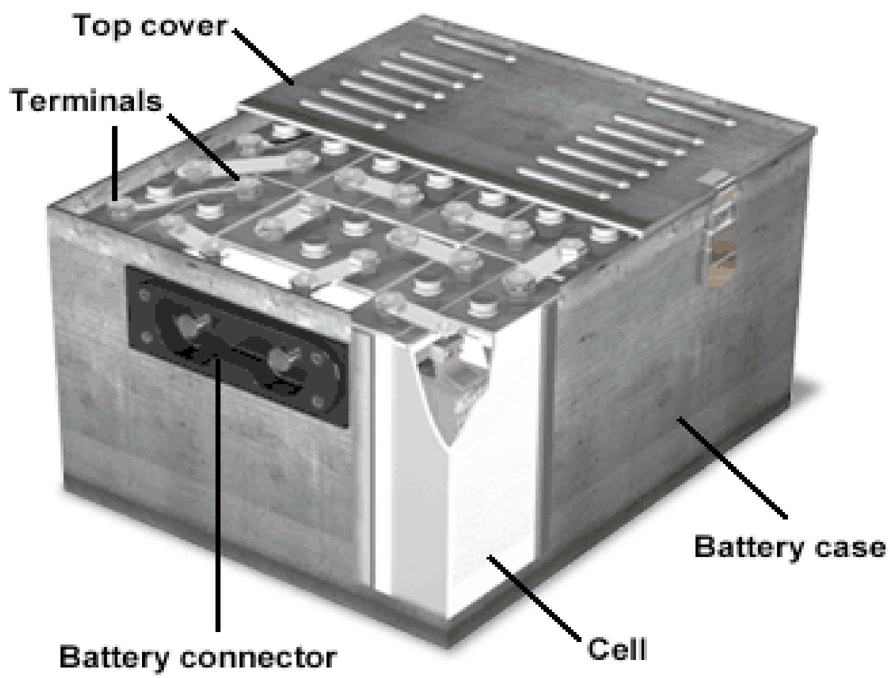
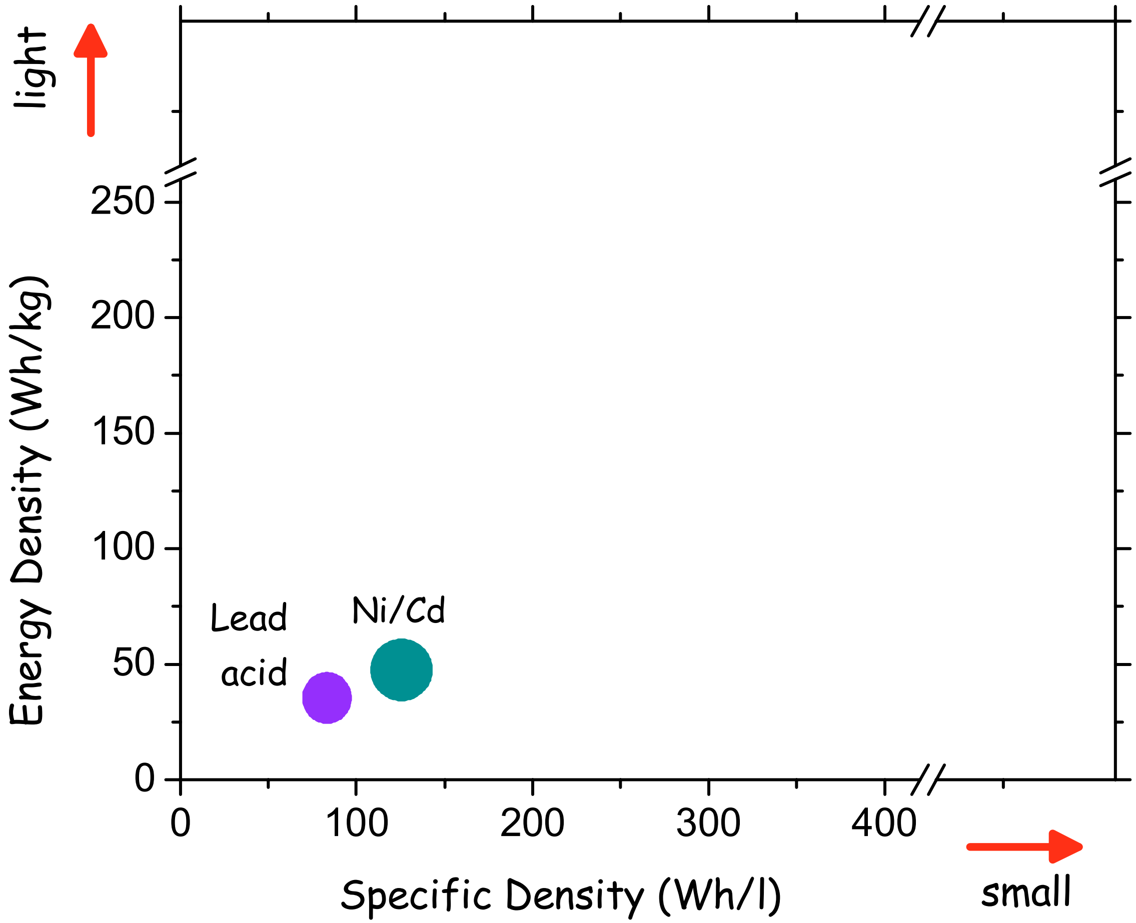



Figure 1

# Energy diagram for conventional batteries

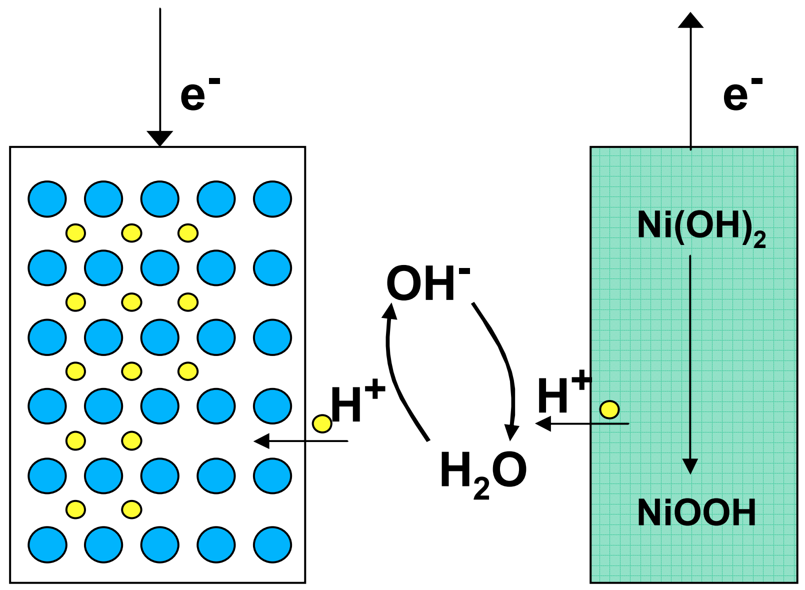


# Alternative battery:

Nickel-Metal Hydride
NiOOH /KOH/ MH
Voltage: 1.6 V
moderate energy density:
≈ 60 Wh/kg
high cost

# Ni/MH charge - discharge mechanism

## CHARGE REACTION



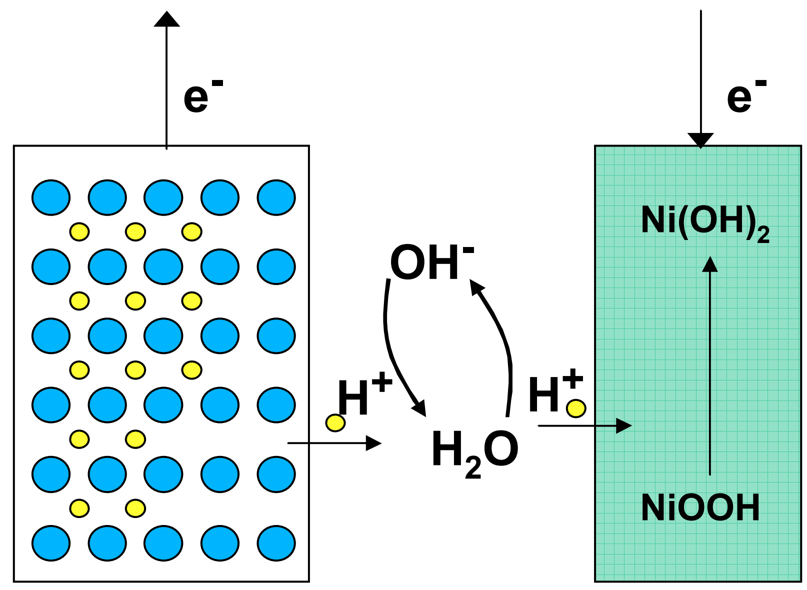

**Metal Hydride Electrode**

**$M + H_2O + e^- \rightarrow MH + OH^-$**

**Nickel Electrode**

**$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$**

## DISCHARGE REACTION




**Metal Hydride Electrode**

**$MH + OH^- \rightarrow M + H_2O + e^-$**

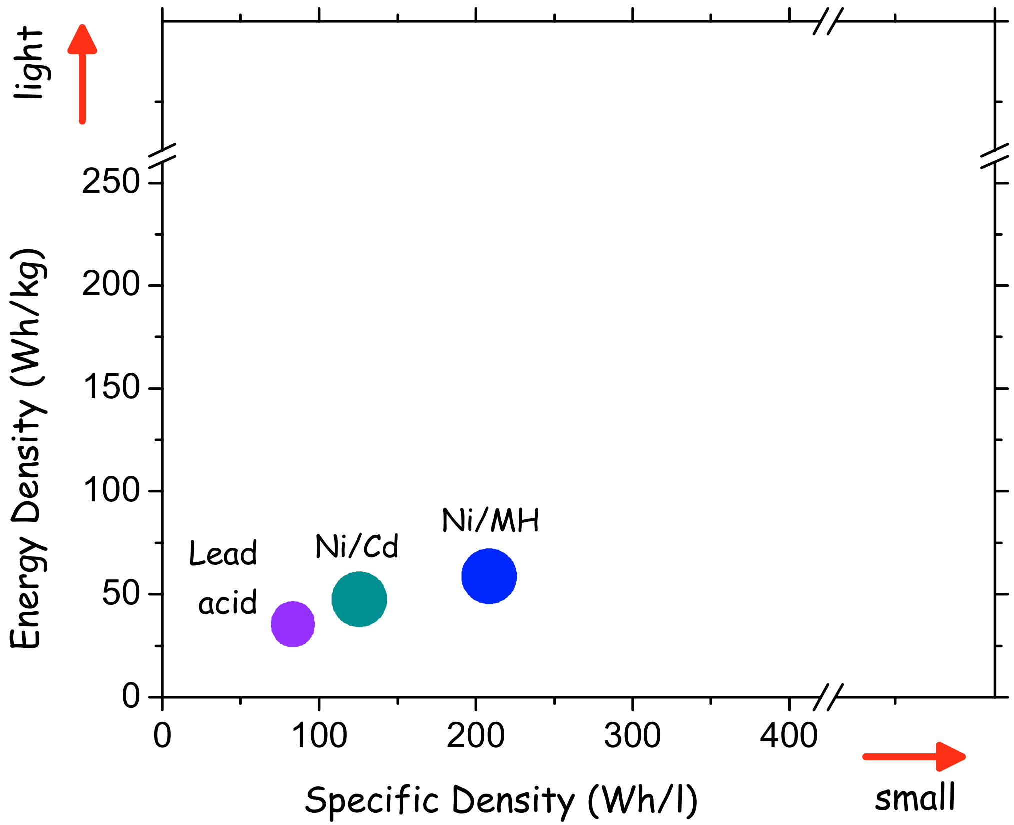
**Nickel Electrode**

**$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$**

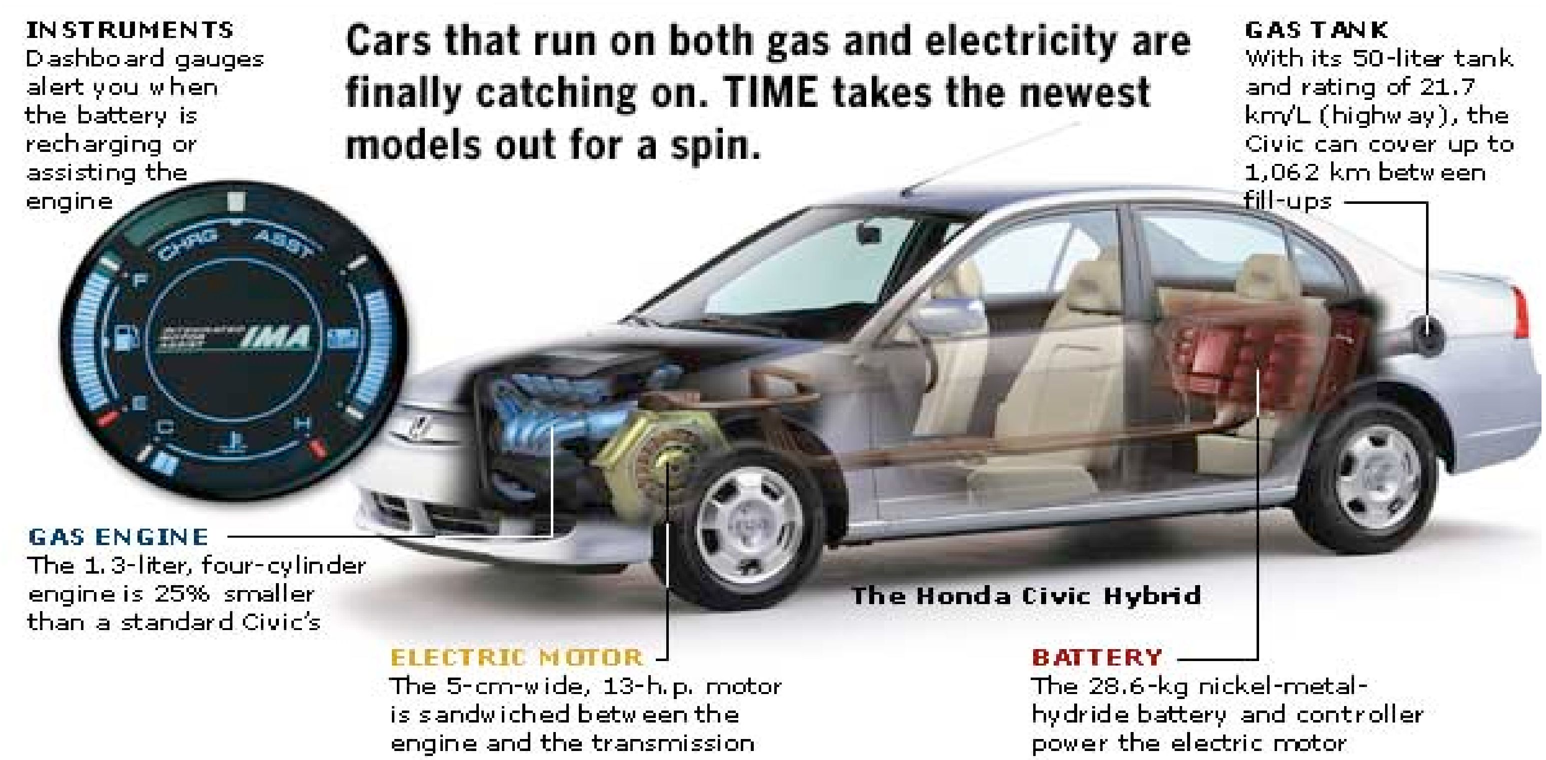
**M: Hydrogen Absorbing intermetallic alloy**

**H: Hydrogen Atom**

# Energy diagram for conventional batteries



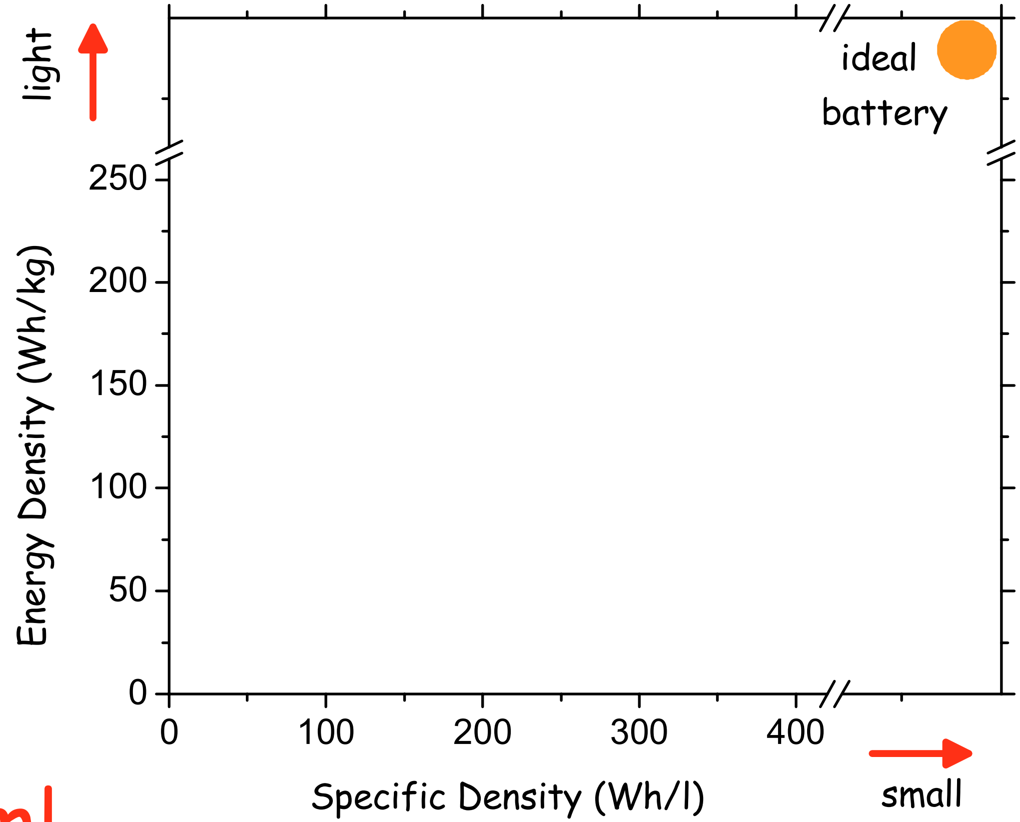
A nickel-metal hydride batteries is presently used as the energy storage unit in HEVs .....




.... however, new types of batteries having higher energy density and lower cost than Ni-MH, are urgently needed to assure high performance and market competitiveness.

# The ideal battery

No mass ! No volume ! No cost ! Infinite voltage! Infinite life!

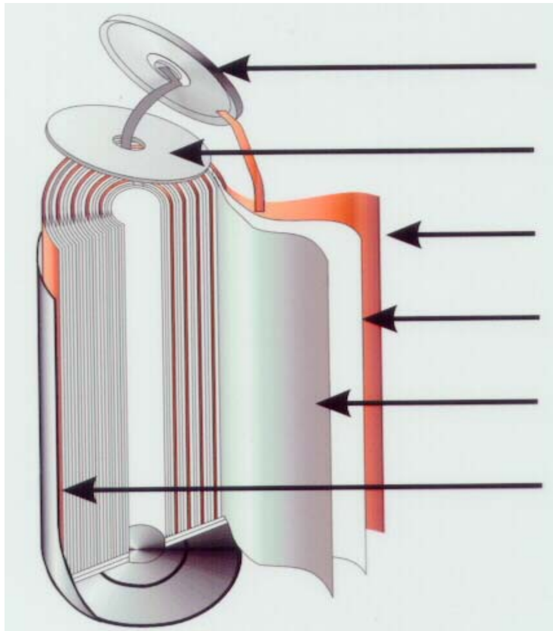



The ultimate dream!

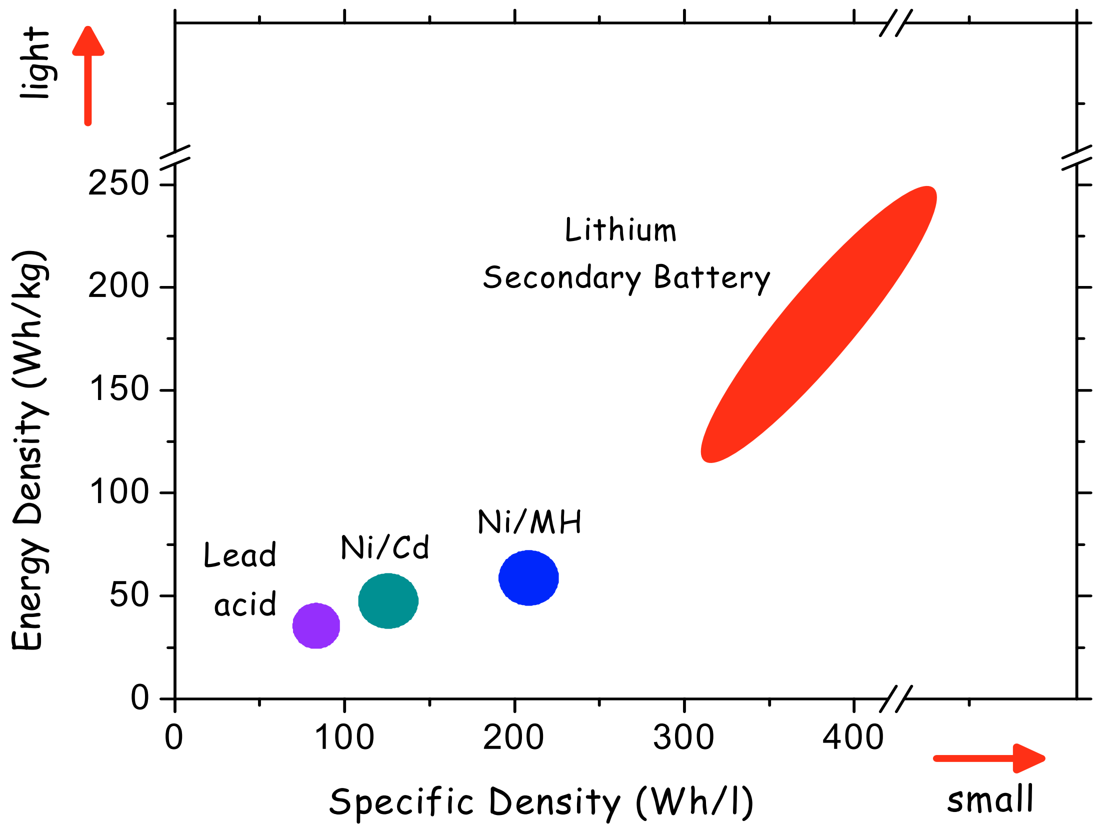
# Advanced batteries

Lithium-ion batteries
$C$ /$LiPF_6$ in EC-DMC /$LiCoO_2$
Voltage: 3.5V
light, ,compact
high energy density,
≈150 Wh/kg

Safety concern ?



# Energy diagram for lithium batteries versus conventional batteries



# Lithium Batteries

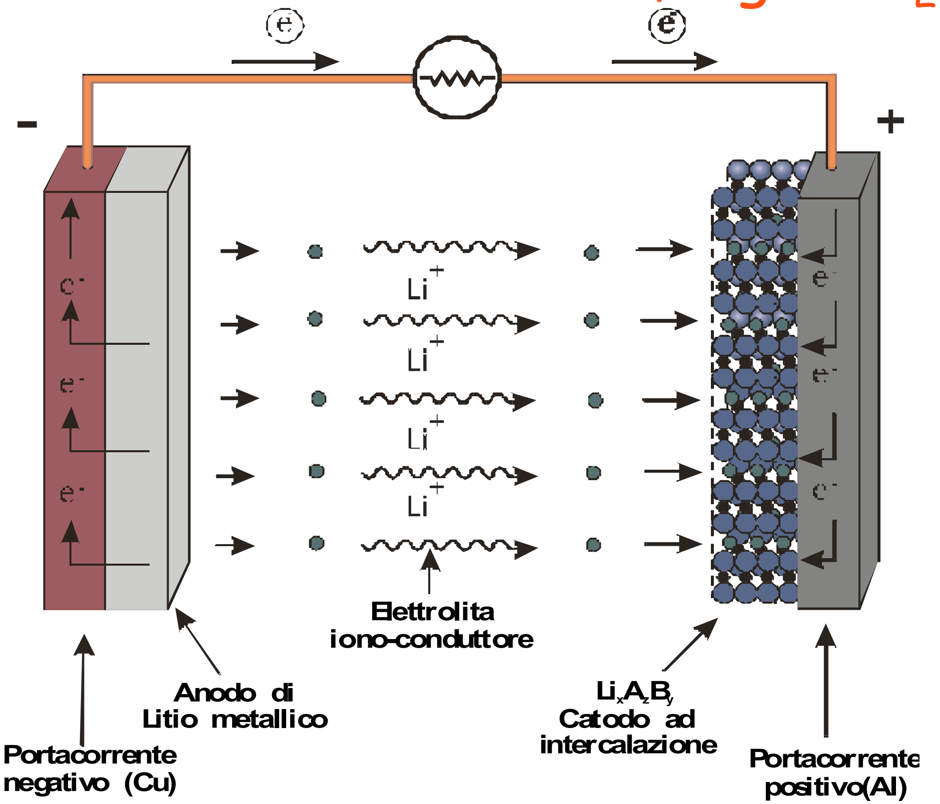
The success of the lithium batteries is in the choice of their components which are all based on innovative electrochemical concepts.

## New concept in the electrode components:

### the intercalation electrodes:

compounds having a soft structure with capability of accepting and releasing guest species, e.g. lithium ions and electrons with reversible structural and electronic changes.

# Scheme of the electrochemical process in an intercalation electrode, e.g. $TiS_2$.

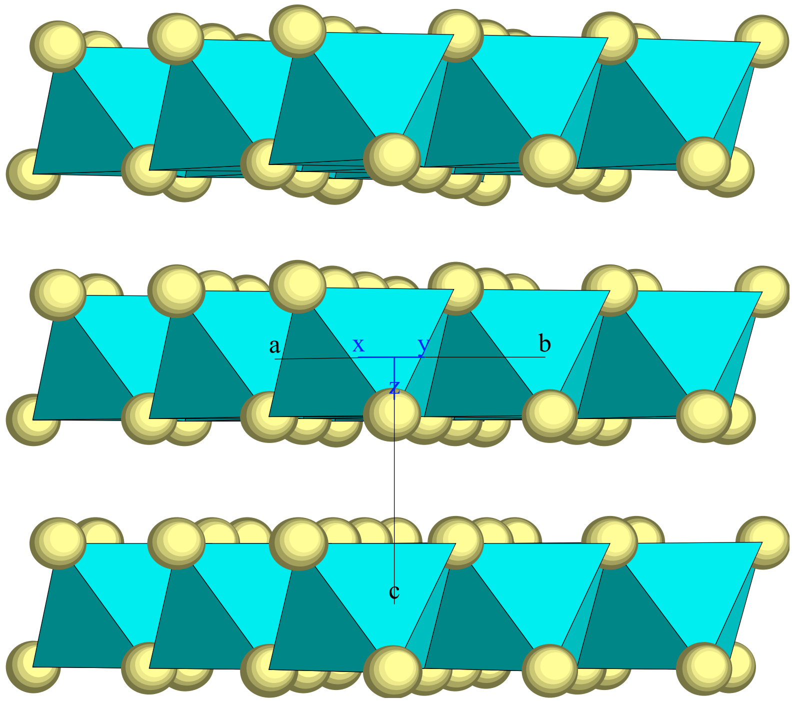



INTERCALATION ELECTRODE: (e.g. $TiS_2$), (negative)

CONTER ELECTODE: metallic lithium (positive)

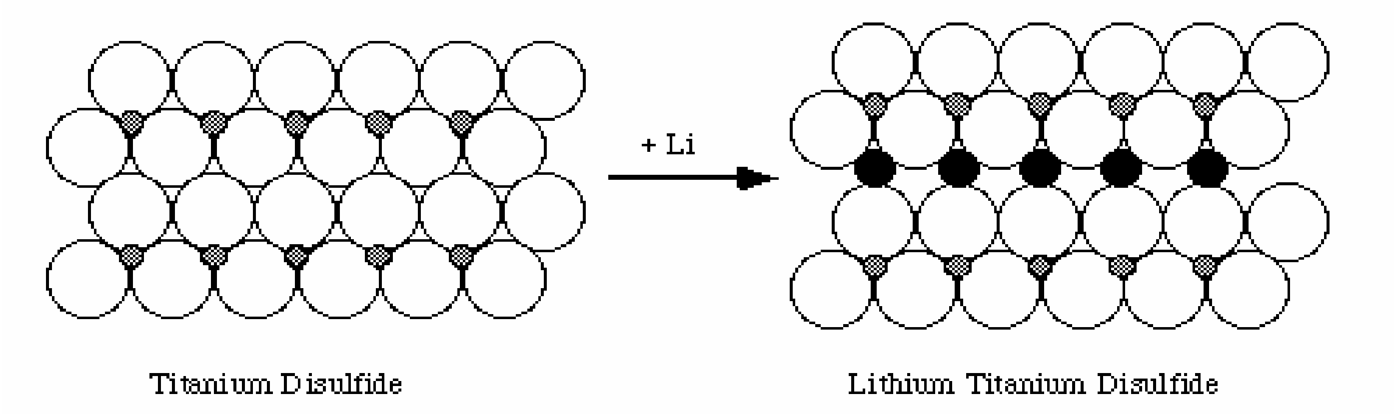
ELECTROLYTE: solution of a lithium salt (e.g, $LiPF_6$) in an organic solvent mixture (e.g., ethylene carbonate-dimetyl carbonate, EC-DMC mixture)

# Layered titanium sulphide: a typical intercalation electrode




**Structure of $TiS_2$ (P-3m1)**

# Scheme of the electrochemical intercalation process of the $Li^+$ ion in a layered structured compound, e.g., $TiS_2$




$$TiS_2 + xLi^+ + xe^- \Leftrightarrow Li_xTiS_2$$

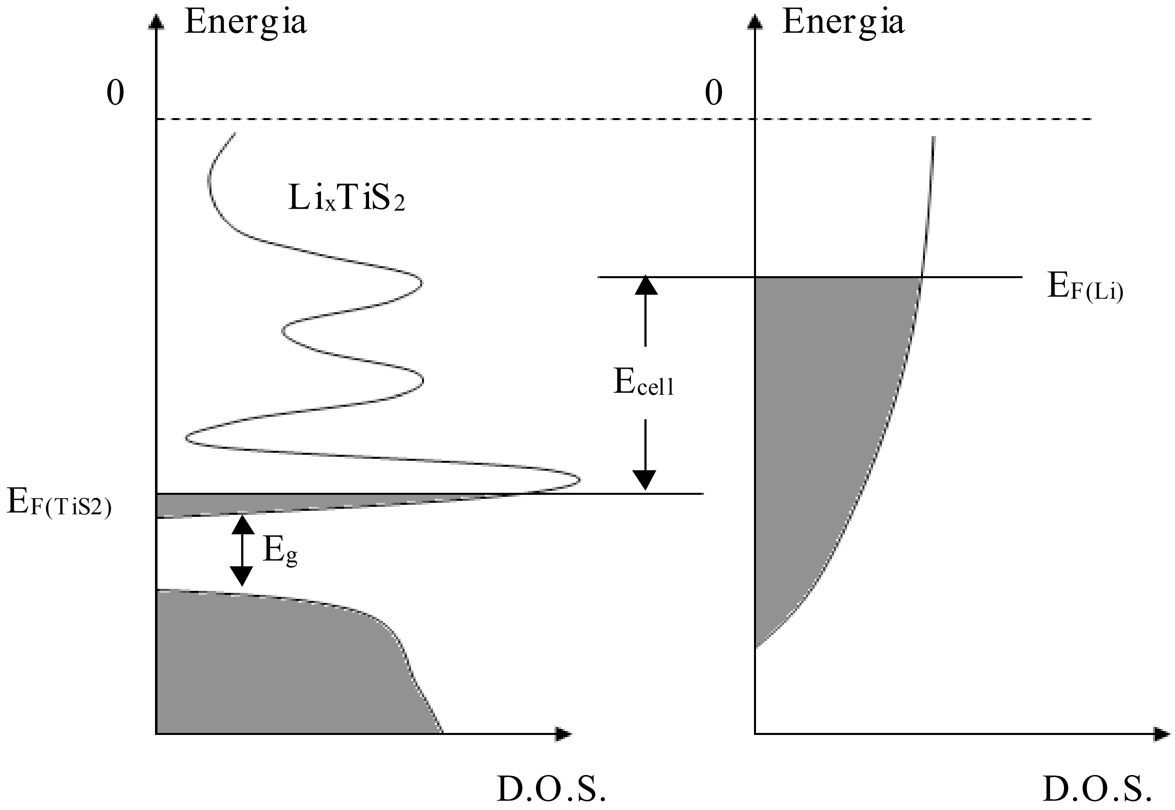
To be noticed that the guest specie, here the lithium ion, keeps its charge when is intercalated in the $TiS_2$ structure. Thus, the electrons which arrive to the intercalating electrode do not reduce the intercalated specie, i.e. $Li^+$, but rather modify the electronic structure of the intercalating specie, i.e. $TiS_2$ . Practically, the insert of the ion is accompanied by a variation of the oxidation state of the transition metal which passes from Ti(IV) to Ti(III).

# Intercalation electrodes

To be effective in terms of reversibility, an intercalation electrode must fulfill the conditions outlined below.
i) The lithium intercalation process must occur with a minimum, yet reversible, perturbation of the structure of the host material.
ii) The intercalation of the guest species, i.e. the lithium ions, should not influence the bonding orbitals of the host material.
iii).In the course of the charge transfer, the electrons should be accommodated in large bands having a high density of states.
iv) The changes in the electronic structure of the host material must be limited to progressive and reversible occupational increase of the anti-bonding conduction band and not to its deformation.

In synthesis, to be effective, the intercalation process should not influence the orbitals of the host material but mainly lead to the progressive filling of the anti-bonding conduction band (*rigid band model*).
In this prospect, the most promising materials are those having a gap separating a full covalent valence band by an empty anti-bonding band. Good examples are materials with *d* bands and narrow anti-bonding bands, such as the chalcogenides of transition metals of group V, e.g., $TiS_2$.

Scheme of density of states of the intercalation electrode ($TiS_2$) and of the counter electrode (Li) in the electrochemical cell.




The cell potential E is given by the difference between the Fermi level of lithium $E_{FLi}$ and the Fermi level of $TiS_2$, $E_{FTiS2}$. When the external circuit is closed, electrons pass from lithium to the titanium sulphide, where they fill the wide anti-bonding band which has a large density of free states . As the process proceeds, the Fermi level of the metal decreases while increases that of the dichalcogenide and thus, the cell potential progressively decreases.

# Electrochemical intercalation process of $Li^+$ in $TiS_2$.

Positive electrode (lithium metal):

$$xLi \rightarrow xLi^+ + xe$$

Negative intercalation electrode ($TiS_2$):

$$xLi^+ + TiS_2 + xe \rightarrow Li_xTiS_2$$

Total process:

$$xLi + TiS_2 \rightarrow Li_xTiS_2$$

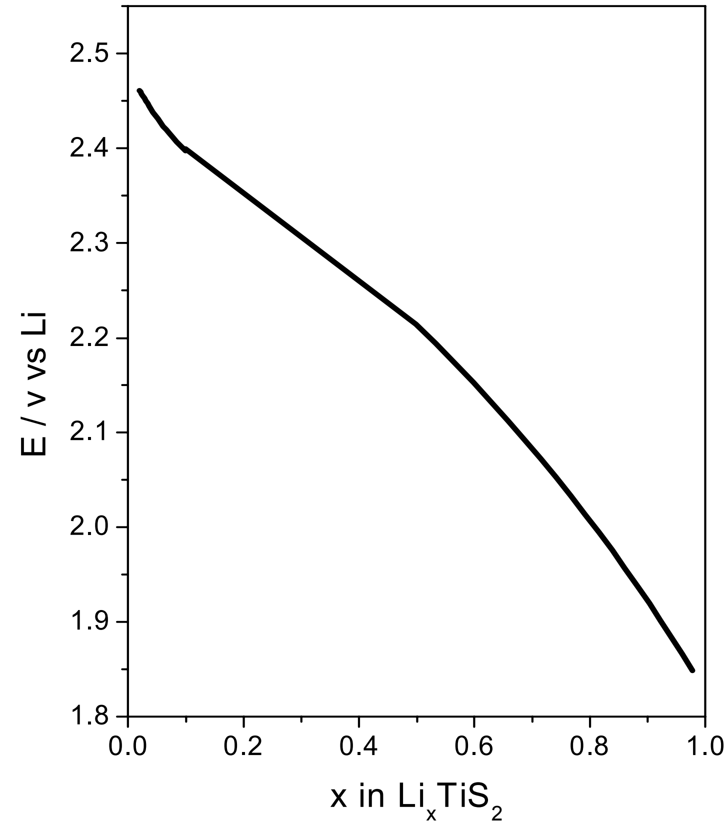
x= intercalation degree

The potential is expressed by the Nernst equation:

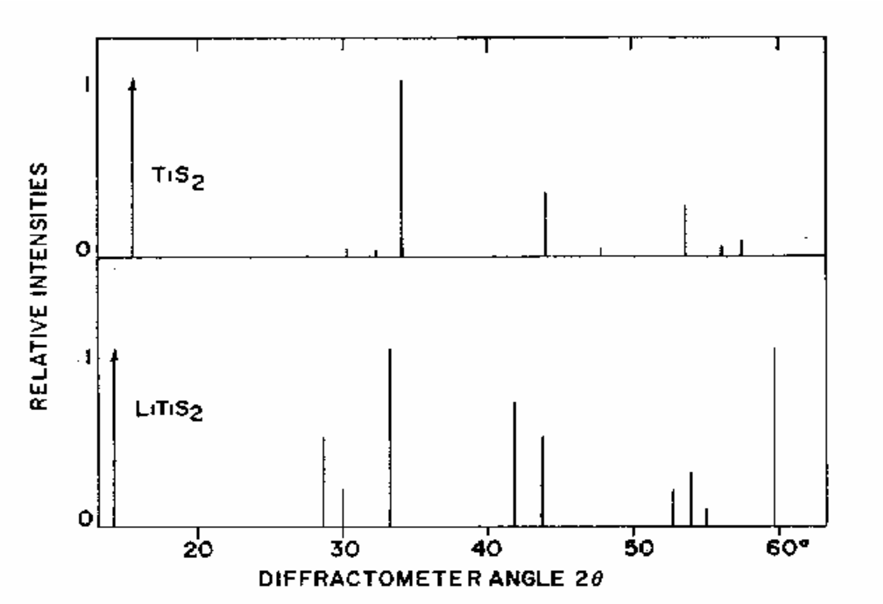
$$E = E^\circ - \frac{RT}{xe} \ln \frac{a_{Li^+}(Li_xTiS_2)}{a_{Li} \cdot a_{TiS_2}} \cong E^\circ - \frac{RT}{xe} \ln a_{Li^+}(Li_xTiS_2)$$

As the intercalation proceeds, the activity of $Li^+$ in $Li_xTiS_2$ increases and thus, E decreases.

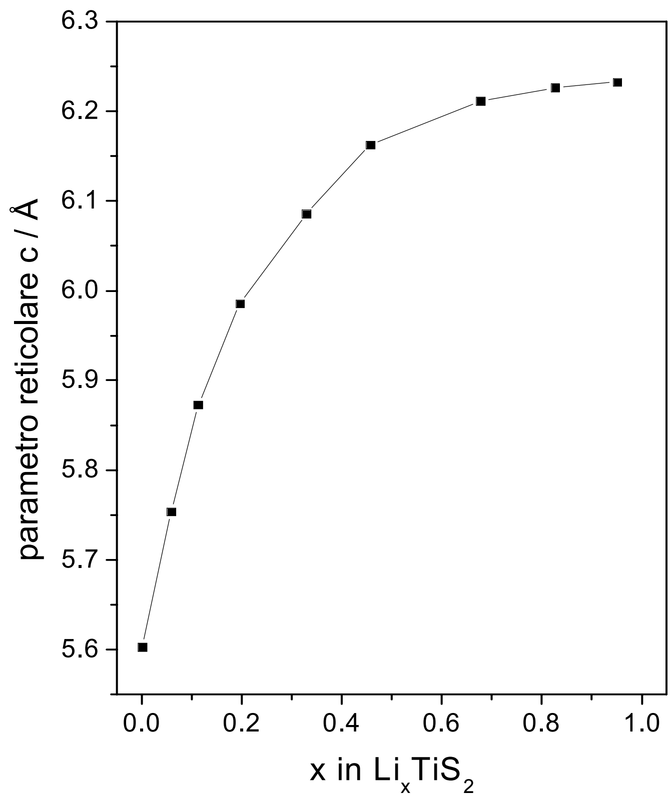
# Change of the $Li_xTiS_2$ potential (vs. $Li^+/Li$) as a function of the intercalation degree, x



# The lithium intercalation process in $TiS_2$ is accompanied by a reversible structural expansion along the c axis




XRD of $TiS_2$ and of $Li_xTiS_2$.

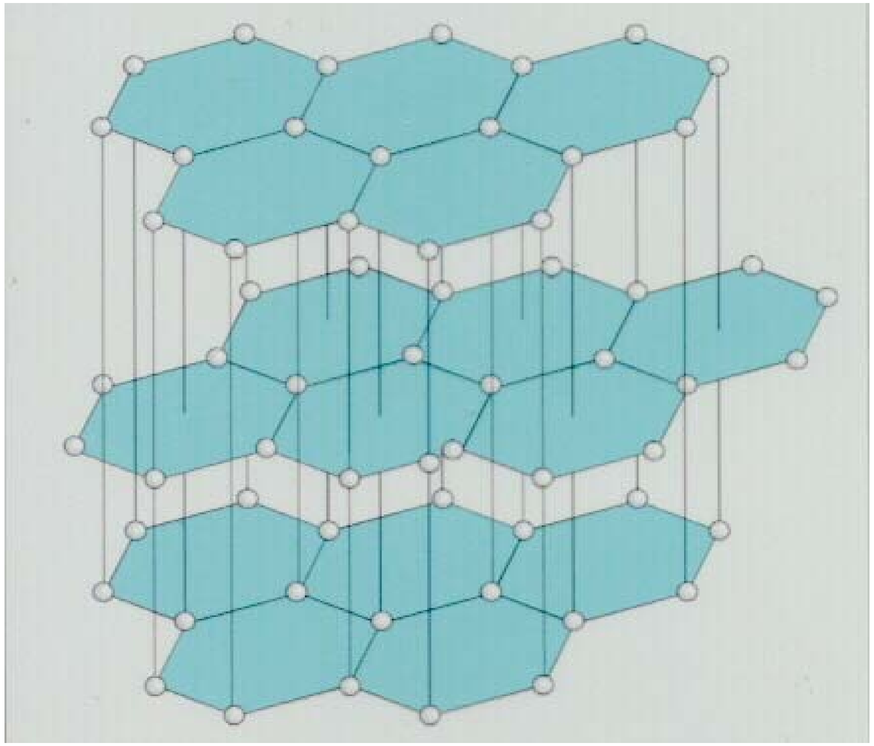



Change of the c axis with the intercalation degree in $Li_xTiS_2$

# Lithium ion batteries

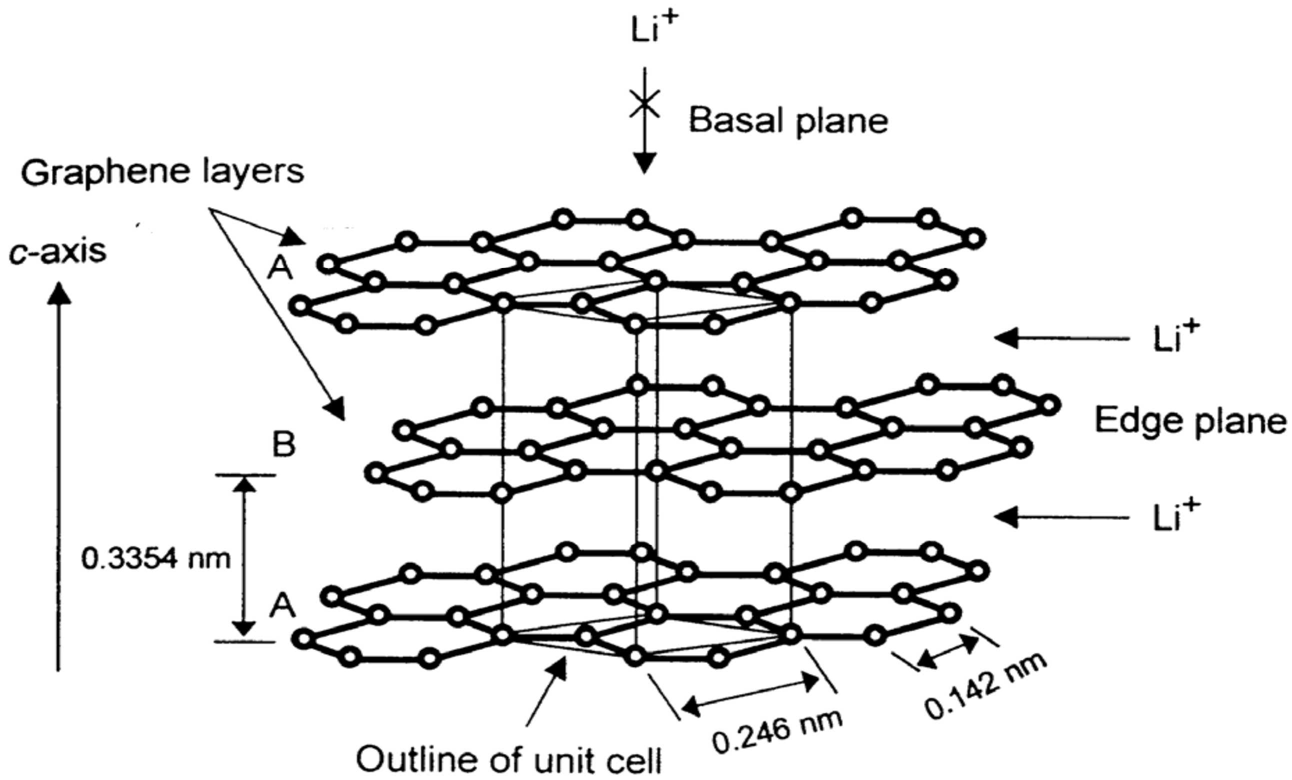
The most successful lithium battery technology relies today on cell configurations based on two intercalation electrodes, i.e., a lithium accepting electrode, e.g. graphite (replacing lithium metal), combined with a lithium donating electrode, e.g., a layered lithium metal oxide.

# Scheme of graphite structure

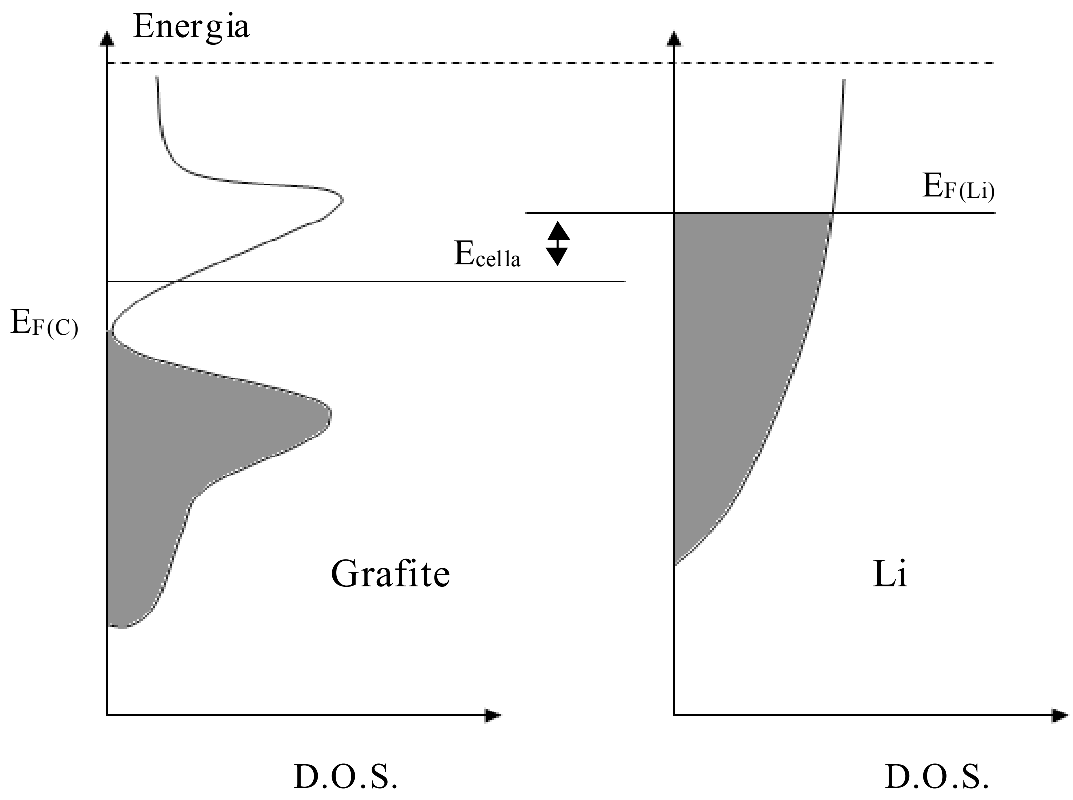


The graphene layers are separated by loose bonds an provide space enough to accept lithium ions: $xLi^+ + yC \Leftrightarrow Li_xC_y$, where x may extend to 1 and y=6

Scheme of the structure of graphite. The unit hexagonal cell ($P6_3/mmc$) is evidenced with the related ABAB packaging and the interplanar distance c/2=0.3354nm

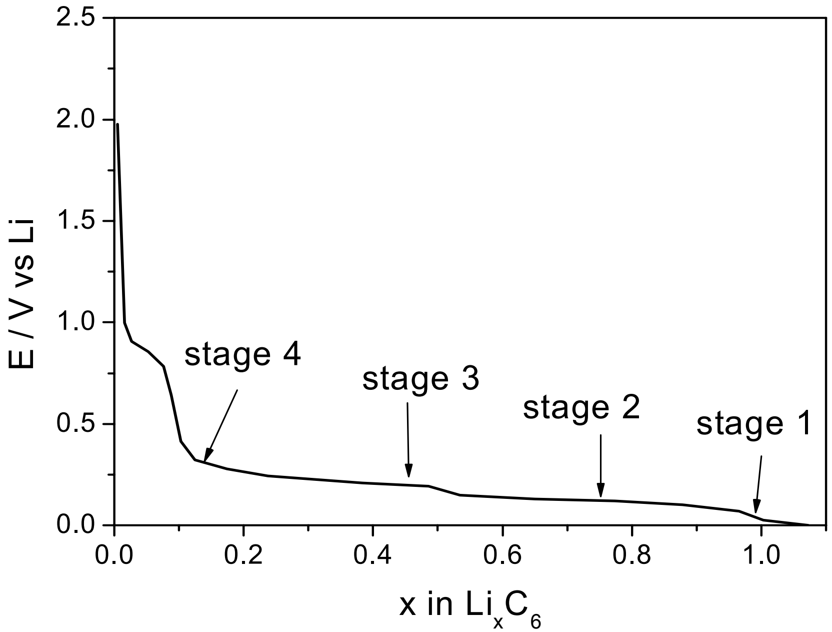


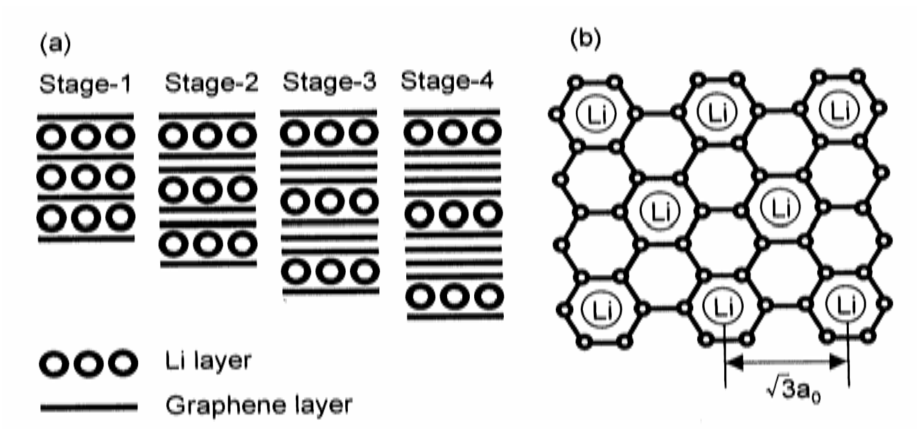
## Scheme of density of states of graphite in comparison with those of a lithium metal




Similarly to the general scheme, as the intercalation process proceeds the electrons fill the empty band of graphite and accordingly, the potential (versus $Li/Li^{+}$) decreases.

## Change of the $Li_xC_6$ potential (vs. $Li^+/Li$) as a function of the intercalation degree, x

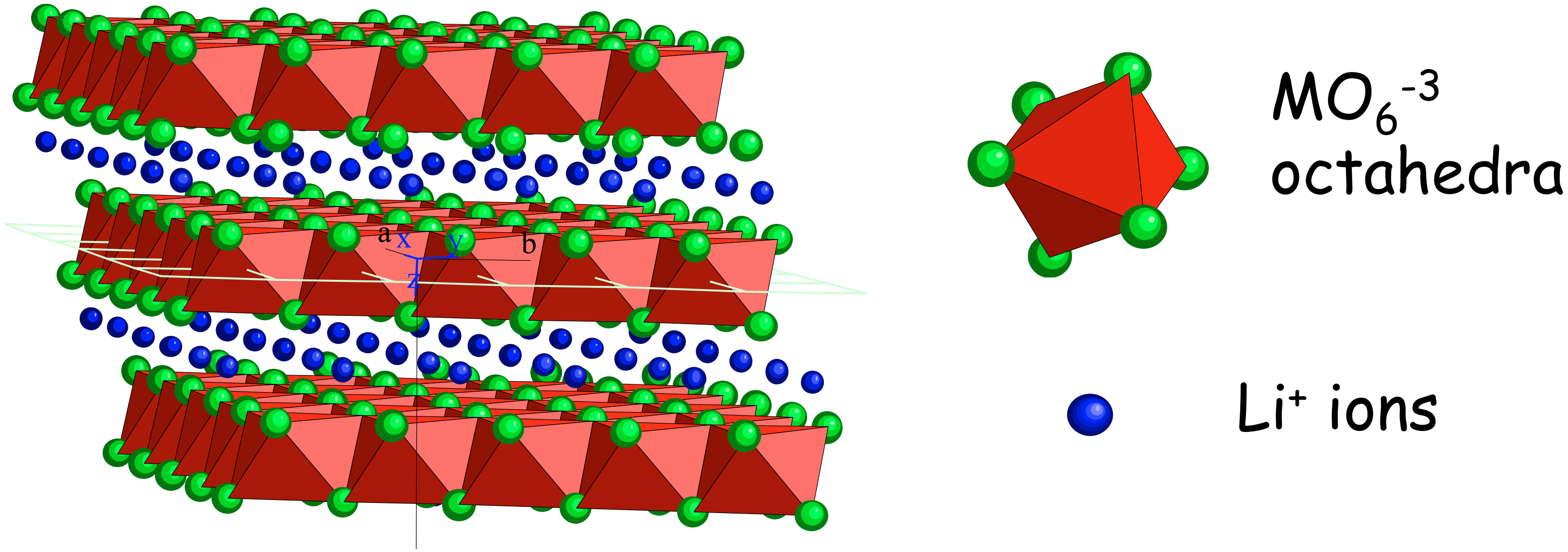



The voltage vs. composition curve develops along various plateaus which are representative of the graphite staging intercalation process.

Proper electrode operation requires the formation of lithium-conducting passivating films on the electrode's surface (Solid Electrolyte Interface, SEI).

# Scheme of layered $LiMO_2$ (M= Co, Ni, …)




Lithium is situated in between the MO6 slabs and can be easily released and accepted back, according to the following de-intercalation-intercalation process:

$LiMO_2 \Leftrightarrow xLi^+ + Li_{1-x}MO_2 + xe^-$ where $0 \leq x \geq 1$

Again, the removal of lithium ions is accompanied by a change in the electronic structure, i.e. by the variation of the oxidation state of the M transition metal.The potential varies from around 4V vs. Li to 3.5V vs. Li, depending on the value of x.

# The lithium ion battery

The electrochemical system:

Anode: grafite

Electrolyte:

liquid solution of a lithium salt in an organic solvent mixture

Cathode: layered $LiMO_2$

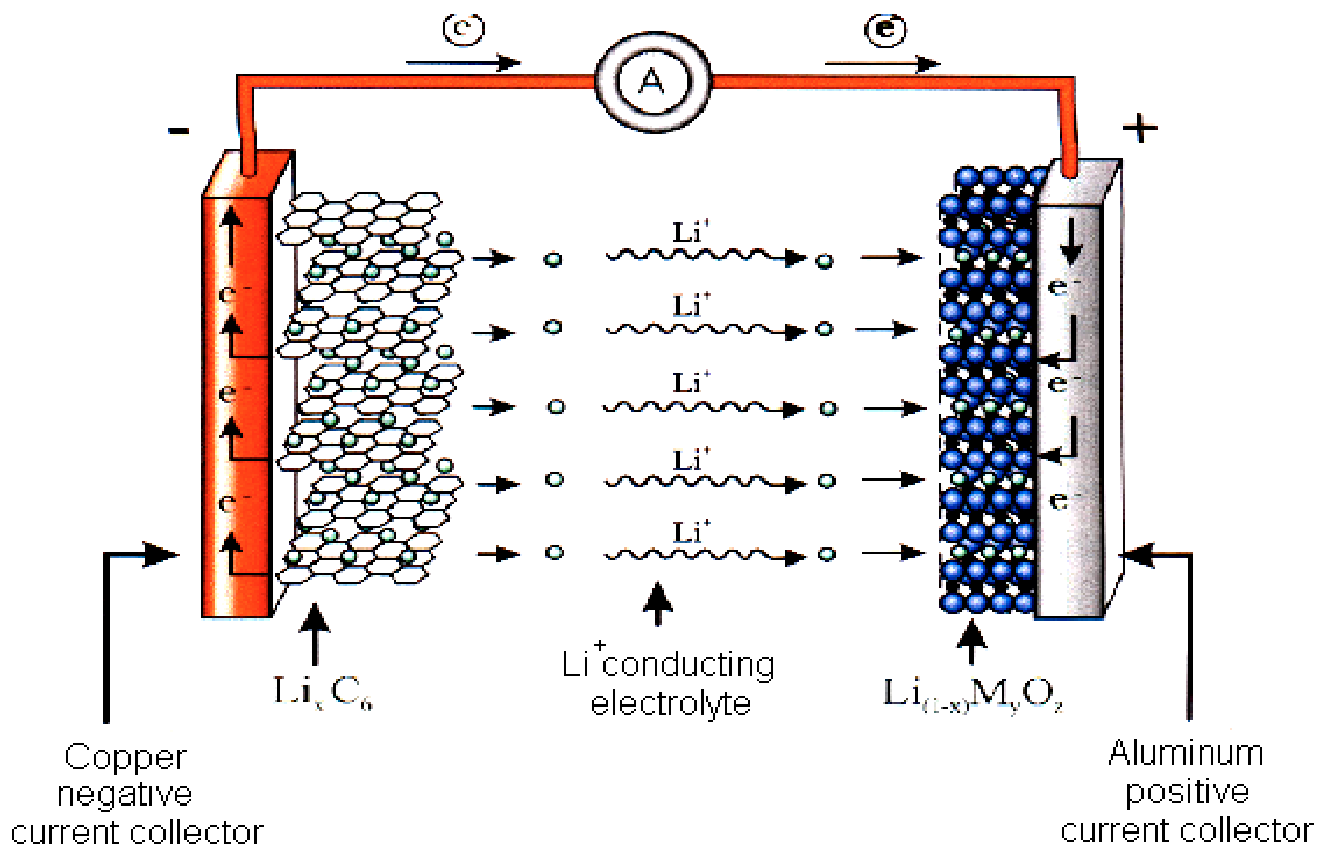
lithium metal

oxide, e.g. $LiCoO_2$

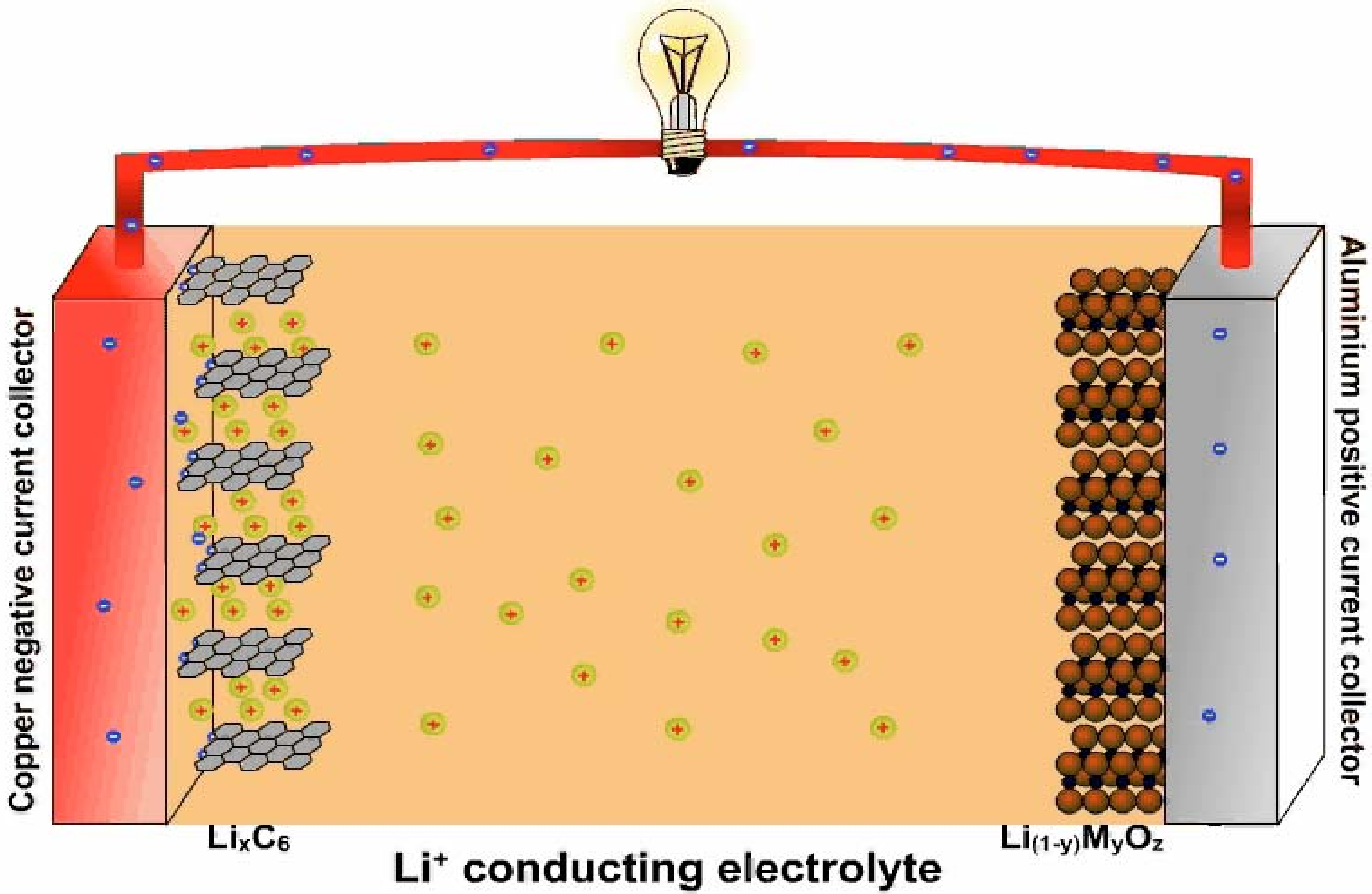
The electrochemical process involves the reversible transfer of lithium ions from lithium cobalt oxide to graphite : xLi + yC+ $LiCoO_2 \Leftrightarrow Li_xC_y + Li_{1-x}CoO_2$ most commonly $x \approx 0.5$ and $y = 6$

Since the intercalation of lithium in graphite develops with a potential evolving around 0.1 V vs. Li and that of $LiCoO_2$ around 3.6 V vs. Li, the combination of the two gives a 3.5 V battery.

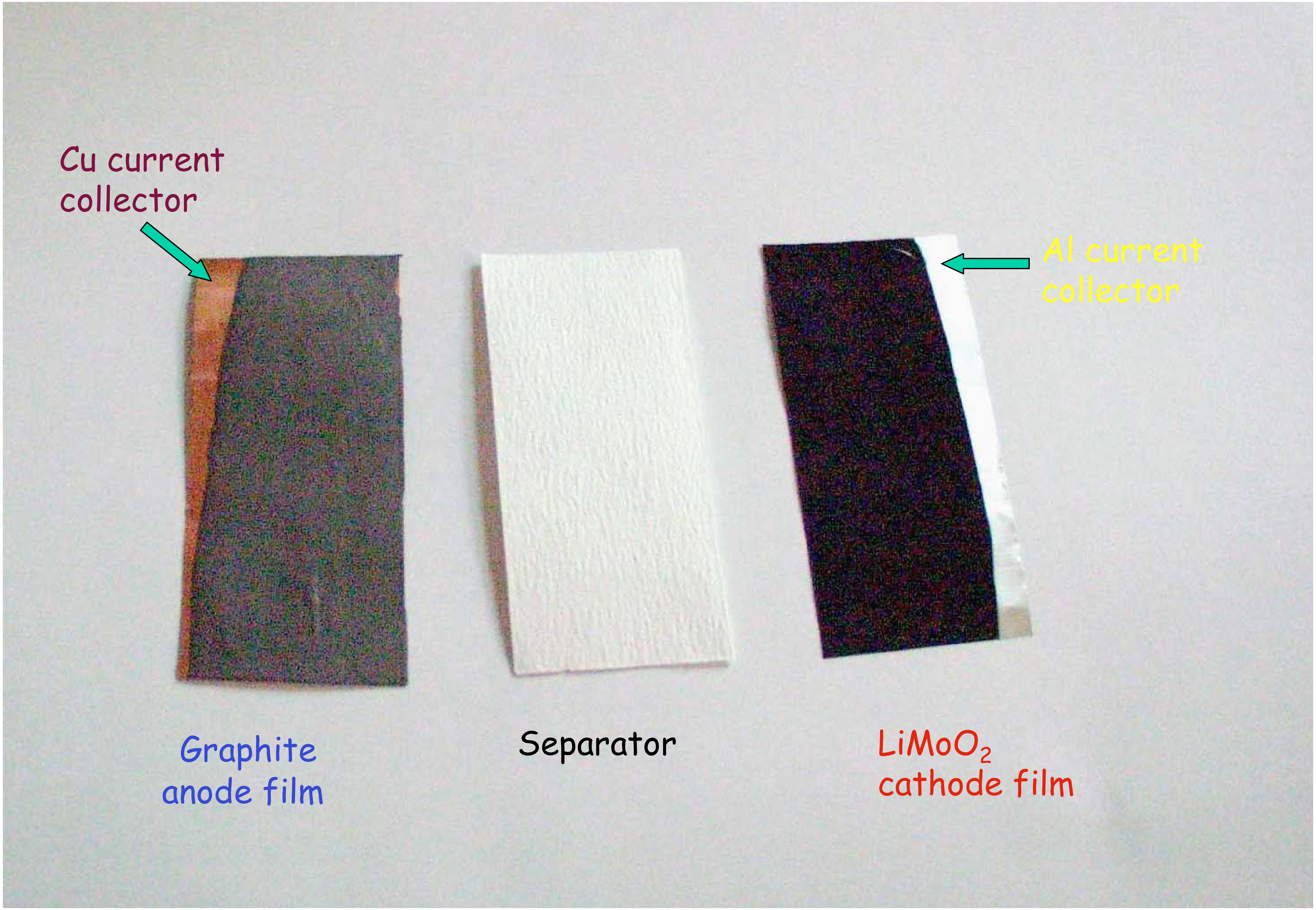
# The lithium-ion rechargeable battery



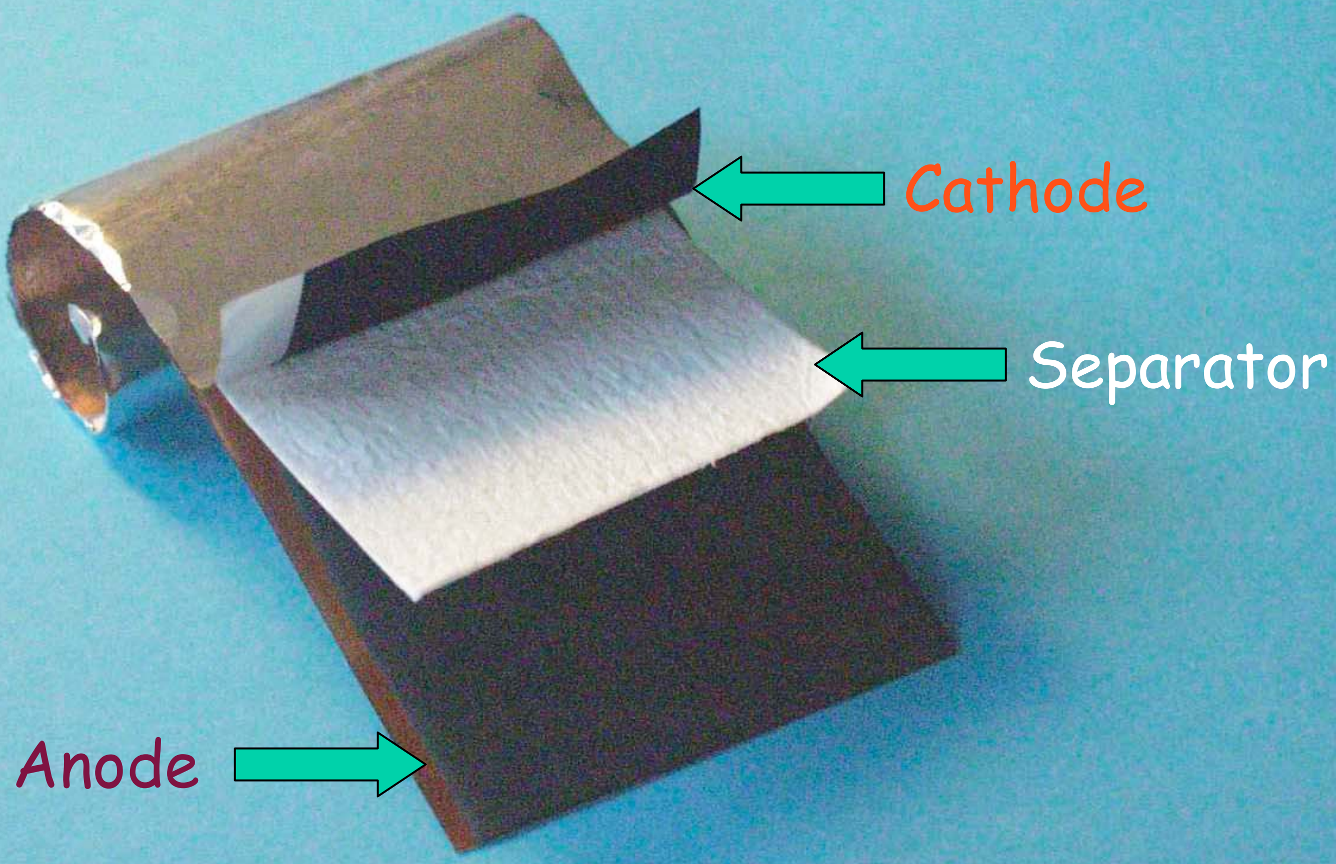
# Batterie litio-ione

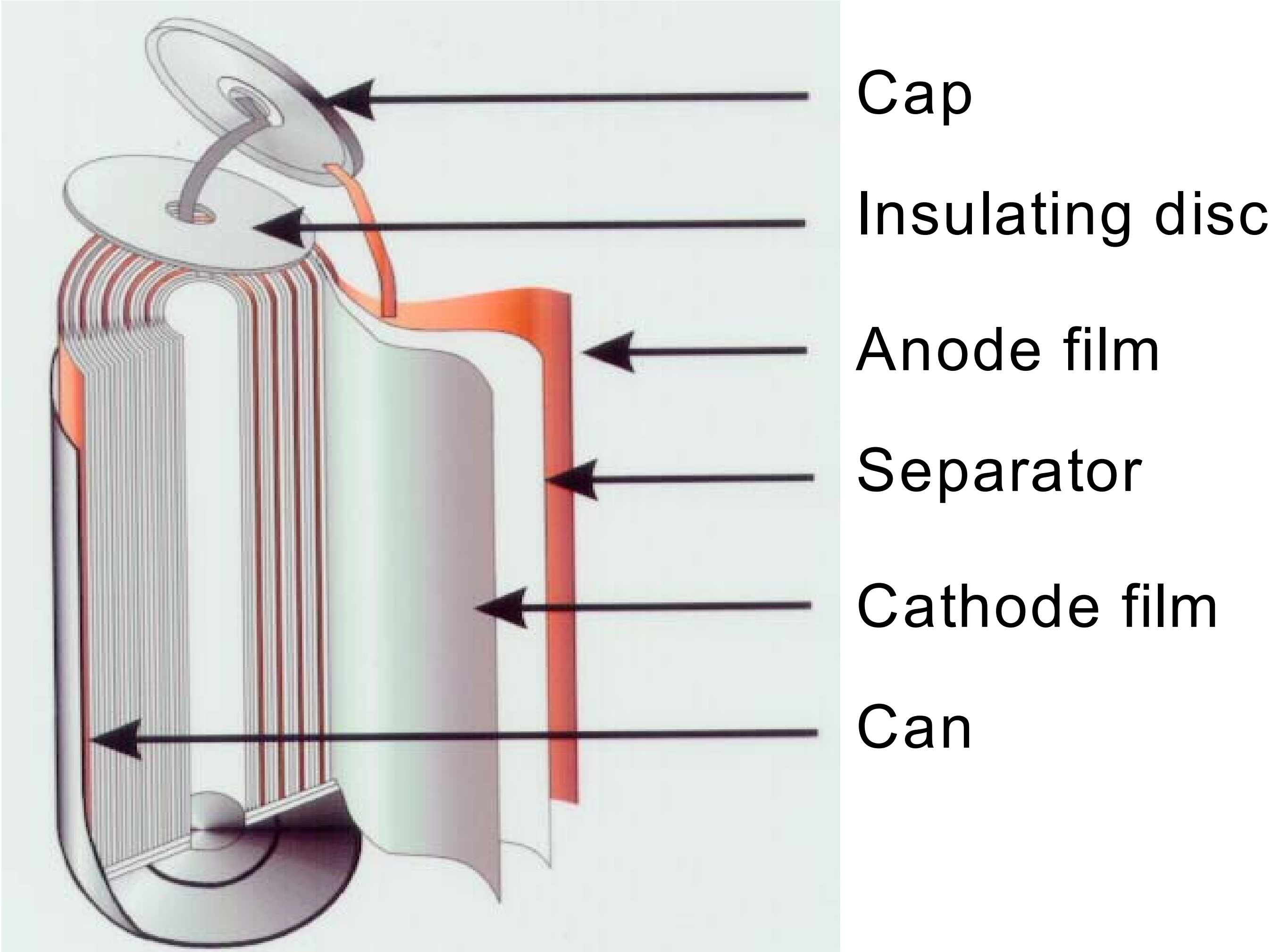



**discharging process**


Cu current collector
Al current collector
Graphite anode film
Separator
$LiMoO_2$ cathode film

# Lithium ion cell assembly




Cap
Insulating disc
Anode film
Separator
Cathode film
Can

# Progress in packaging materials and methods for lithium ion batteries

Polymer battery

| | | | |
|---|---|---|---|
| Case material | steel, SUS | aluminum | Al/resin laminated film |
| Seal method | crimp | laser welding | heat seal |
| Features | | thin<br>lightweight | very thin |

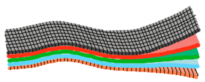
# Where do we stand after two centuries of evolution of batteries ?

**Alessandro Volta, 1801**
(Cu/Zn)

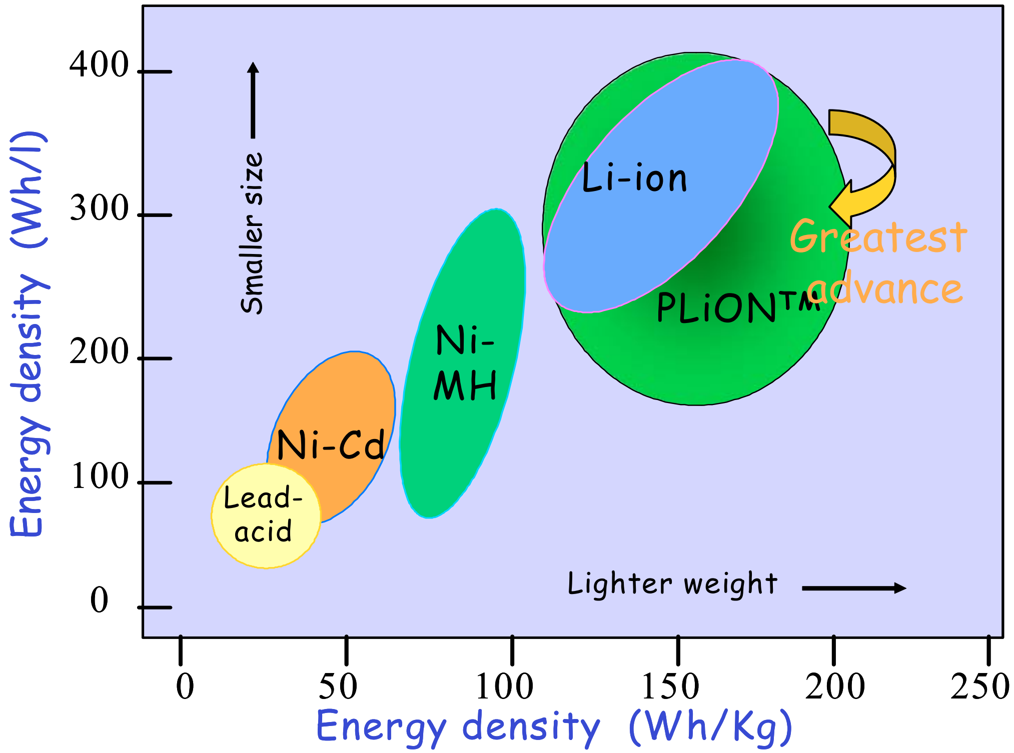
| | |
|---|---|
| 1839 | Fuel cell |
| 1859 | Pb battery |
| 1899 | Ni-Cd |
| 1973 | Li metal |
| 1975 | Ni-MH |
| 1979 | Li-polymer |

**Li-ion: Sony 1990**

**Plastic Li-ion: 2000**



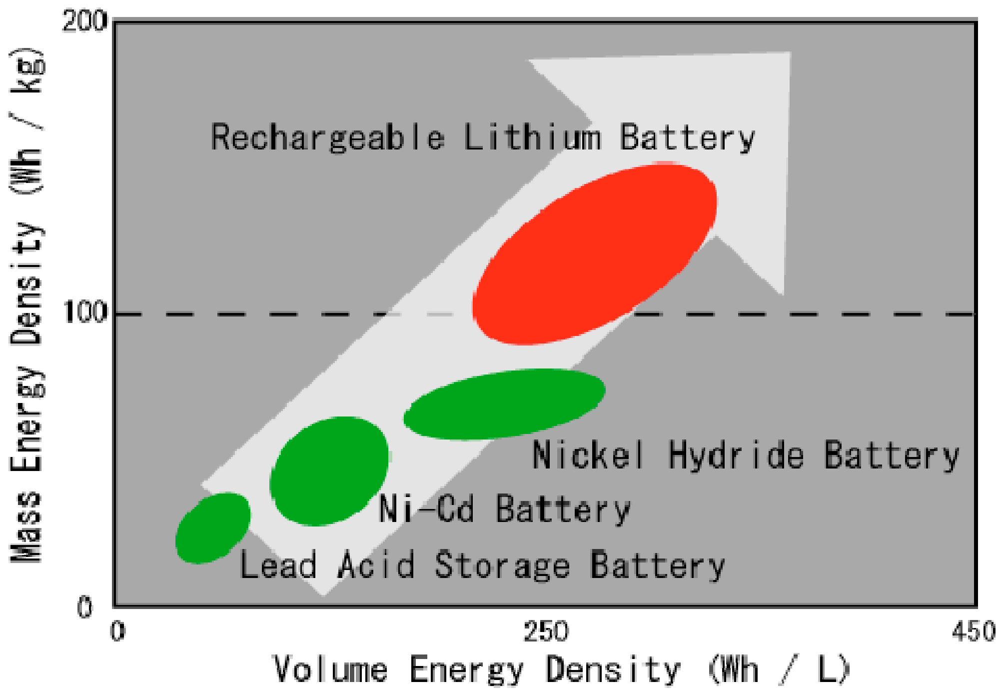
Courtesy of Dr. J-M. Tarascon, Amiens



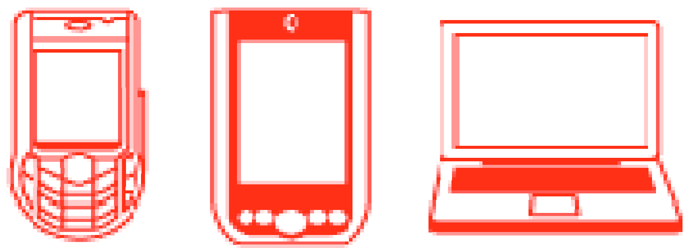

Lithium ion batteries are the power sources of choice for portable electronics.....


Lithium-ion batteries are produced at a rate of several millions per year in a variety of shape configurations.

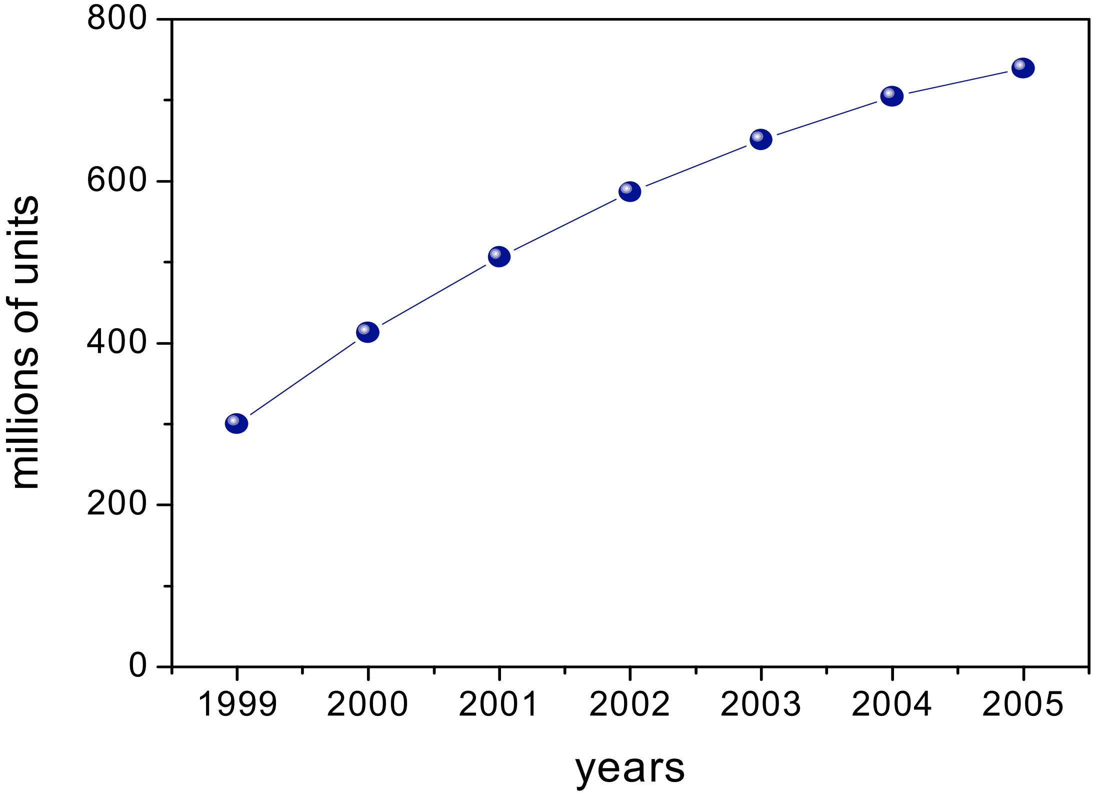
These batteries are the power sources of choice for portable electronics, e.g. cell phone, PDAs, laptops.




Cell Phone, PDA, Laptop

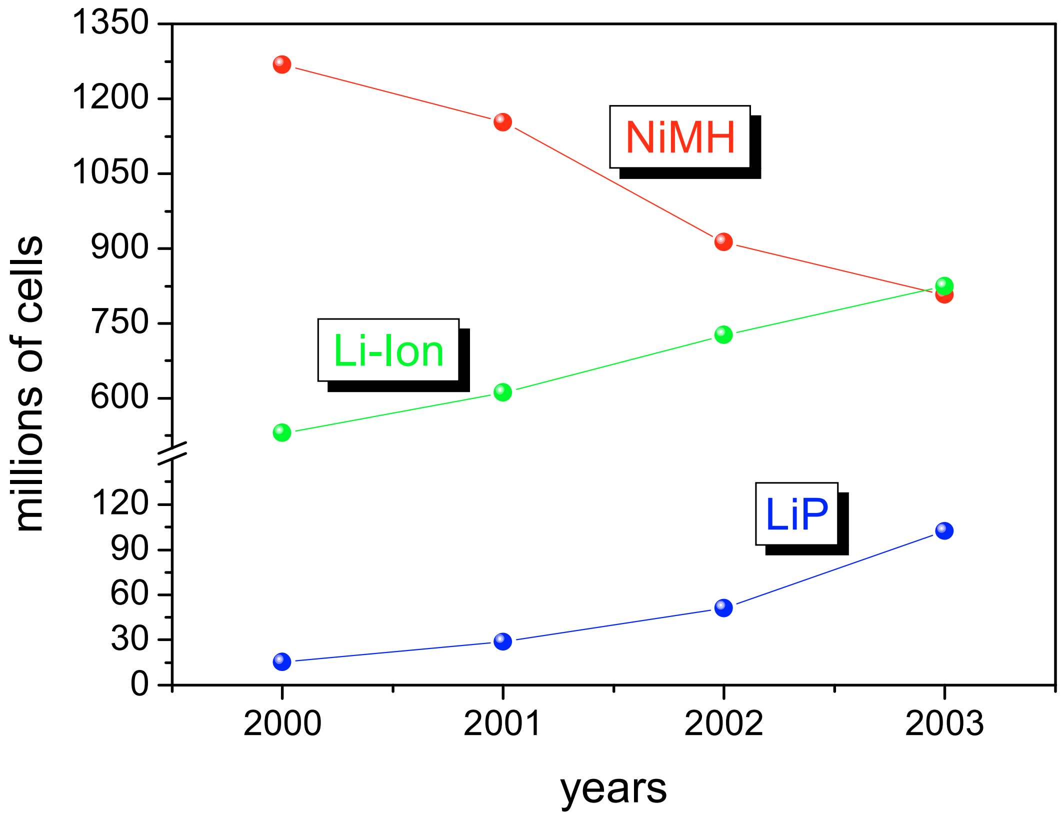


# Sale prospect of cellular phones (millions of units)



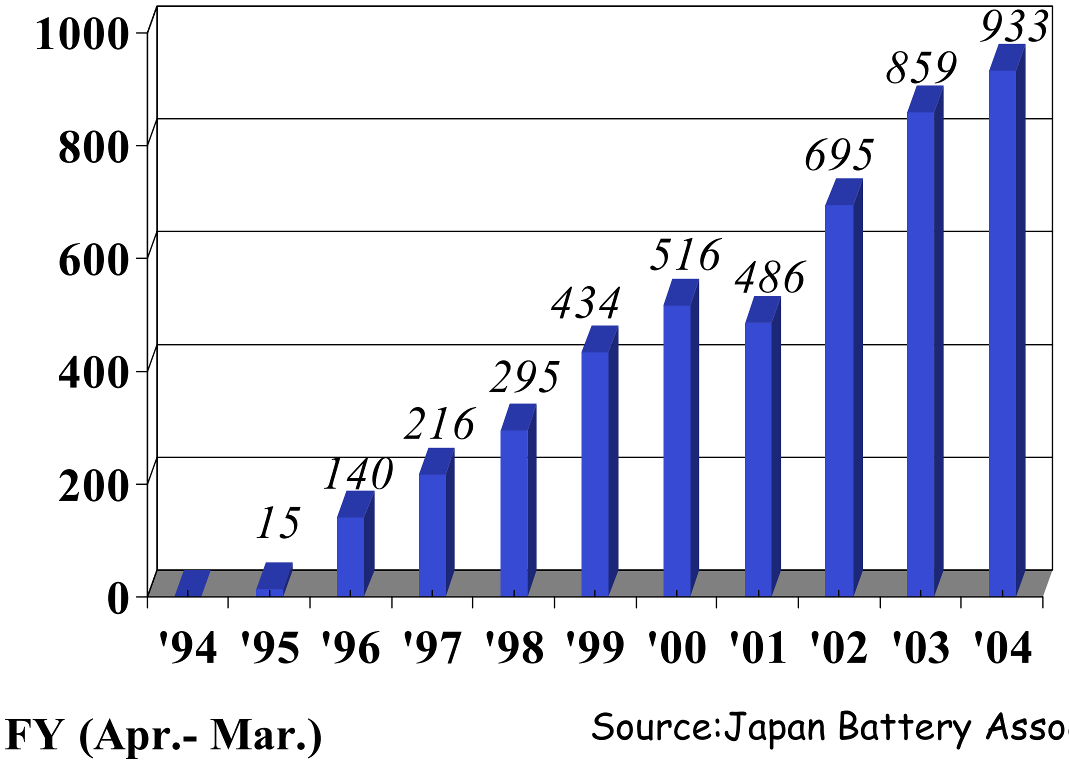

Source: Gartner Dataquest

# Sale prospect of batteries for portable electronics




Source: Takeshita

Lithium ion battery sales (millions)




Source:Japan Battery Association

Lithium-batteries: a multi-billion dollar market for popular devices, e.g. cellular phones, PDAs, laptops….

This winning technology may be applied to more demanding systems, e.g. electric cars (EVs) or hybrid cars (HEVs)

Success in these area requires improvements in terms of safety, cost, environmental compatibility.

B. Scrosati, *The Chem. Records*, 5 (2005) 286

Effectively, lithium ion battery modules are presently under development for EV and HEV applications.

## LiPB Pack System for HEV Applications


| Items | Specification |
|---|---|
| Pack Voltage | 144V |
| Nominal Capacity | 7.5Ah |
| Pack Weight | 28kg |
| Pack Volume | 28L |
| Operating Temp | -30°C ~ 60°C |
| Discharage Power(10s) | 25kw |
| Regen. Power(10s) | 17kw |
| Self-discharge | < 10%/7days |

# The hybrid car, HEV

A nickel-metal hydride batteries is presently used as the energy storage unit in HEVs .....

.... however, new types of batteries having higher energy density and lower cost than Ni-MH, are urgently needed to assure high performance and market competitiveness.

.

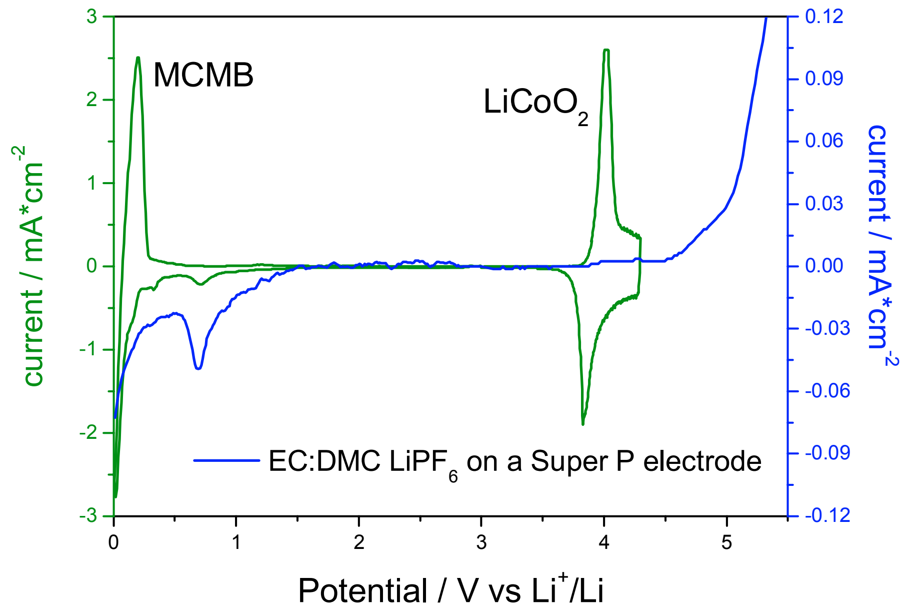
Lithium batteries can do the job.....

...provide that they can assure **safety**, high energy, low cost and high rates!

# *SAFETY*

A conventional C/ $LiPF_6$-EC-DMC/ $LiCoO_2$ lithium-ion battery operates ***beyond*** the stability window of the electrolyte.

Proper cell operation requires the formation of lithium-conducting passivating films on the electrodes' surface (Solid Electrolyte Interface, SEI).




Cyclic response of the C and the $LiCoO_4$ in a $LiPF_6$ in EC-DMC electrolyte

The films result from the decomposition processes of the electrolyte with the release of sub-products; these processes may affect the safety of the battery!

Safety is the major concern in the use of lithium ion battery modules for HEV!

The electrode materials, both anode and cathode, operate in voltage ranges which extend beyond the stability window of the electrolyte.

Safety hazards in lithium ion battery operation are associated to electrolyte decomposition phenomena.

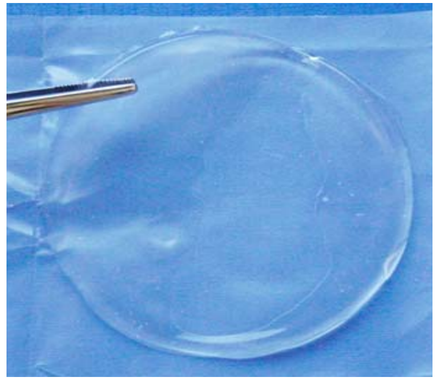
## Approaches to improve safety:

Development of liquid electrolytes having stability windows exceeding 5V vs. Li (*difficult to achieve*)

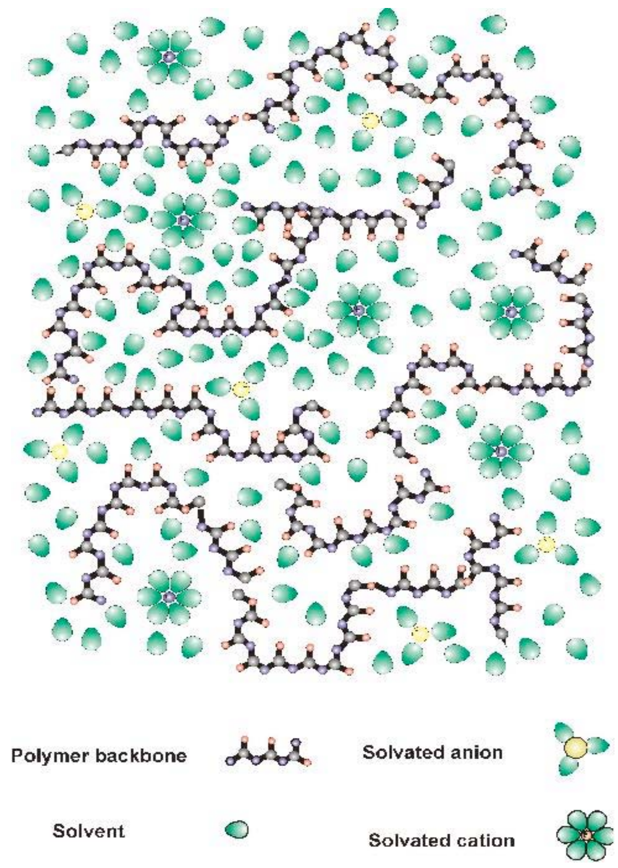
Use of a solvent-free polymer electrolyte (*plastic lithium metal rechargeable batteries*)

Use of electrode combinations operating within the stability window of the (polymer) electrolyte (*plastic novel types of lithium-ion batteries*)

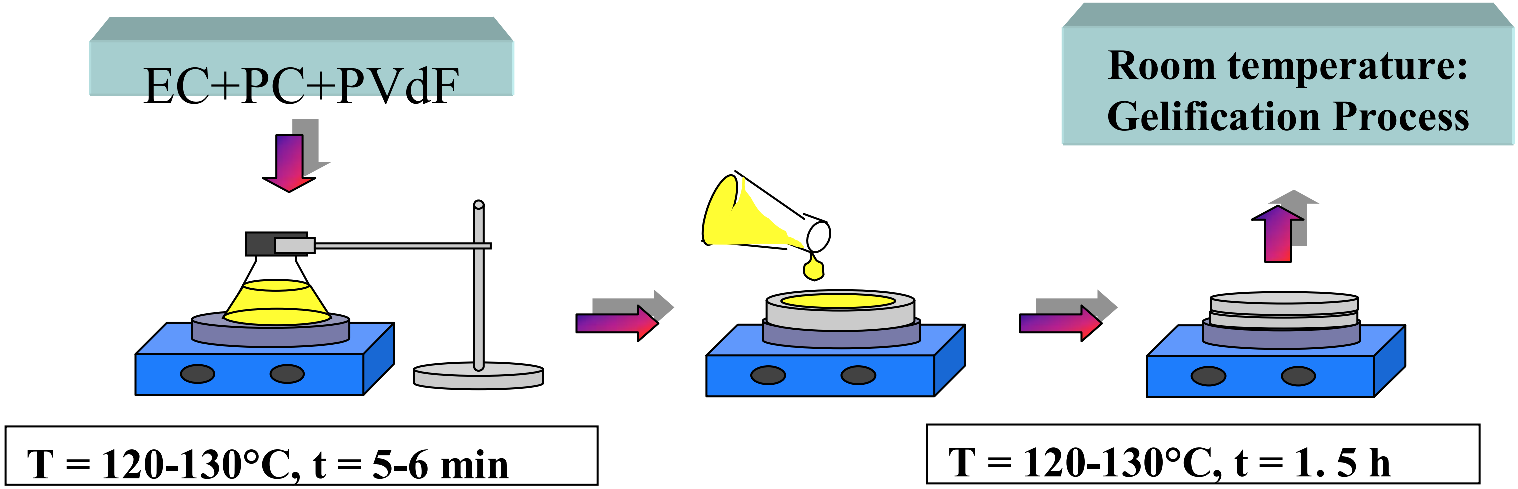
Gel-type membranes, formed by trapping liquid solutions (e.g., a $LiPF_6$-PC-EC solution ) in a polymer matrix (e.g. a poly(vinylidene fluoride), PVdF matrix (*GPE*).



SCHEMATIC OF GEL POLYMER ELECTROLYTE STRUCTURE

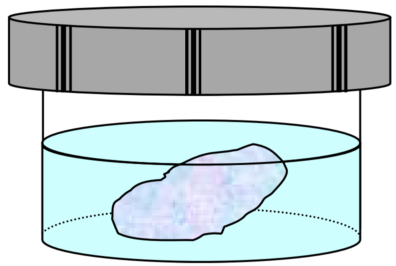


# Preparation of PVdF-based Gel Polymer Electrolytes




***Preparation of Gel Polymer Electrolyte membrane:***

The Gel Polymer membrane is dipped into a swelling solution: EC-PC (1:1 w/w), $LiPF_6$ 1M.
Swelling time: 2 hours.

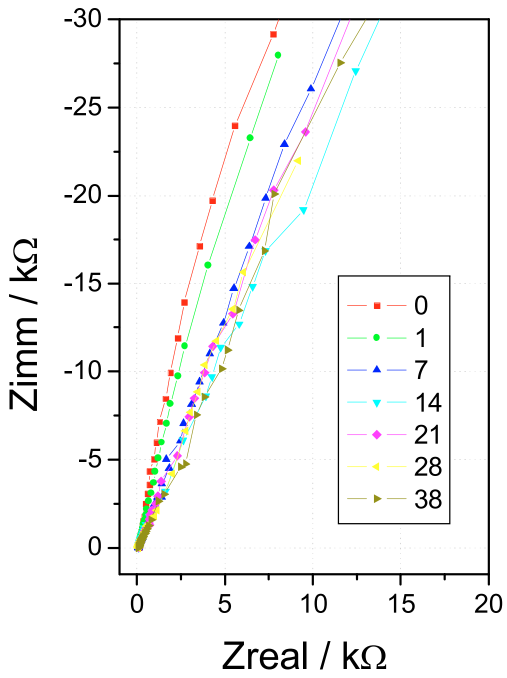


***Gel Polymer Electrolyte composition:***

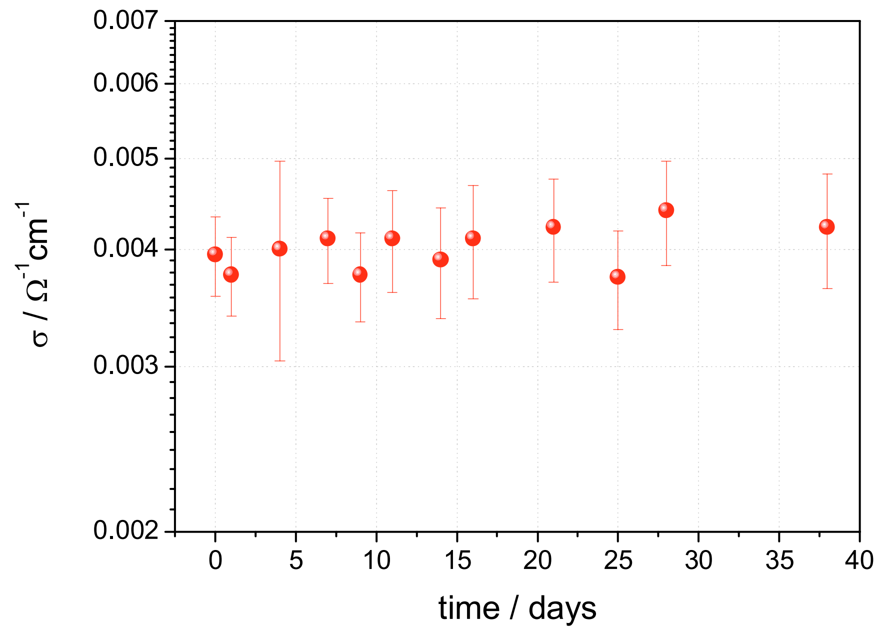
Membrane: 80 wt% EC-PC (1:1 w/w), 20 wt% PVdF;
Swelling solution: EC-PC (1:1 w/w), $LiPF_6$ 1M.

# Polymer gel electrolyte: membrane formed by trapping a $LiPF_6$-PC-EC solution into a poly(vinylidene fluoride) PVdF matrix $LiPF_6$-PC-EC -PVdF PGE

## Conductivity

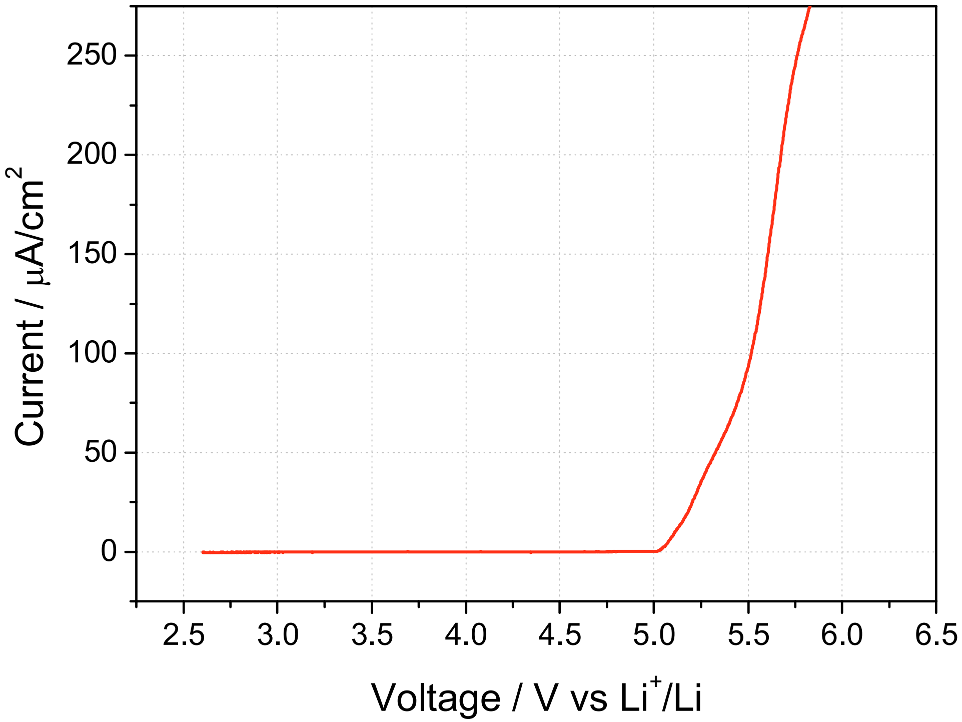



Impedance response versus time



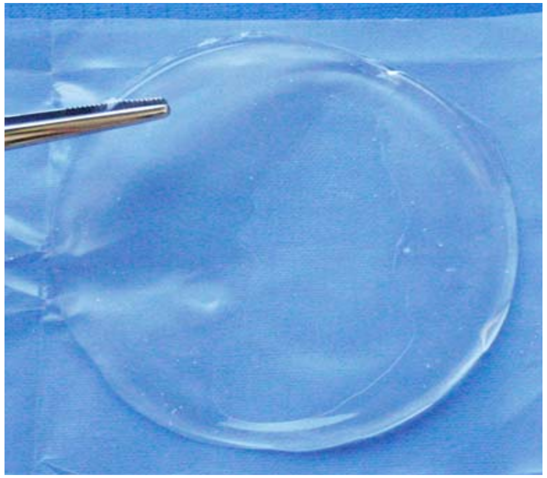

Time dependence of conductivity

# $LiPF_6$-PC-EC -PVdF PGE




Stability window exceeding 5 V vs. Li!

Polymer electrolyte



Gel-type, lithium conducting membrane

High conductivity, high stability

# High safety lithium ion batteries

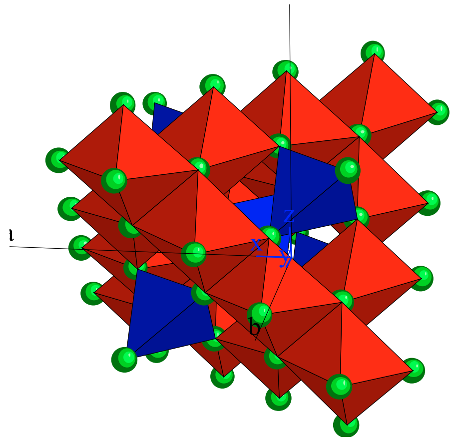
Cell combination based on a $Li_{4/3}Ti_{5/3}O_4$ anode and a $LiFePO_4$ cathode and a gel-type polymer electrolyte

F. Croce, L. Persi, B. Scrosati .Electrochem.Solid State Lett, 2000
P.Reale, S. Panero, B. Scrosati,J. Garche, M. Wohlfahrt-Mehrens, M.Wachtler, J.Electrochem.Soc, 151 (2004) A2138

# Structure, morphology and characteristics of the electrode materials

# Anode:

# Lithium Titanium Oxide



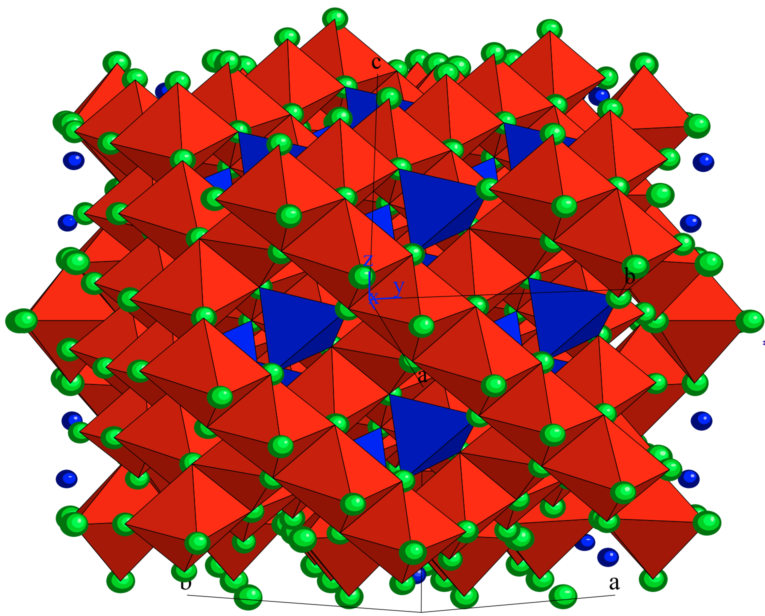
$$Li_4Ti_5O_{12} + Li^+ + e^- \Leftrightarrow FePO_4$$

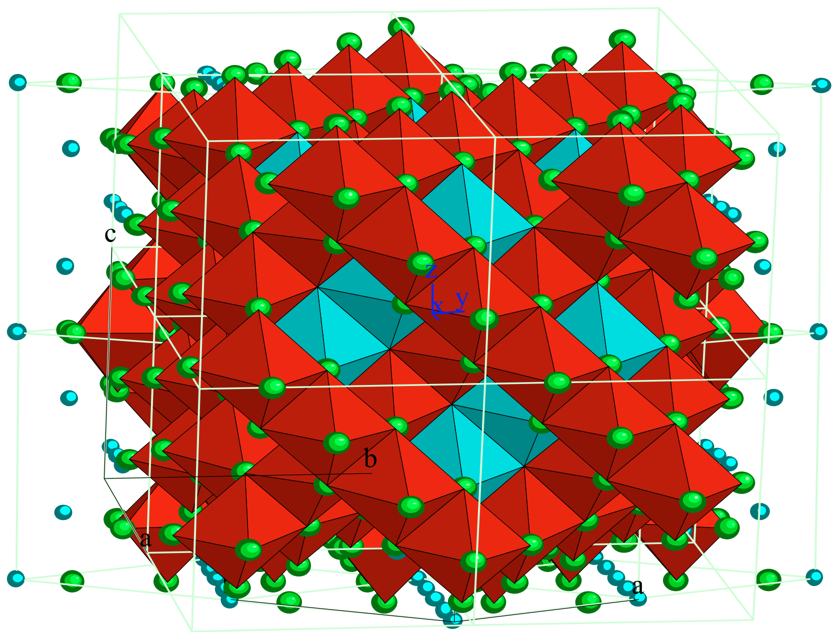
Two-phase process (constant voltage: 1.5 V vs. $Li^+$ /Li)

# $Li_{4/3}Ti_{5/3}O_4$

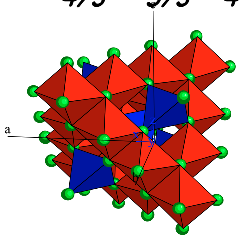
$$Li_{(8a)}[Li_{1/3}Ti_{5/3}]_{(16d)}O_{4(32e)} + Li^+ + e^- \rightleftarrows Li_{2(16c)}[Li_{1/3}Ti_{5/3}]_{(16d)}O_{4(32e)}$$

$Fd\bar{3}m$ $\qquad\qquad$ $Fd\bar{3}m$



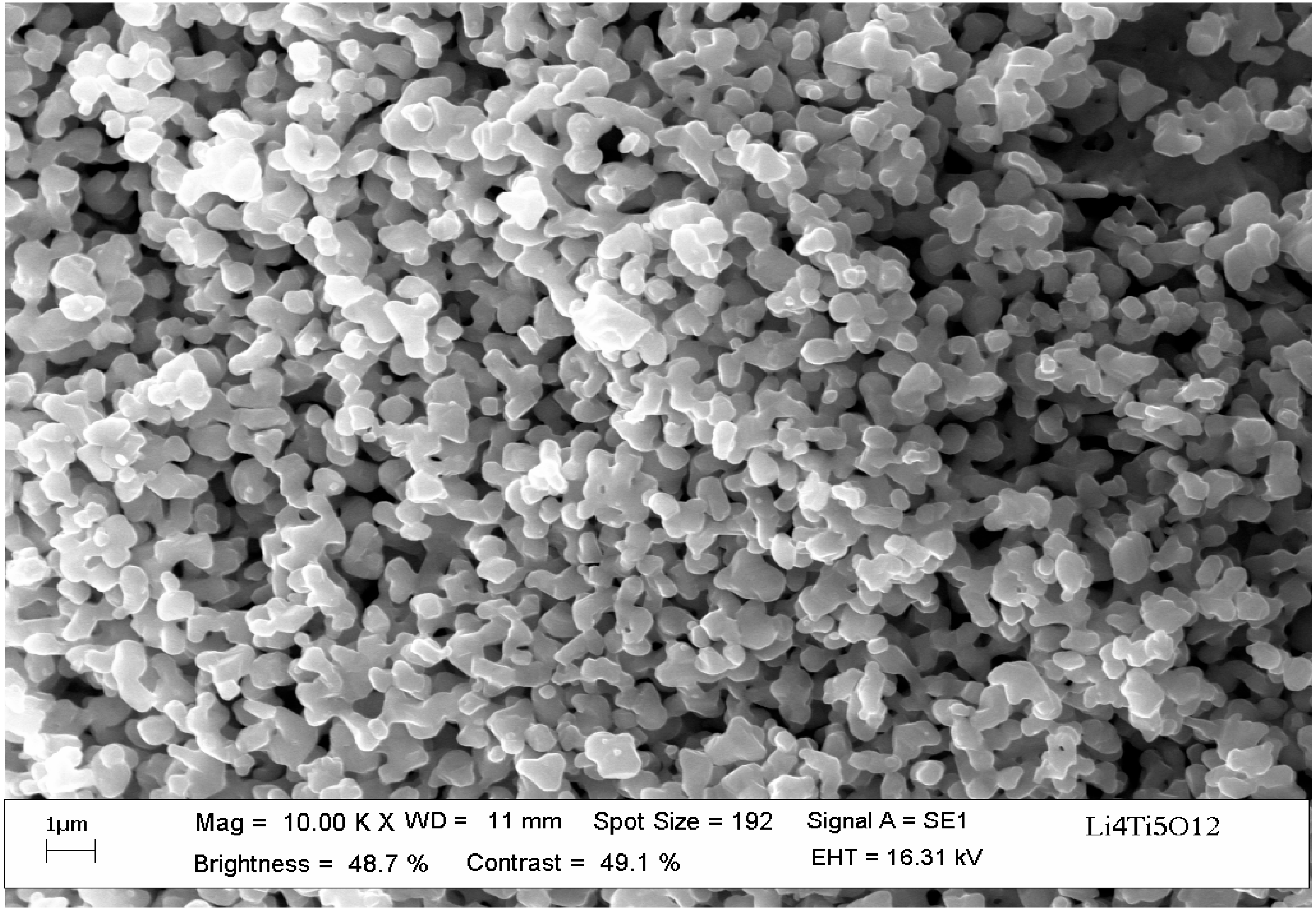


$Li_{4/3}Ti_{5/3}O_4$

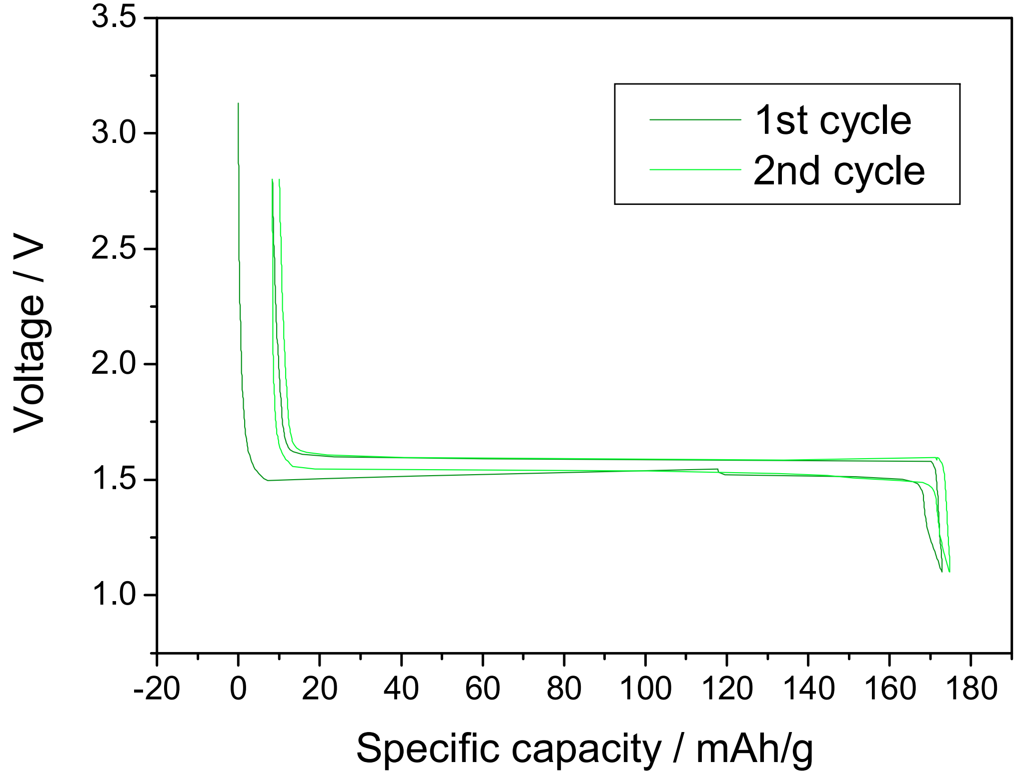


Two phase process ⇒ constant voltage (1.56V vs $Li^+/Li$)

# $Li_4Ti_5O_{12}$electrode

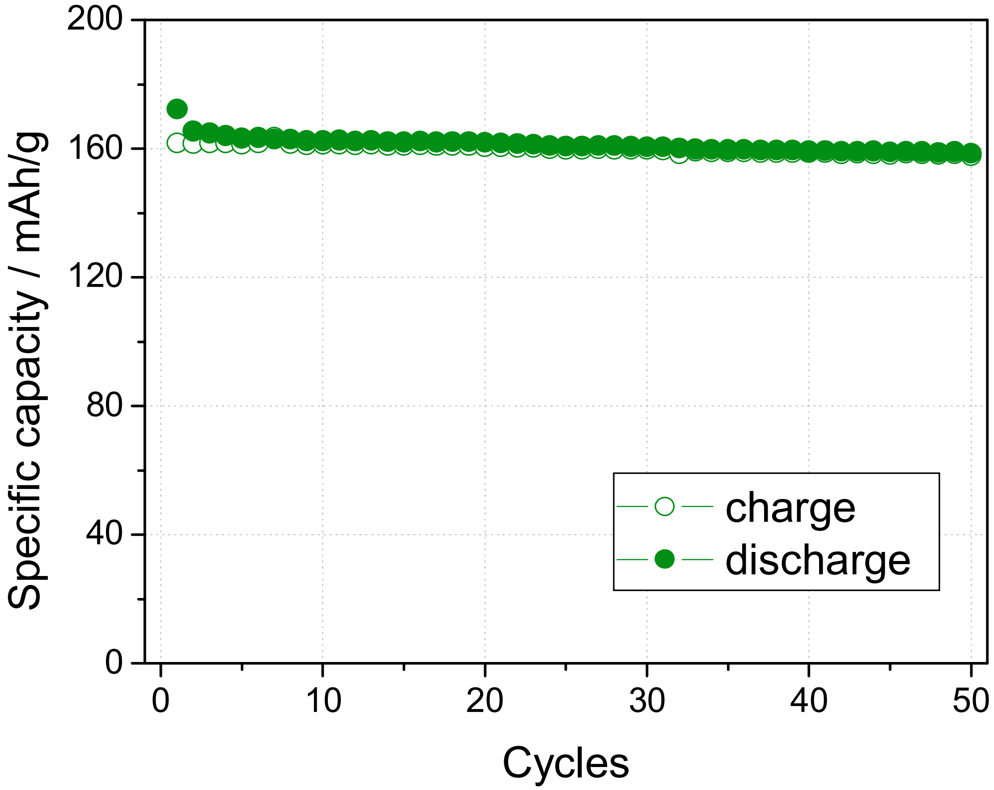


# $Li_4Ti_5O_{12}$ electrode




Voltage evolution (vs. Li) of the electrochemical process (lithium uptake) - (lithium removal) in a Li/ $LiPF_6$-PC-EC -PVdF gel cell. Current rate: C/20. Room temperature.

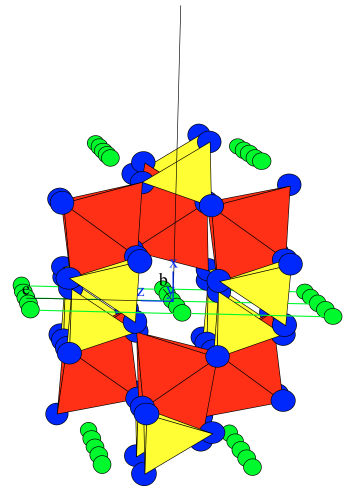
# $Li_4Ti_5O_{12}$ electrode




Galvanostatic cycles at C/5 in a Li/ $LiPF_6$-PC-EC -PVdF gel cell. Room temperature.

## Cathode:

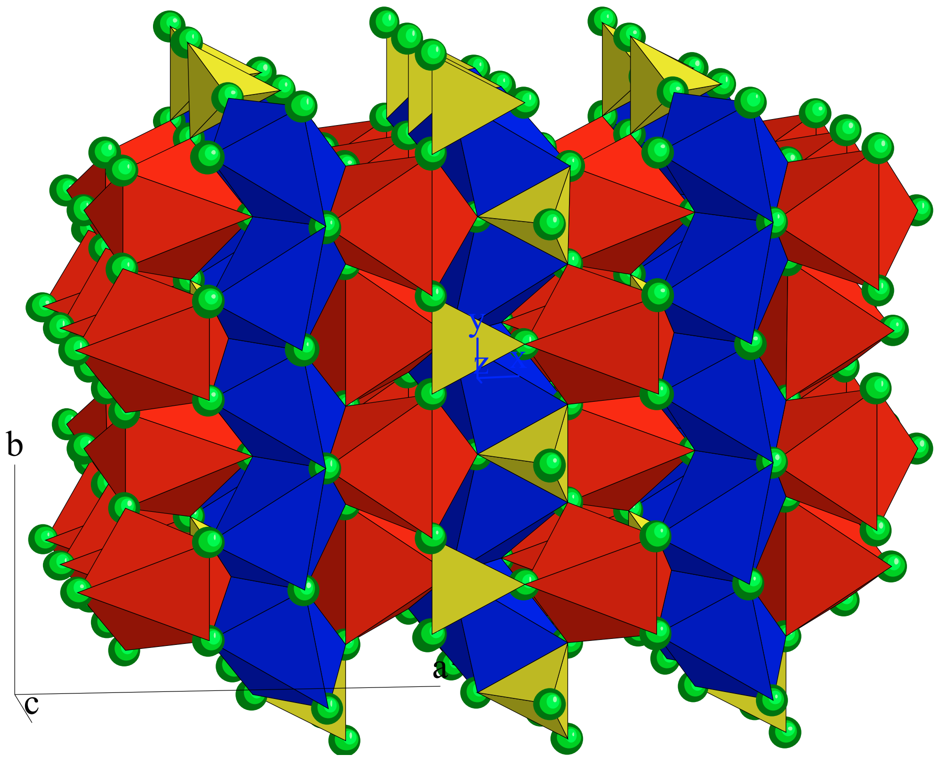
## Lithium iron phosphate

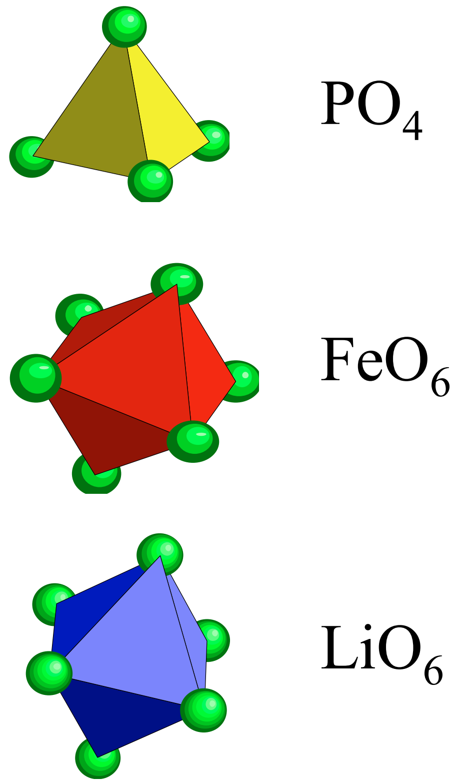


$$LiFePO_4 \Leftrightarrow Li^+ + FePO_4 + e^-$$

Two-phase process (Constant voltage: 3.5 V vs. $Li^+$ /Li)

# Olivine lithium iron phosphate

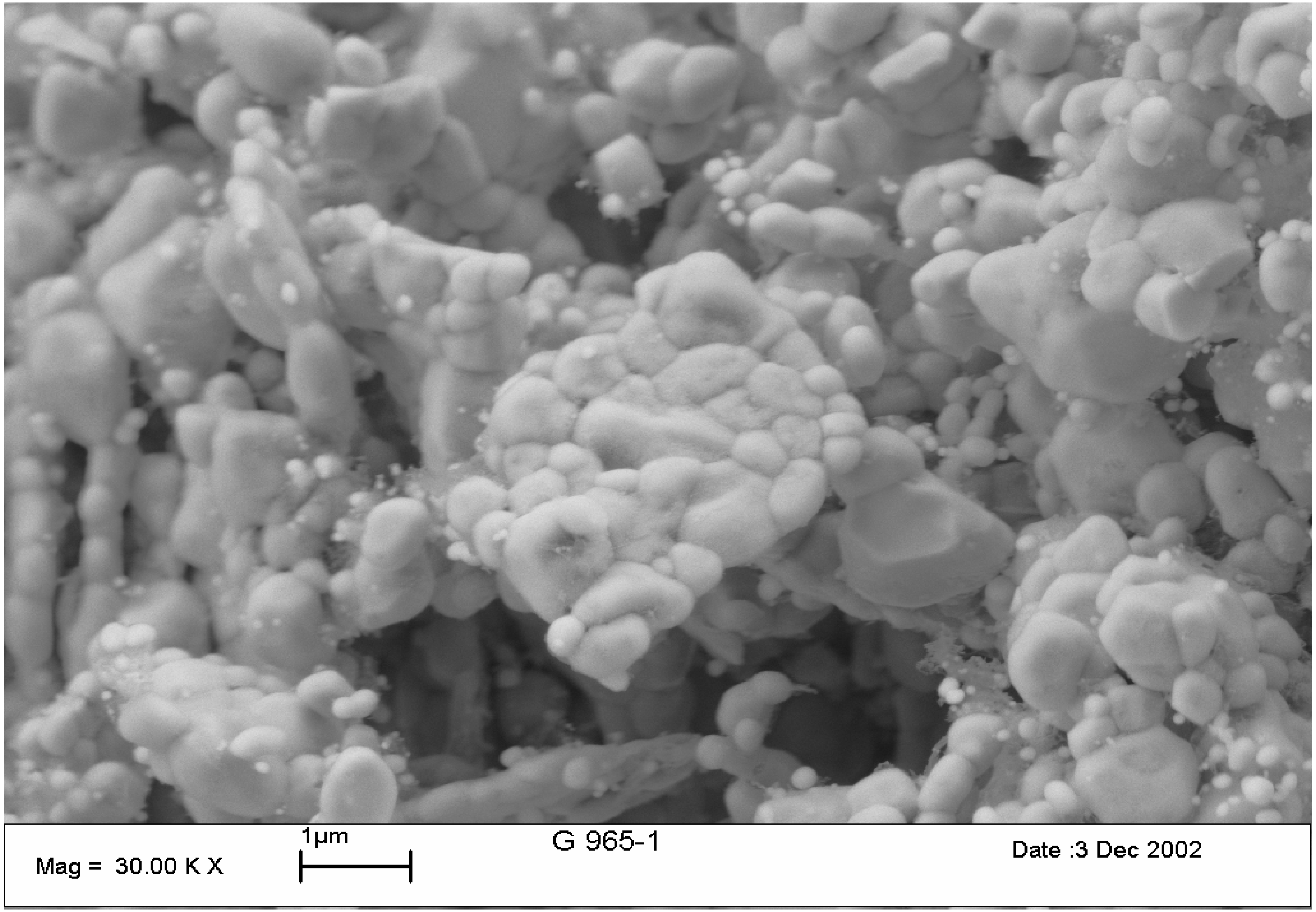



$LiFePO_4 \Leftrightarrow Li^+ + FePO_4 + e$

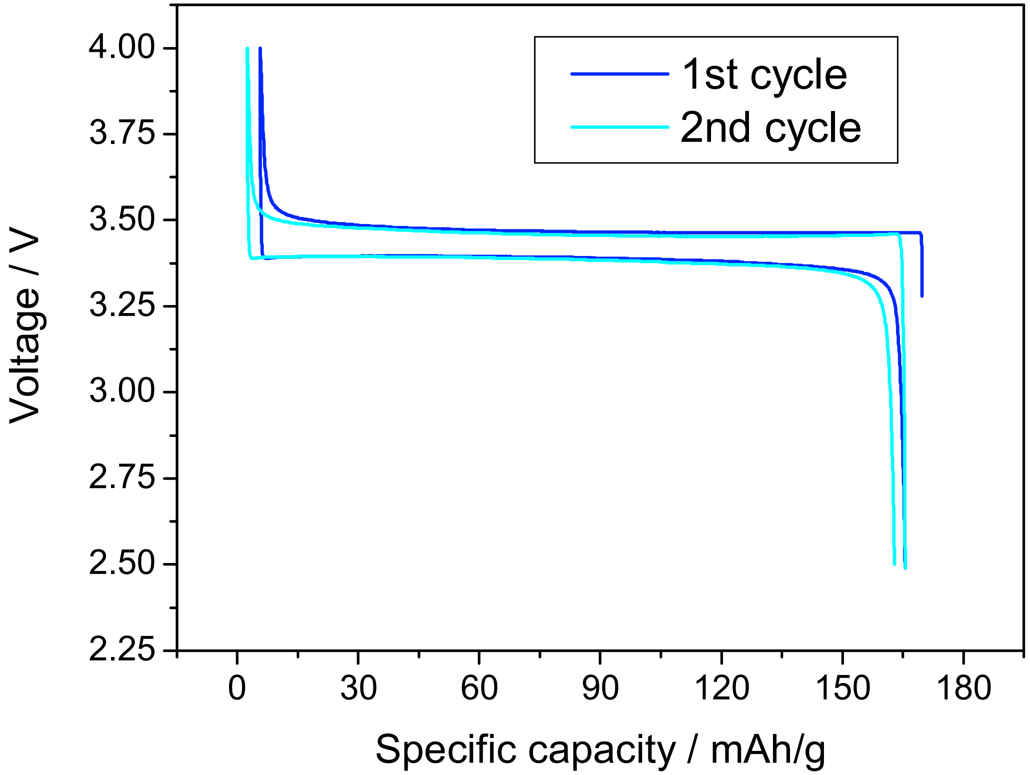
Two-phase process (3.5 V vs. $Li^+$/Li)

# $LiFePO_4$ electrode



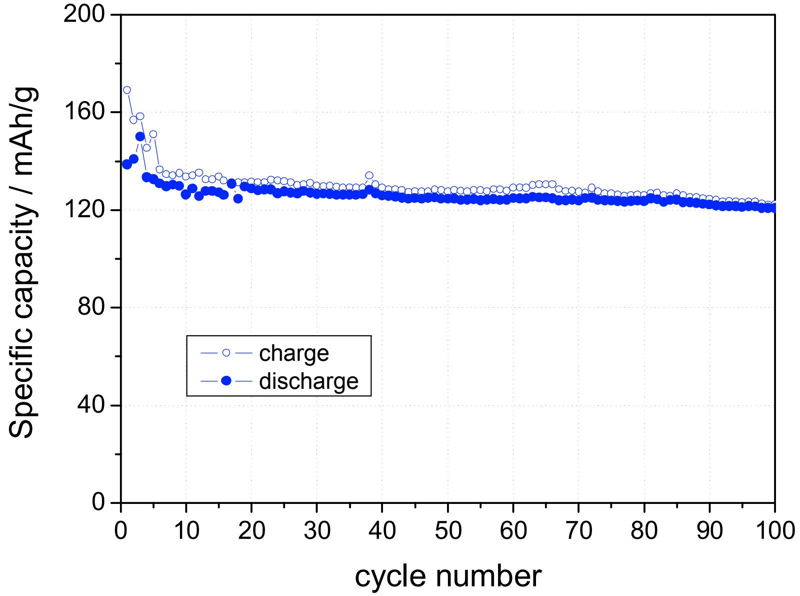

Material prepared in Professor Garche's Laboratory, ZSW, Ulm

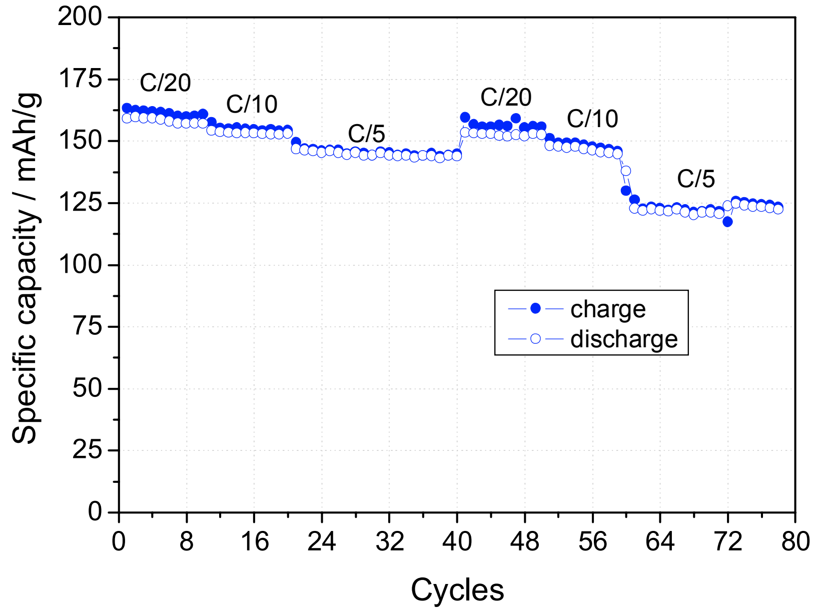
# $LiFePO_4$ electrode




Voltage evolution vs. Li of the electrochemical process (lithium uptake) - (lithium removal) in a Li/ $LiPF_6$-PC-EC -PVdF gel cell. Current rate: C/20. Room temperature.

# $LiFePO_4$ electrode

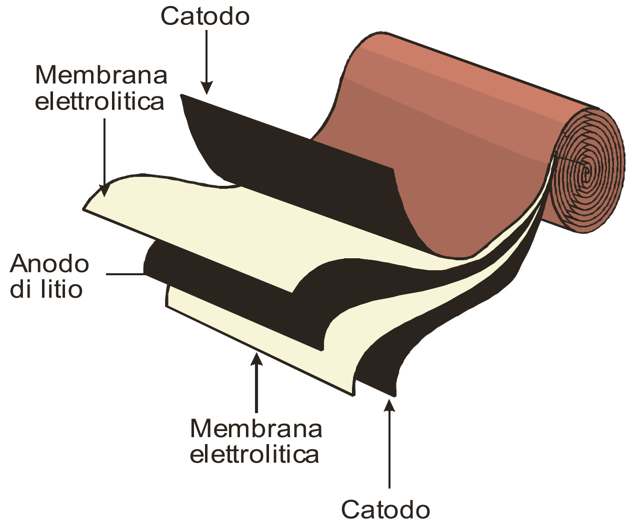



Galvanostatic cycles at various rates in a Li/ $LiPF_6$-PC-EC -PVdF gel cell. Room temperature.

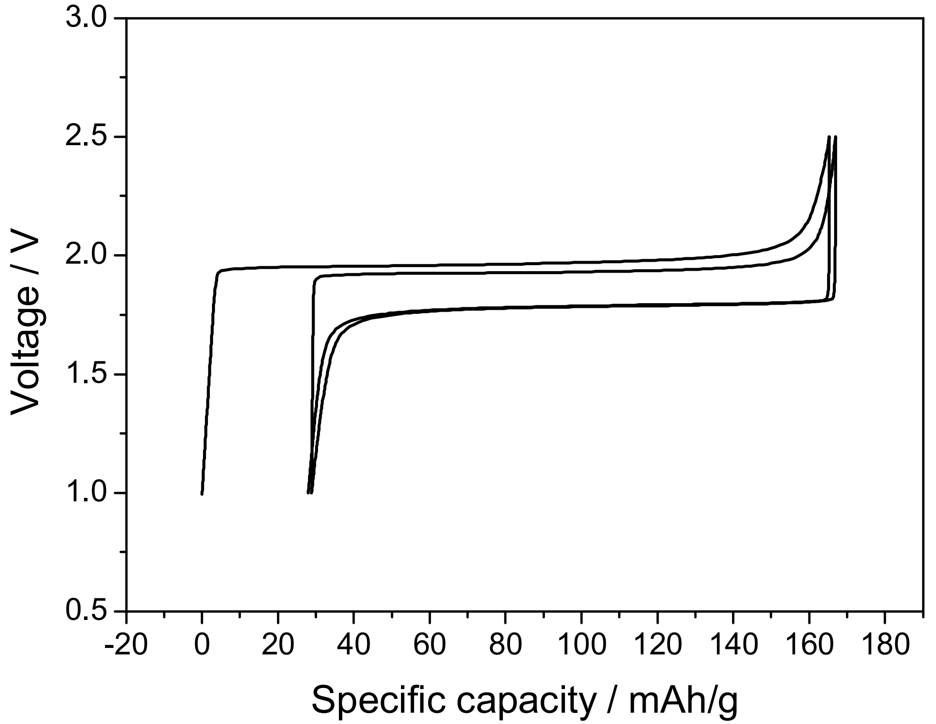
## $Li_4Ti_5O_{12}$ / $LiPF_6$-PC-EC -PVdF / $LiFePO_4$

## lithium ion polymer cell




Combination of a 1.5 V anode with a 3.5V cathode gives a 2V battery!

# $Li_4Ti_5O_{12}$ / $LiPF_6$-PC-EC -PVdF / $LiFePO_4$ lithium ion polymer cell

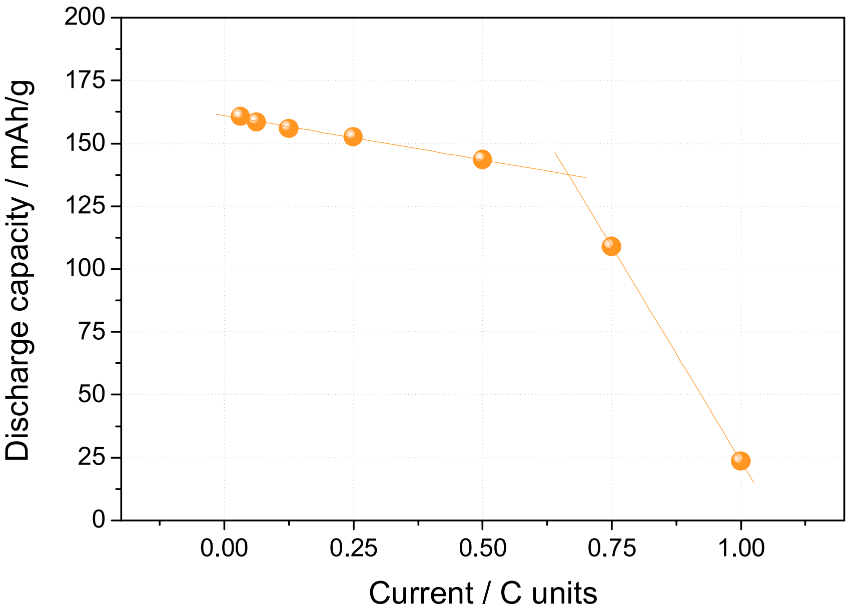



Galvanostatic charge-discharge voltage profile

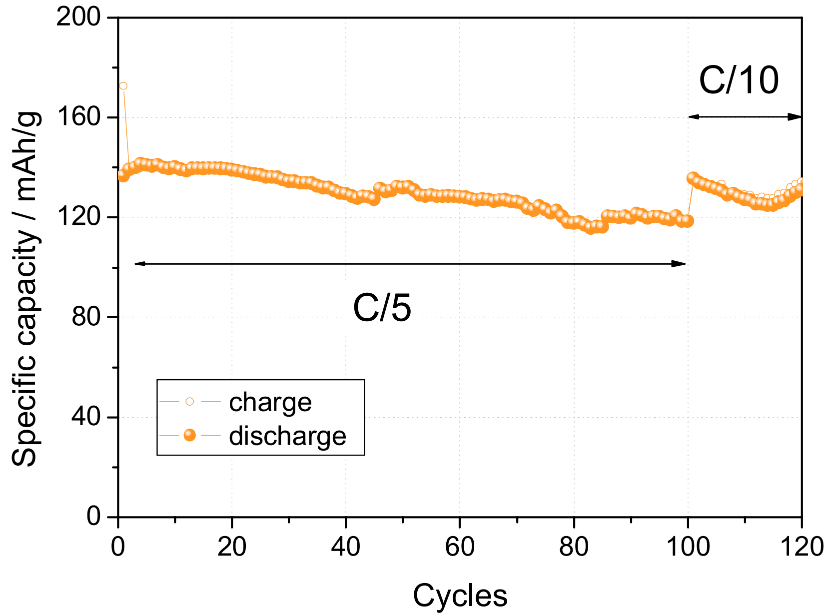
Current rate: C/20. Room temperature.

P.Reale, S. Panero, B. Scrosati,J. Garche, M. Wohlfahrt-Mehrens, M.Wachtler, J.Electrochem.Soc, 151 (2004) A2138

# $Li_4Ti_5O_{12}$ / $LiPF_6$-PC-EC -PVdF / $LiFePO_4$ lithium ion polymer cell




Discharge capacity vs current rate. Room temperature.




Capacity versus cycle number. Room temperature.

P.Reale, S. Panero, B. Scrosati,J. Garche, M. Wohlfahrt-Mehrens, M.Wachtler, J.Electrochem.Soc, 151 (2004) A2138

# High safety lithium ion batteries

Electrode combination based on a $Li_{4/3}Ti_{5/3}O_4$ anode and a $LiFePO_4$ cathode.

Both electrodes operate within the stability window of the electrolyte, are cheap, not toxic and evolve along a flat, two-phase lithium acceptance-removal process with minor structure modifications.

Extra step towards reliability and cell design modularity is achieved by moving from the standard liquid-like electrolyte to a polymer electrolyte configuration.

Reliable and safe batteries.

P.Reale, S. Panero, B. Scrosati,J. Garche, M. Wohlfahrt-Mehrens, M.Wachtler, J.Electrochem.Soc, 151 (2004) A2138

# High safety lithium ion batteries

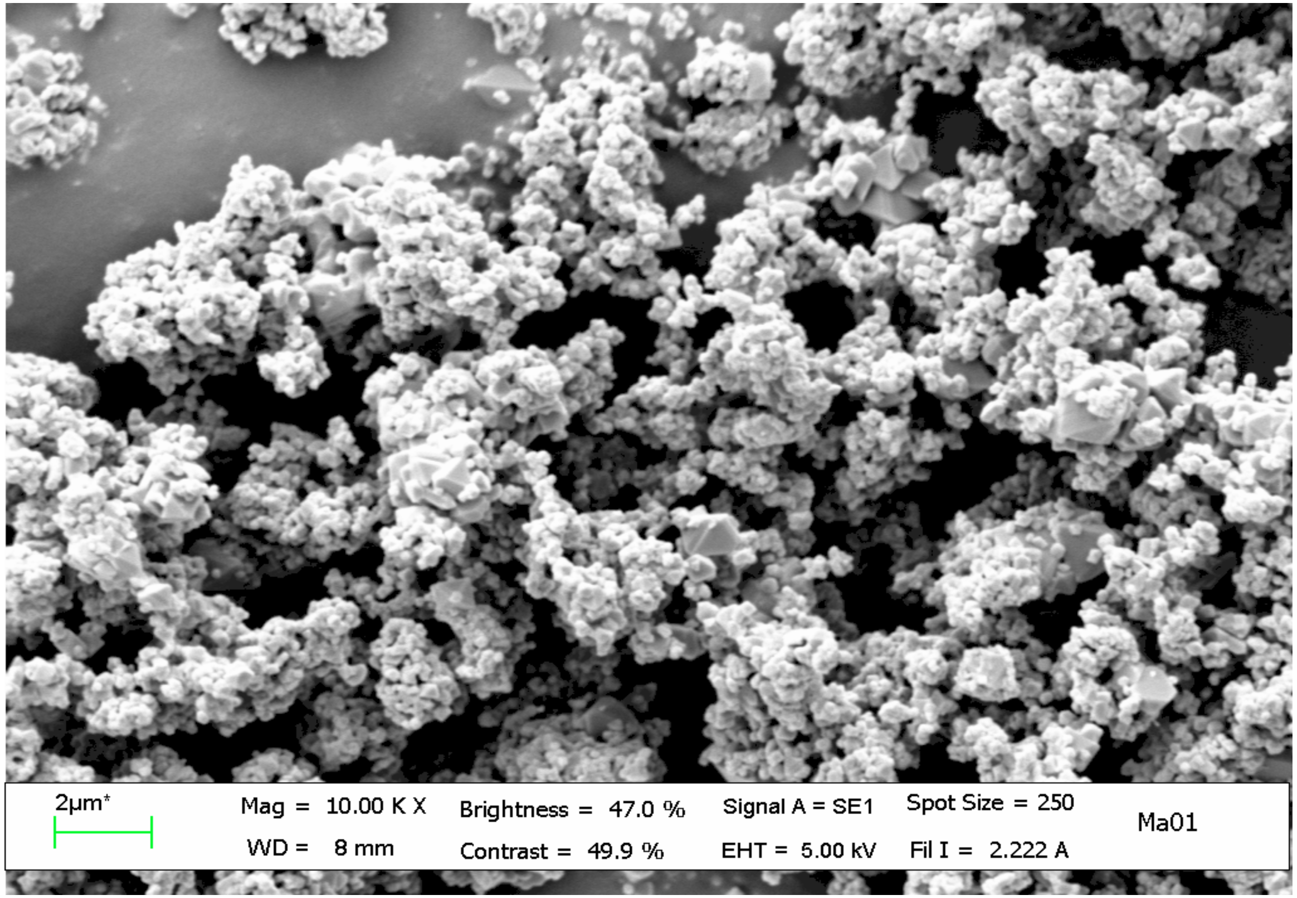
## Strategies for further improving the battery performance:

High voltage cathodes (higher voltage)

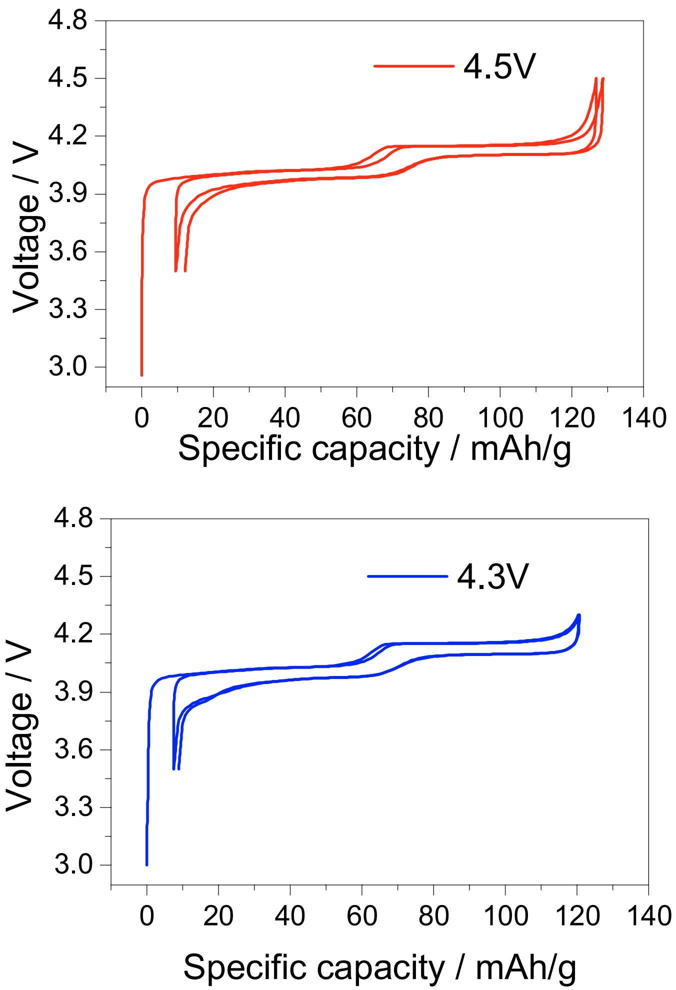
Electrode nano morphology (higher rate)

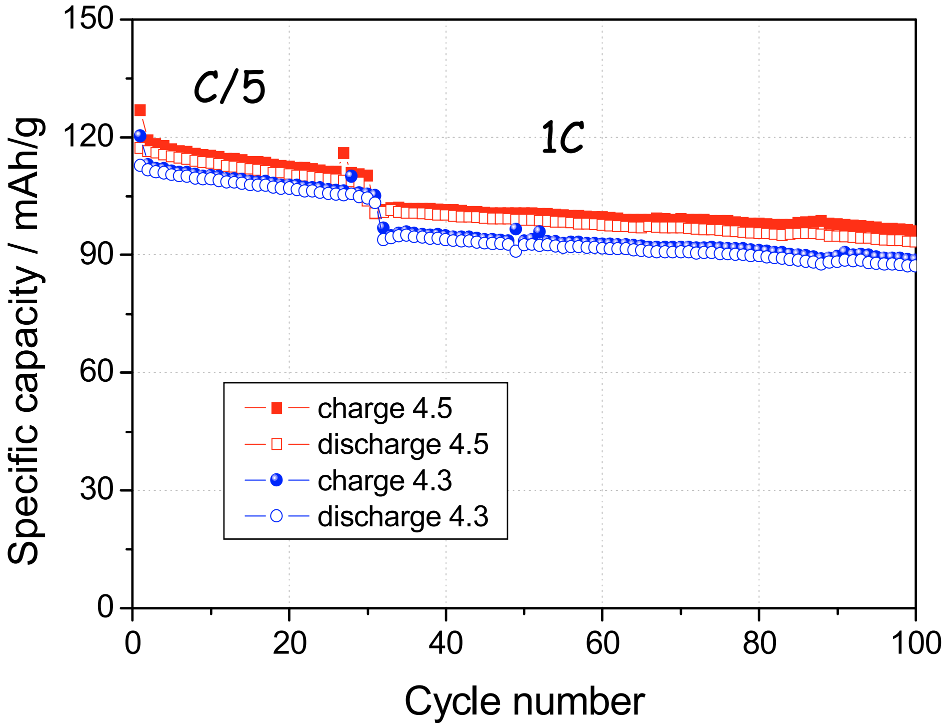
# 4V volt cathodes
# $LiMn_2O_4$ - solid state synthesis

Li :Mn=0.98 : 2



# Voltage evolution vs. Li of the electrochemical process



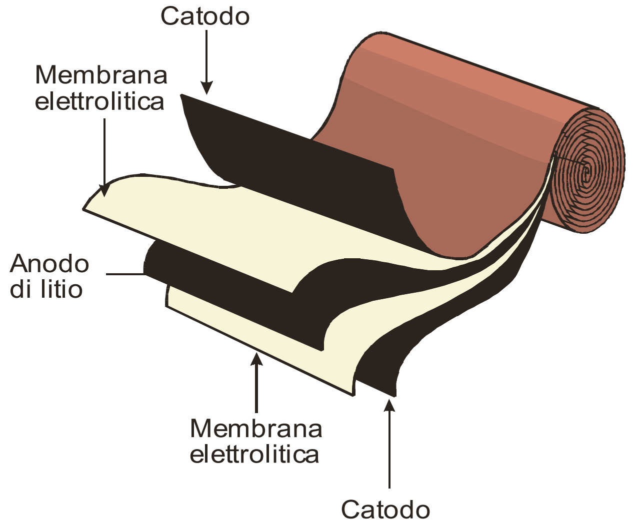




Solid State

$LiMn_2O_4$

# $Li_4Ti_5O_{12}$ / $LiPF_6$-PC-EC -PVdF /$LiMn_2O$

# lithium ion polymer cell

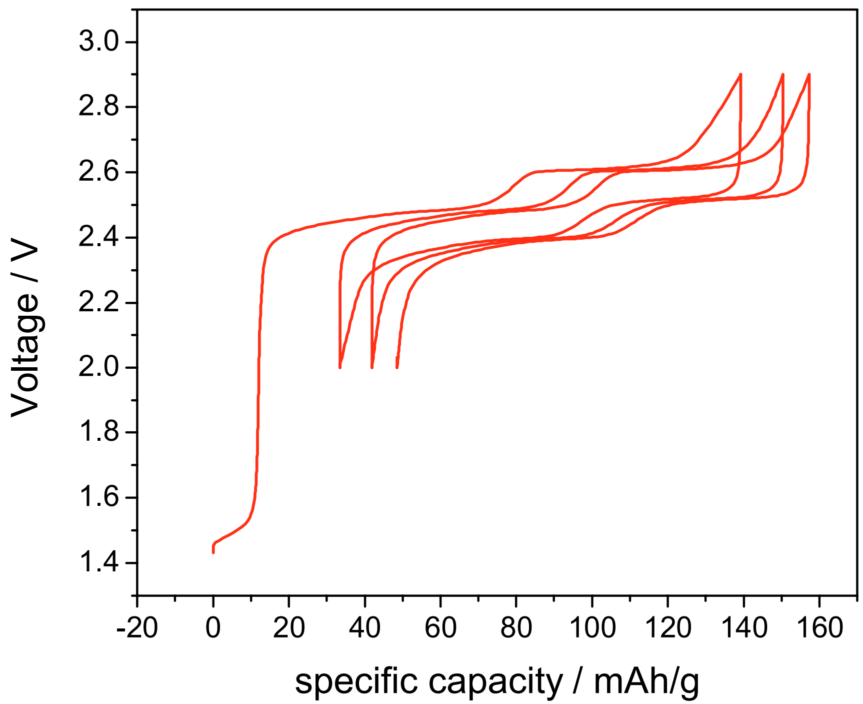


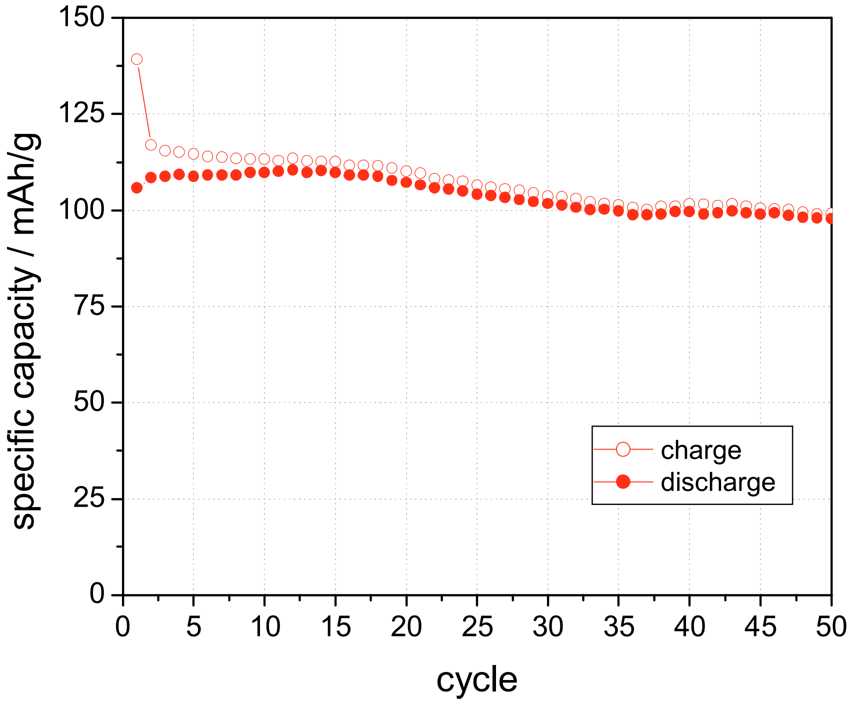

Combination of a 1.5 V anode with a 4.0V cathode gives a 2.5V battery!

# Lithium-ion battery

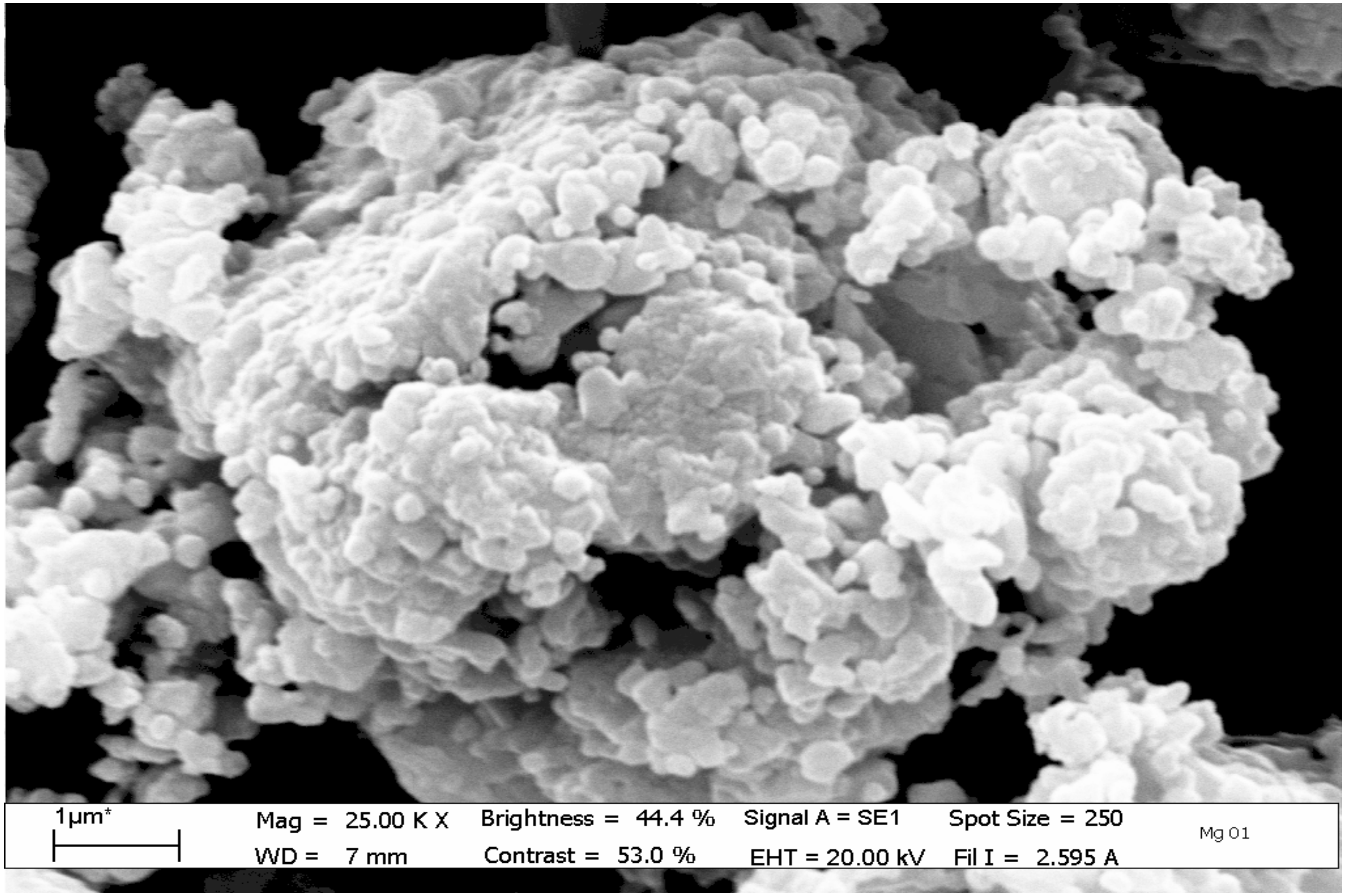
## $Li_4Ti_5O_{12}$ /PVdF EC:PC $LiPF_6$ / $LiMn_2O_4$

## Galvanostatic cycles at **C/5** respect $LiMn_2O_4$
## 2.0-2.9 V voltage range



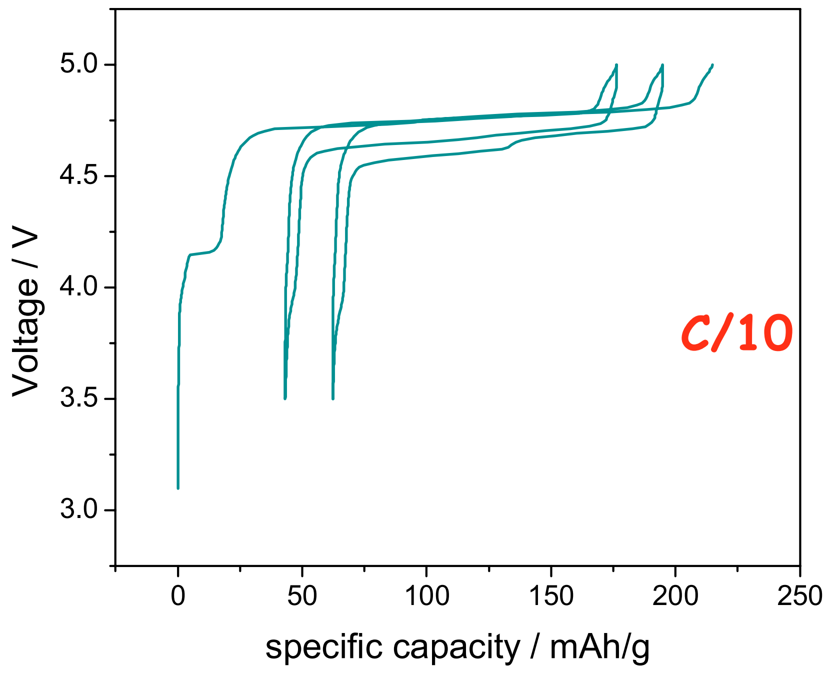
# 5V cathodes $LiNi_{0.5}Mn_{1.5}O_4$ - Wet chemistry

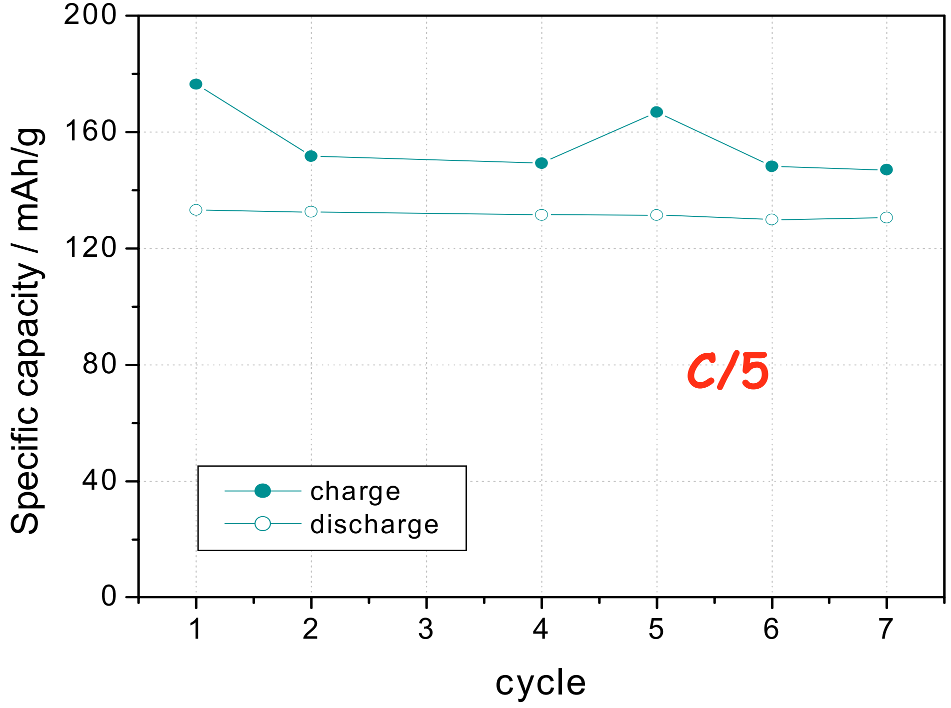



ICP analysis:

$Li_{0.98}Ni_{0.51}Mn_{1.49}O_z$

# Galvanostatic cycling of $LiNi_{0.5}Mn_{1.5}O_4$ in a lithium cell.



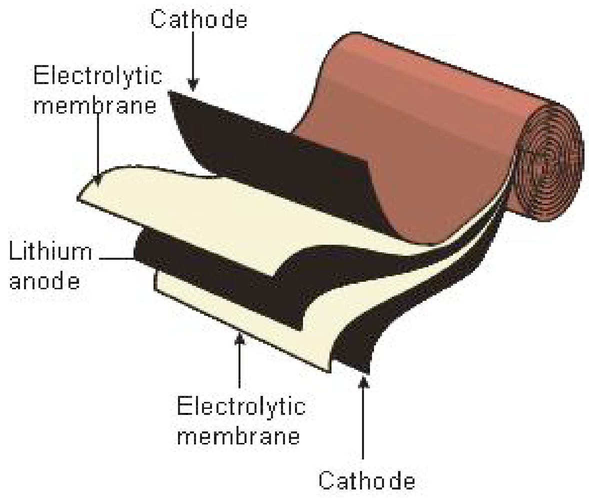




Voltage profiles vs. Li

Capacity vs. cycle number

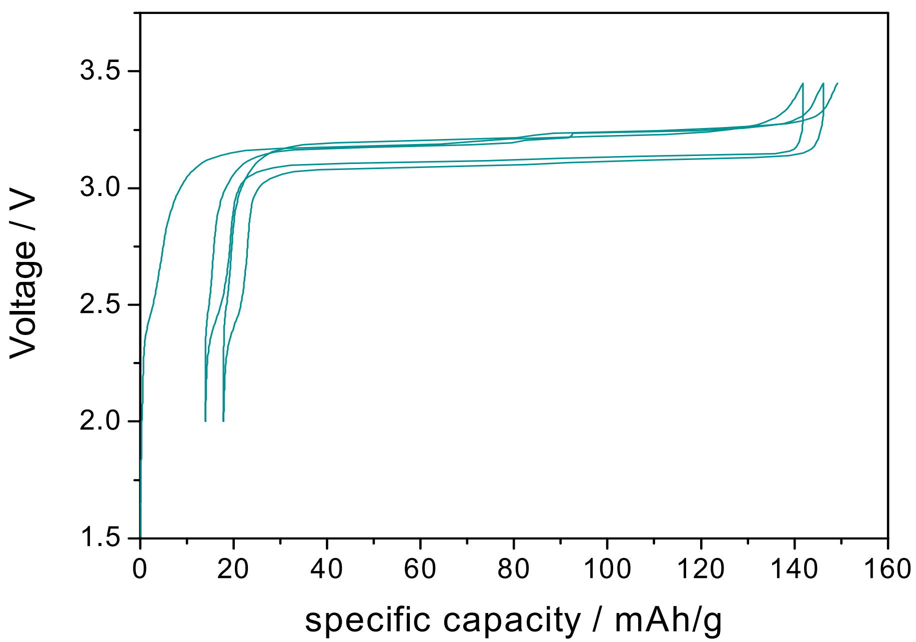
# $Li_4Ti_5O_{12}$ / PGE / $LiNi_{0.5}Mn_{1.5}O_4$

# lithium ion polymer cell

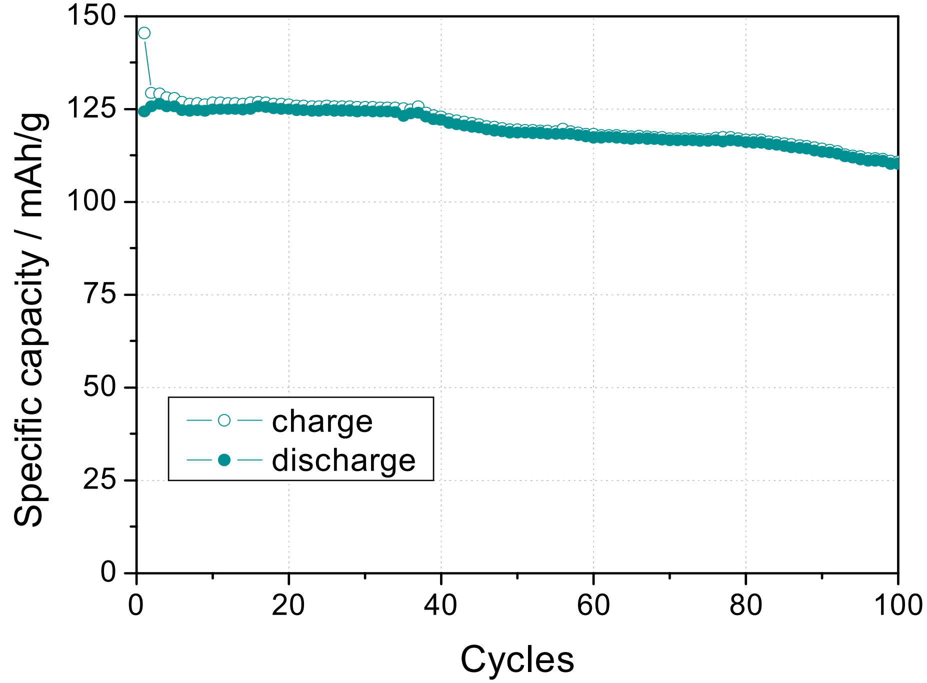



Combination of a 1.5 V anode with a 4.5 V cathode gives a 3V safe battery!

# $Li_4Ti_5O_{12}$ / GPE/ $LiNi_{0.5}Mn_{1.5}O_4$ lithium ion polymer battery




Galvanostatic charge-discharge voltage profile. Current rate: C/20. Room temperature.




Capacity versus cycle number at C/5. Room temperature.

P.Reale, S. Panero, B. Scrosati, J.Electrochem.Soc, 152 (2005) A1949

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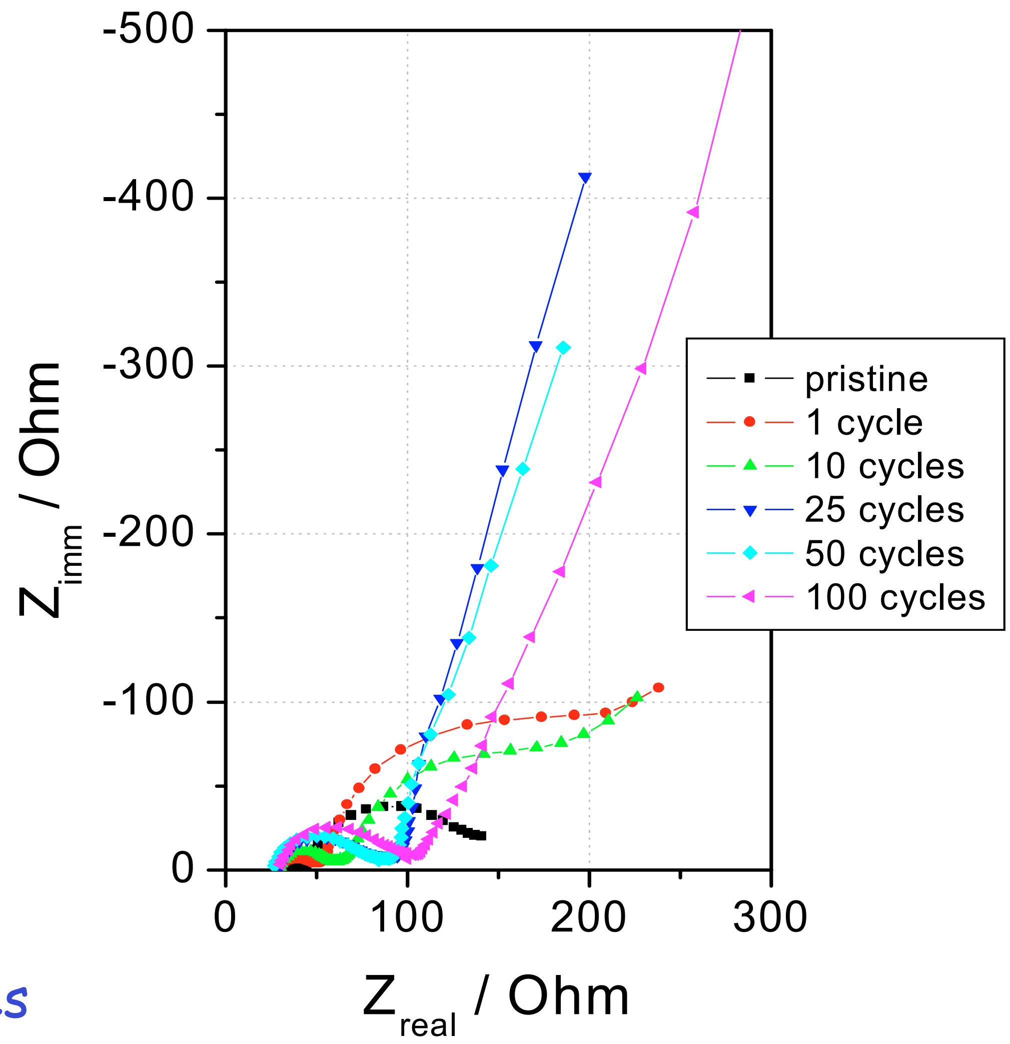
## *Specific features*




Impedance response recorded at various cycles. Frequency range: 50kHz-50mHz; ΔV=10mV. Room temperature.

- -High safety
- -low cost
- -long cycle life
- -environmental compatibility
- -high stability
- -acceptable rates

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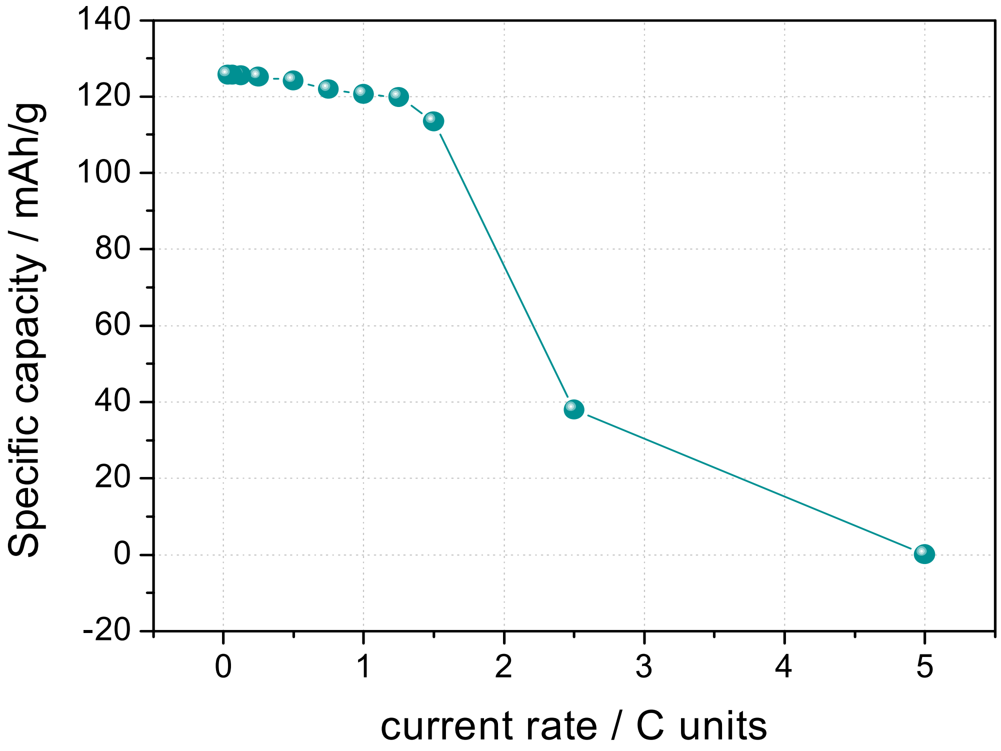


Discharge capacity vs current rate of the lithium ion $Li_4Ti_5O_{12}$/GPE/$LiNi_{0.5}Mn_{1.5}O_4$ battery. Room temperature.

-High safety
-low cost
-long cycle life
-environmental compatibility
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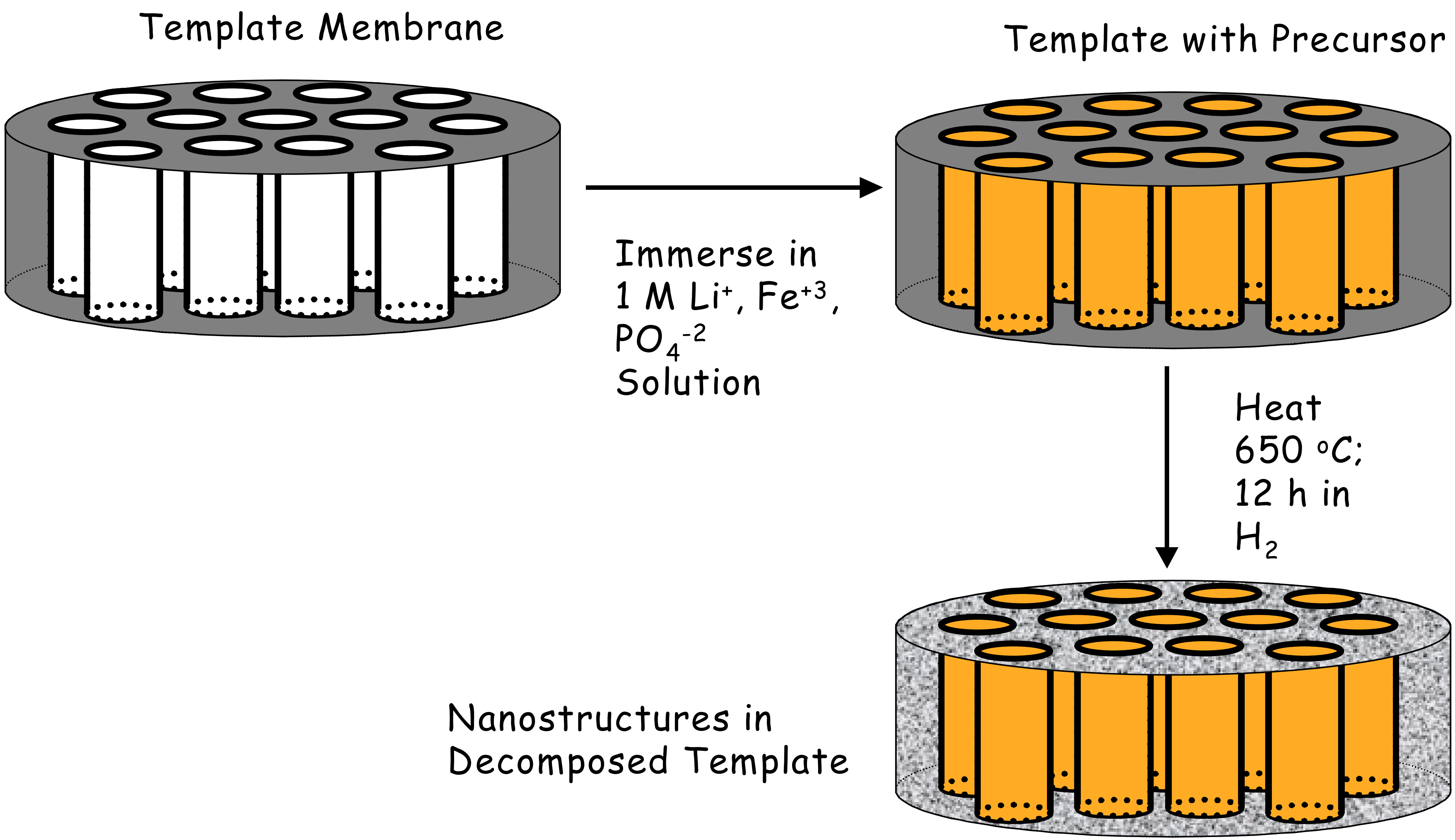
-acceptable rates

# High safety lithium ion batteries

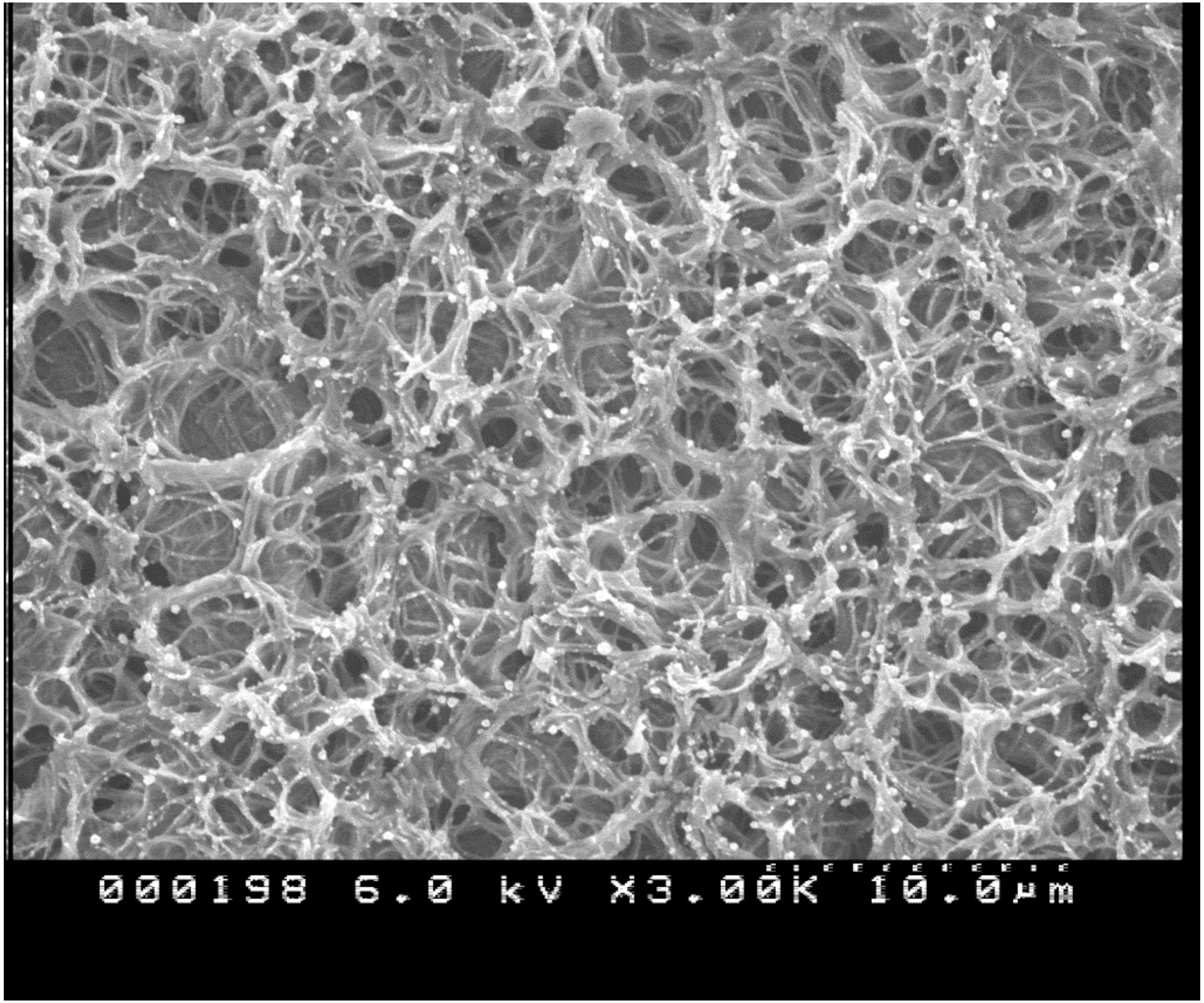
## Strategies for further improving the battery performance:

Electrode nano morphology (higher rate)

# Schematic of Template Synthesis of $LiFePO_4$ Nanostructures in Carbon



# Morphology of nanostructured $LiFePO_4$



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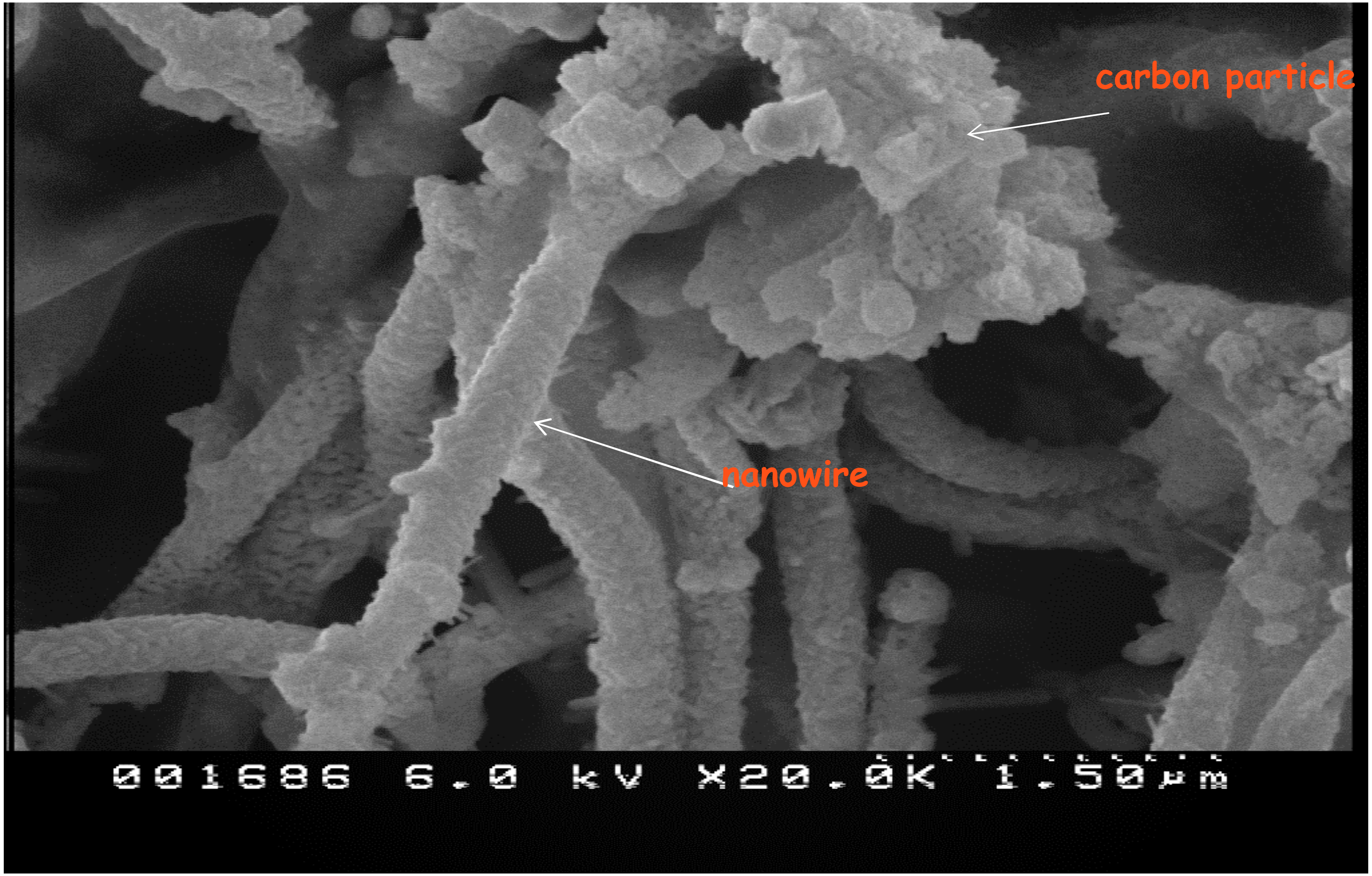

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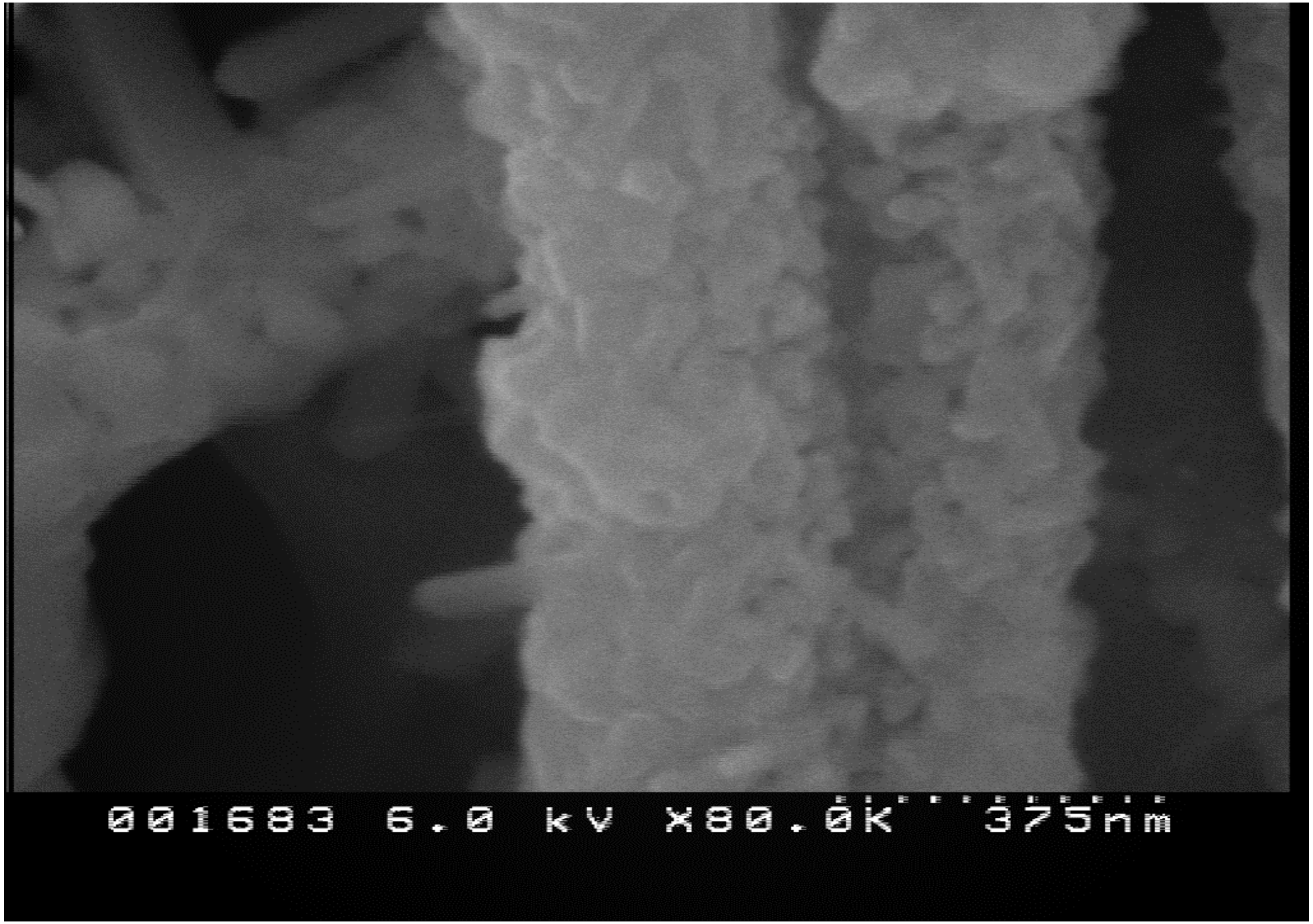
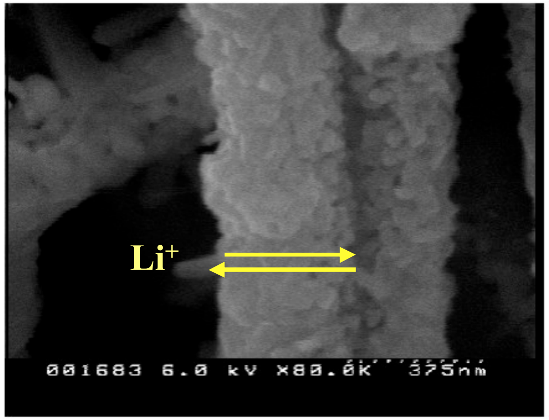
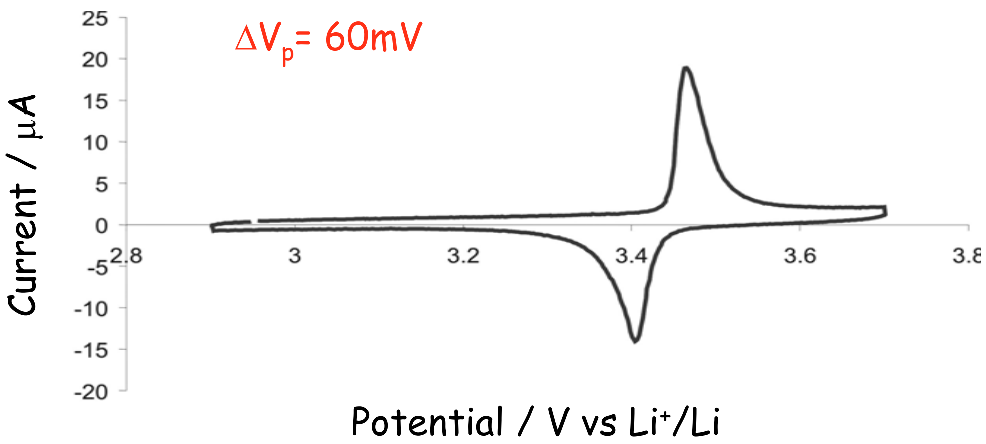
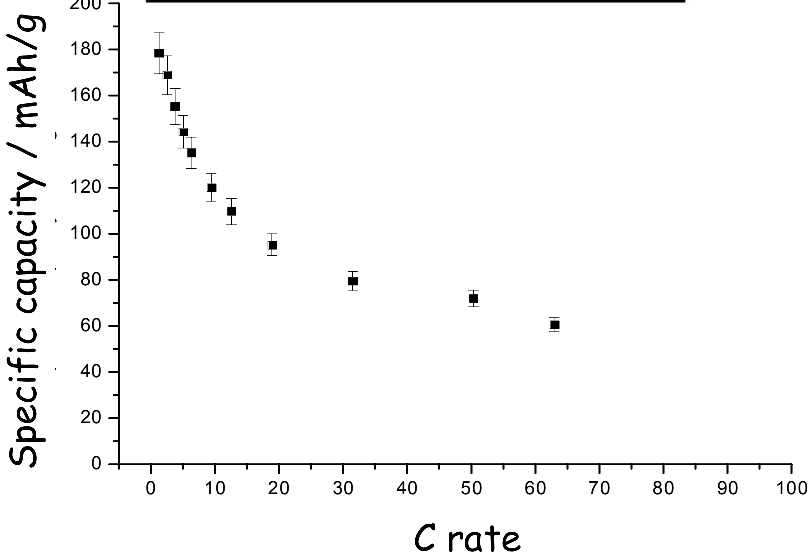


# Nanostructured, lithium iron phosphate: reduced lithium ion diffusion length: fast kinetics!




High reversibility




High power

F. Croce, R. Sides, C. Martin, B. Scrosati, Electrochem & Solid-State Lett, in press

# Conclusion

Optimized, advanced lithium batteries are needed to assure progress in HEV technology.

Valid approaches:

use of modified solvent-free polymer electrolytes for the development of ***long-life, reliable lithium polymer batteries***

use of gel-type electrolytes in combination with selected electrodic couple for the development of ***stable lithium-ion polymer batteries***

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Italian Ministry of Education , University and Resarch,
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"*Advanced Lithium Energy storage System Based on the Use of Nano-powders and Nano-composite Electrodes/Electrolytes*"

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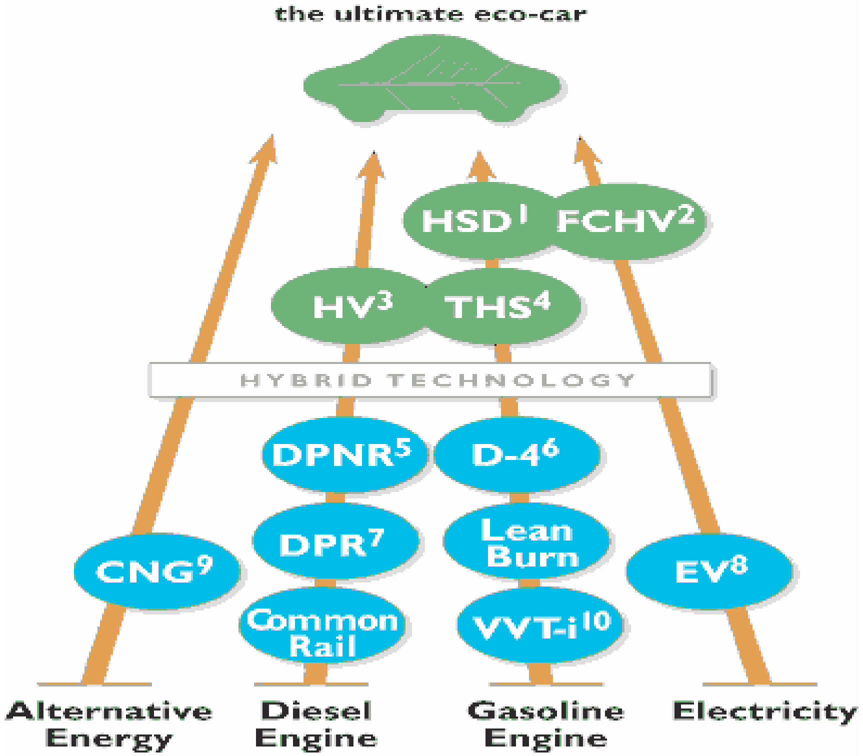


[1] **HSD**: Hybrid Synergy Drive, [2] **FCHV**: Fuel Cell Hybrid Vehicle, [3] **HV**: Hybrid Vehicle, [4] **THS**: Toyota Hybrid System, [5] **DPNR**: Diesel Particulate NOx Reduction, [6] **D-4**: Direct Injection 4-stroke, [7] **DPR**: Diesel Particulate active Reduction System [8] **EV**: Electric Vehicle, [9] **CNG**: Compressed Natural Gas, [10] **VVT-i**: Variable Valve Timing with intelligence