The Abdus Salam
International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

International Atomic Energy Agency

ICTP Experts Meeting on "Science & Renewable Energy"
January 15 - 18, 2007

Venue: ICTP Adriatico Guest House - Lundqvist Lecture Hall

310/1905

"Electrochemical Power Sources for Fighting Global Warming"

B. Scrosati
Università degli Studi di Roma "La Sapienza"
Italy

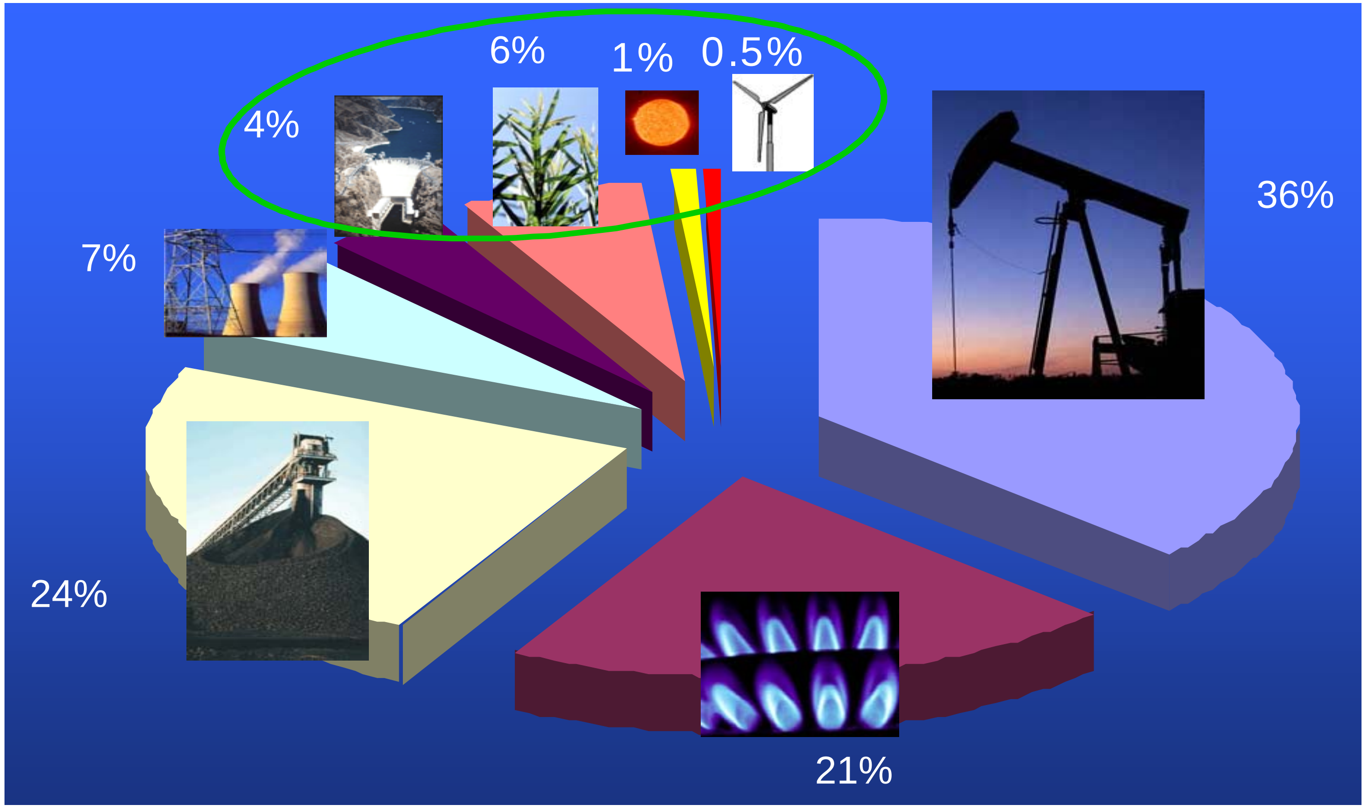
Electrochemical Power Sources for fighting Global Warming

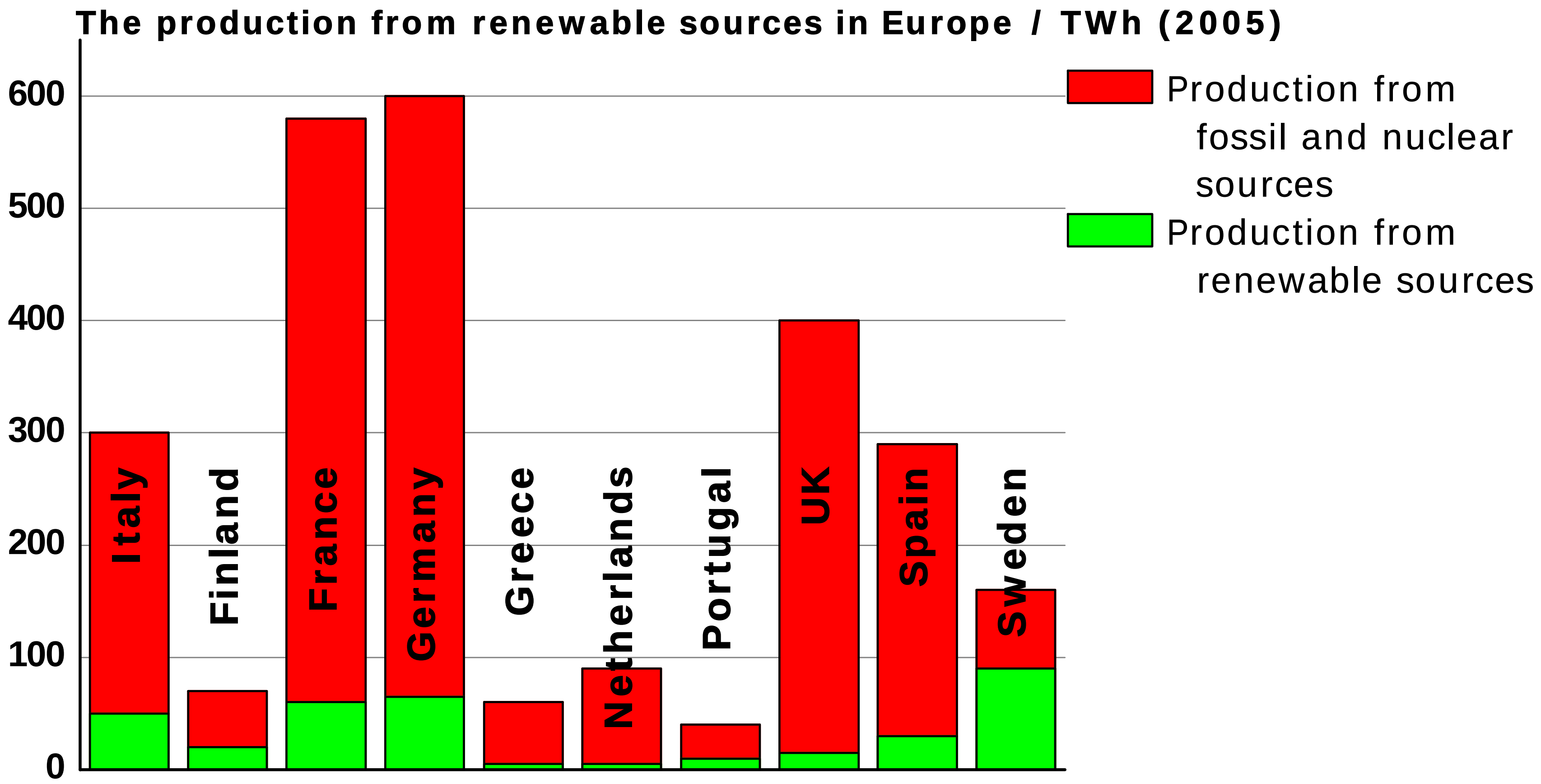
Bruno Scrosati
Laboratory for Advanced Batteries
and Fuel Cell Technology

LAB-FCT

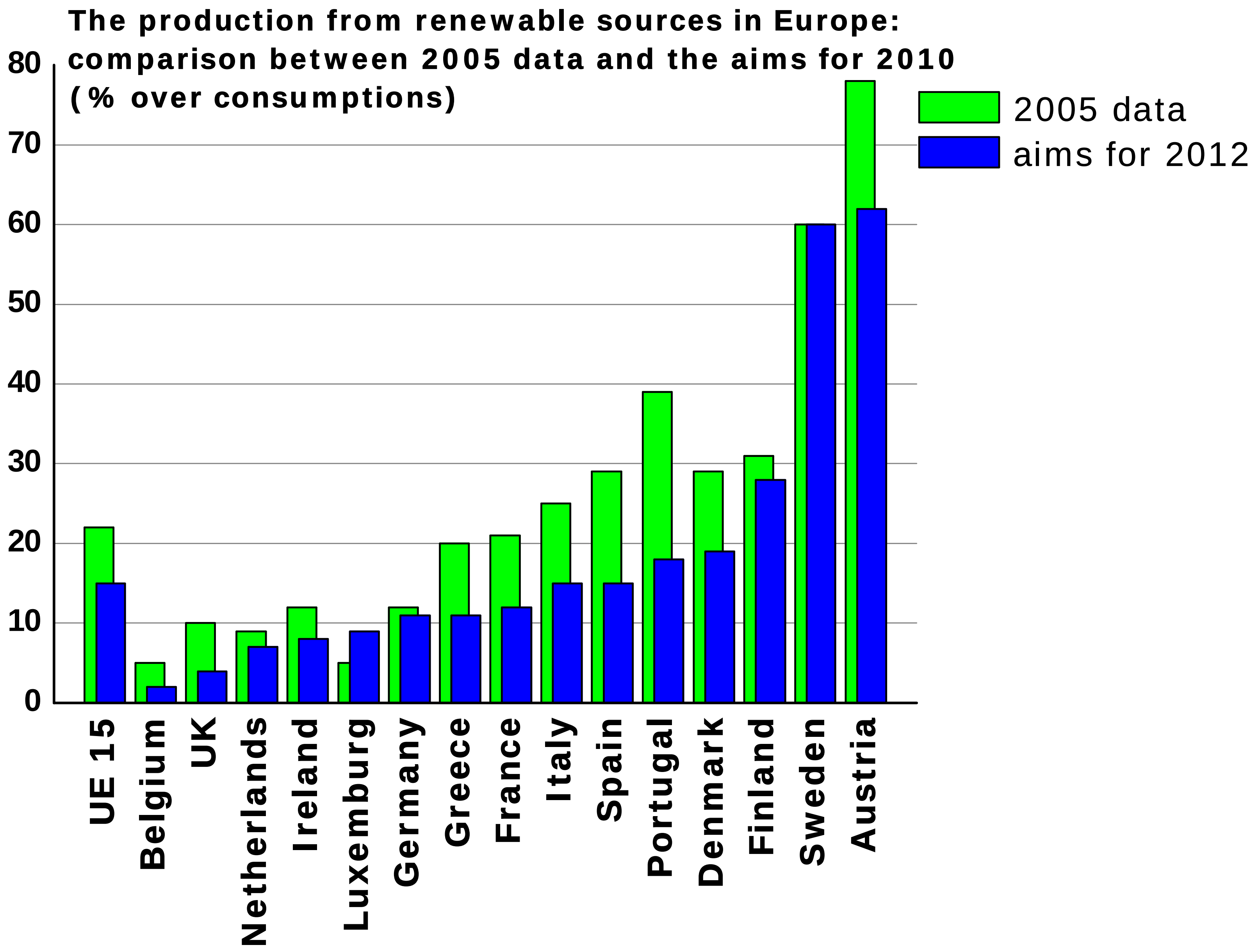
Dipartimento di Chimica,
Università "La Sapienza" Rome, Italy

The energy forms used in the World today





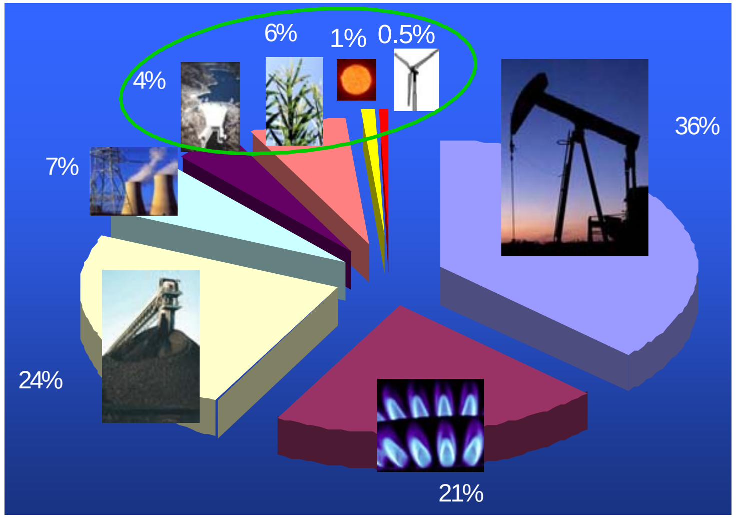
Derived from “Nuova Energia”N. 6, 2006



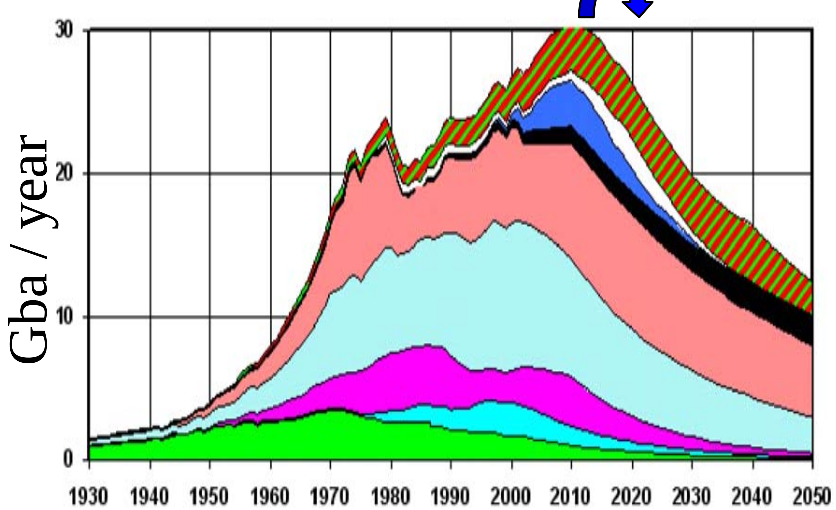
Derived from “Nuova Energia”N. 6, 2006

Oil: social and economic stakes

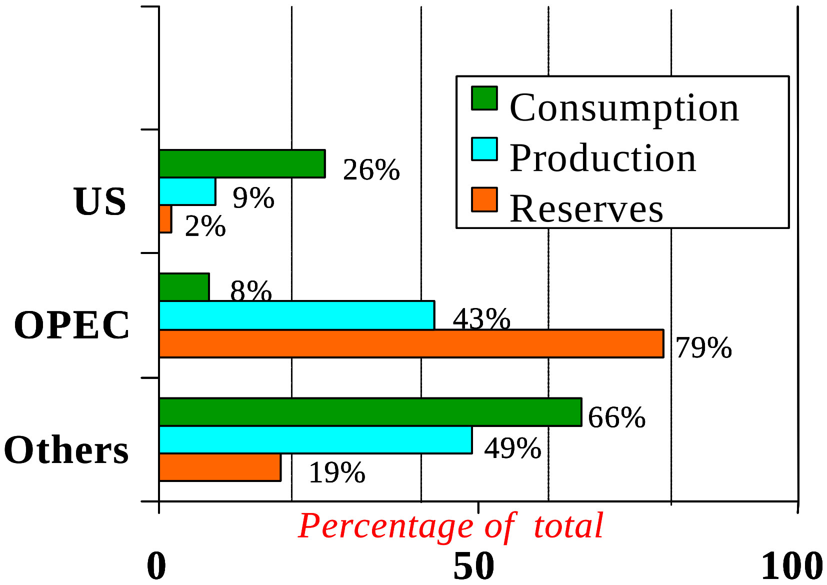
The energy forms used in the World today?



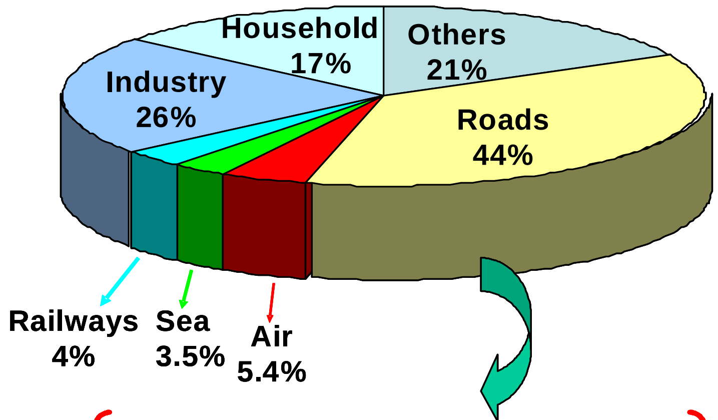
Worldwide production of oil & natural gas



World oil reserves/consumption



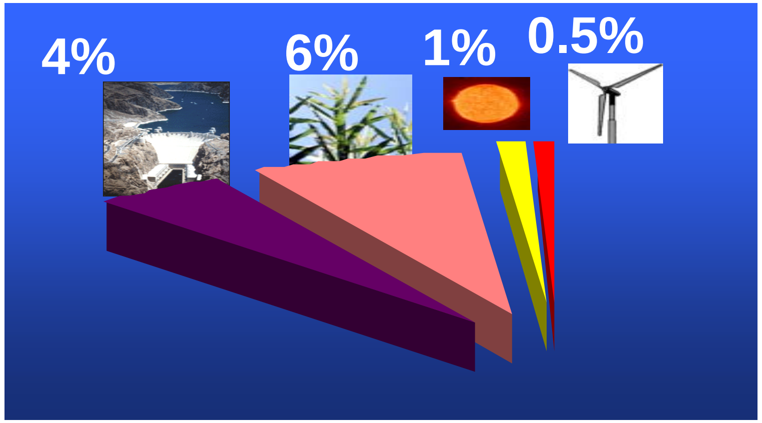
Detailed oil consumption



$$\left\{ \begin{array}{l} C_8H_{18} + 12.5\ O_2 \rightarrow 8CO_2 + 9\ H_20 \\ \text{-----------} \qquad \rightarrow NO_x \\ \qquad\qquad\quad\ \rightarrow C.O.V \end{array} \right\}$$

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..



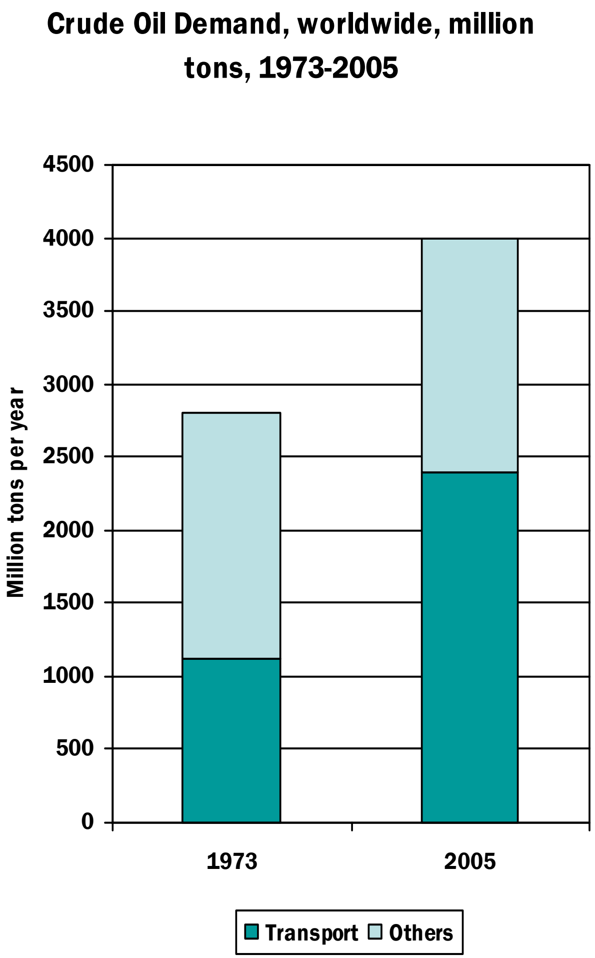
Cost-efficient, long-life, high-power energy electrochemical power sources (e.g. batteries or fuel cells) are urgently needed!

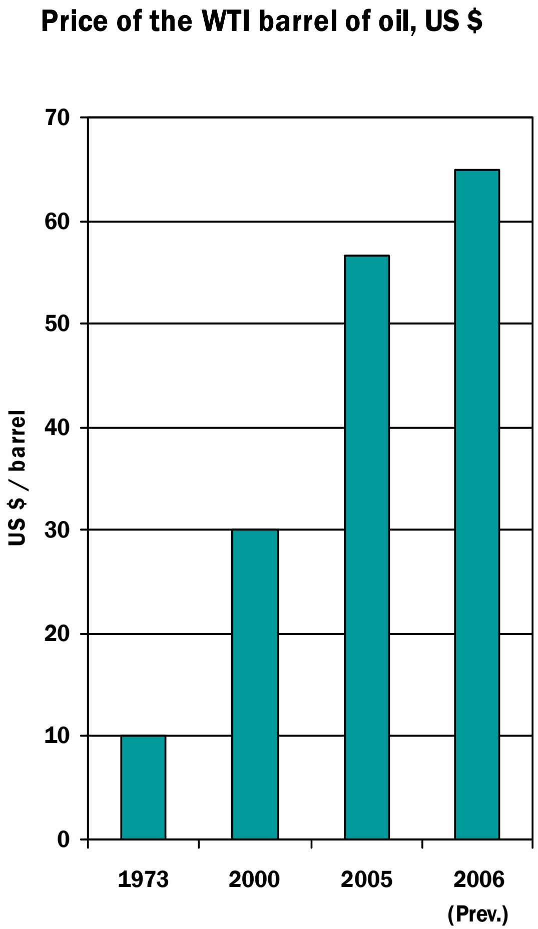
How we can we address the CO_2 issue
and control the pollution in urban area ?

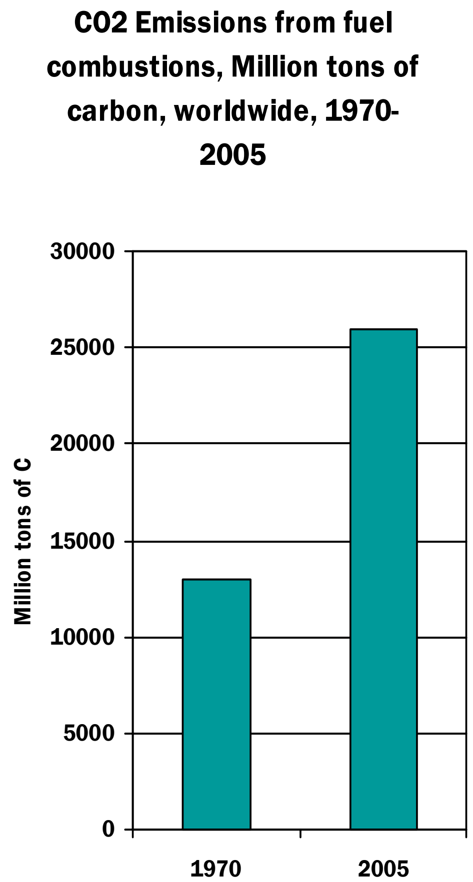
Among other actions, the replacement of a large fraction of internal combustion vehicles with controlled-emission (hybrid car) or zero emission (hydrogen car) is urgently needed!

Advanced energy storage systems, i.e. cost-efficient, long-life, high-power energy storage systems, i.e., batteries or fuel cells, are needed to meat this goal!

WHY HEV?





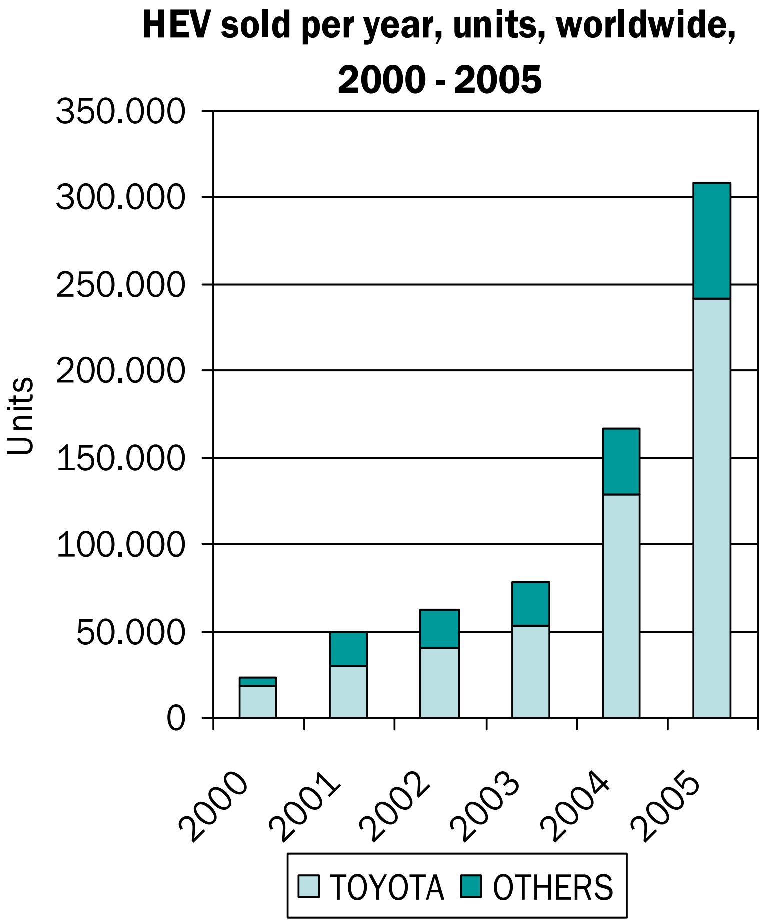


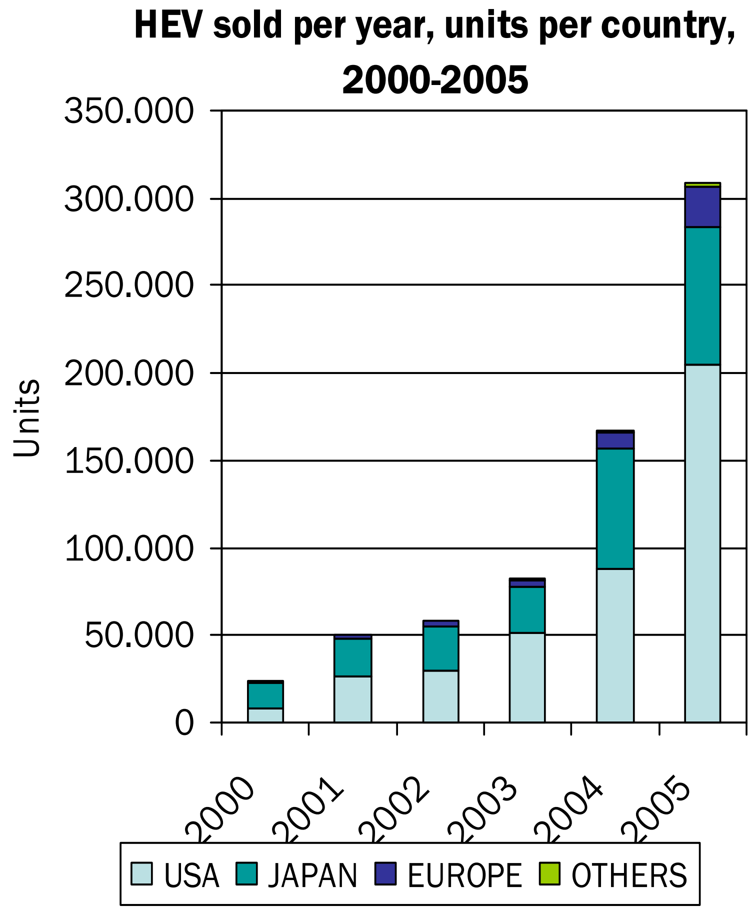
Source : International Energy Agency - http://omrpublic.iea.org/ - Feb 2006

From A. Madani, BATTERIES 2006, Paris, June 2006

HEV MARKET

HEV MARKET WORLDWIDE GROWTH 04/05: +86%





Source : The Rechargeable Battery Market 2005-2015, AVICENNE, March 2006

From A. Madani, BATTERIES 2006, Paris, June 2006

FOTO HYBRID CAR

The hybrid car, HEV

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

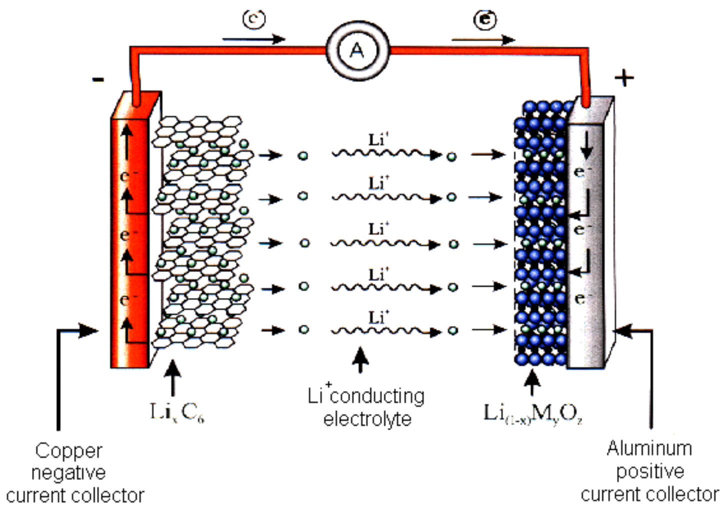
.... however, new types of batteries having higher energy density and lower cost than Ni-MH, are urgently needed to assure high performance and market competitiveness.

Lithium batteries can do the job.....

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

The lithium ion battery

The lithium-ion rechargeable battery



Conventional lithium/ion batteries are based on the following electrochemical system:

Anode: grafite

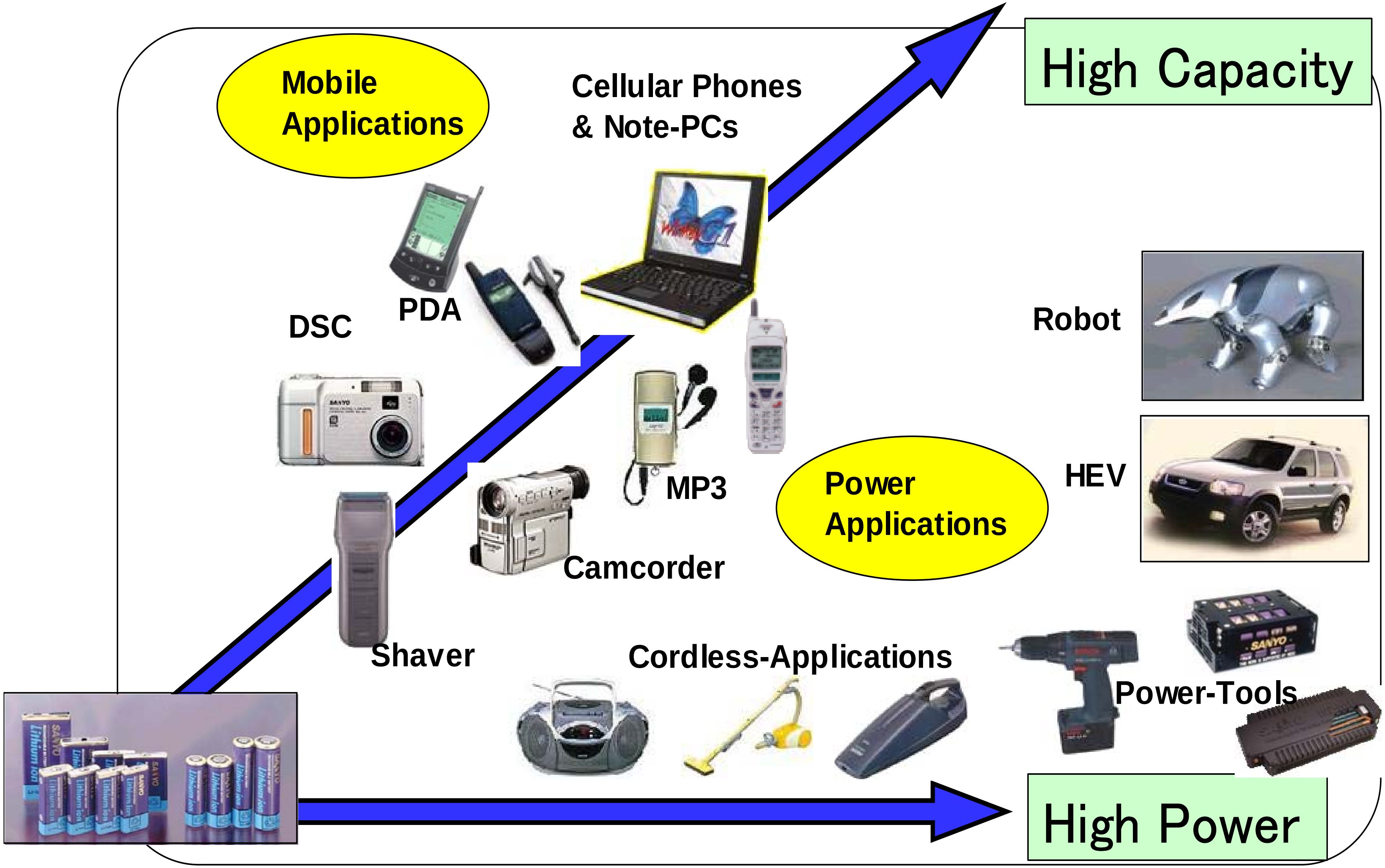
Electrolyte: liquid solution of a lithium salt in an organic solvent mixture

Cathode: layered $LiMO_2$ lithium oxide, e.g. $LiCoO_2$

Process: $yC + LiCoO_2 \leftrightarrows Li_xC_y + Li_{(1-x)}CO_2$; $x \sim 0.5$; ~ 4V

Lithium ions are exchanged between the two electrodes by reversible extraction and insertion from and in open host structures with a concomitant removal and addition of electrons.

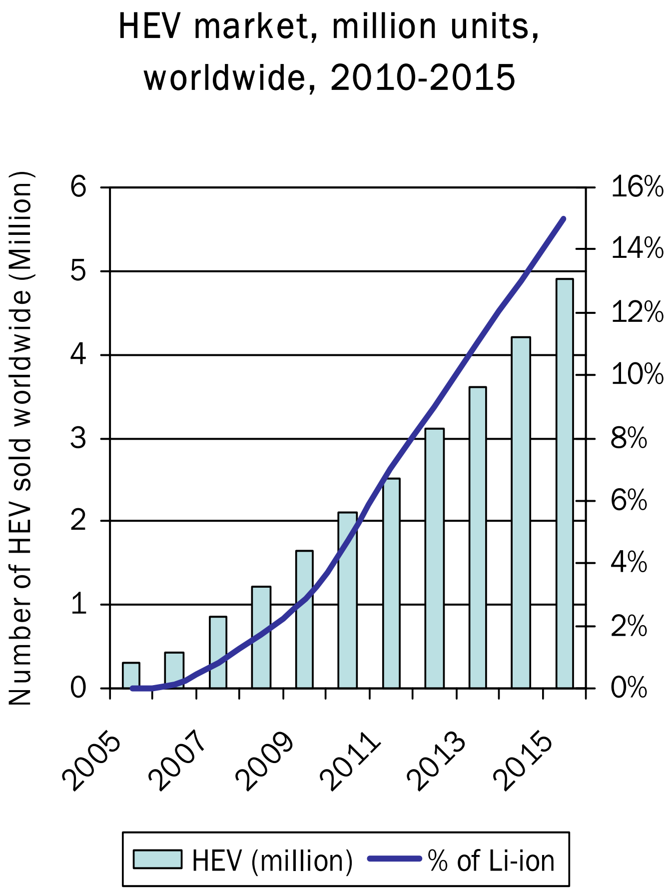
Lithium ion battery is the power sources of choice in a large range of consumer electronic devices!

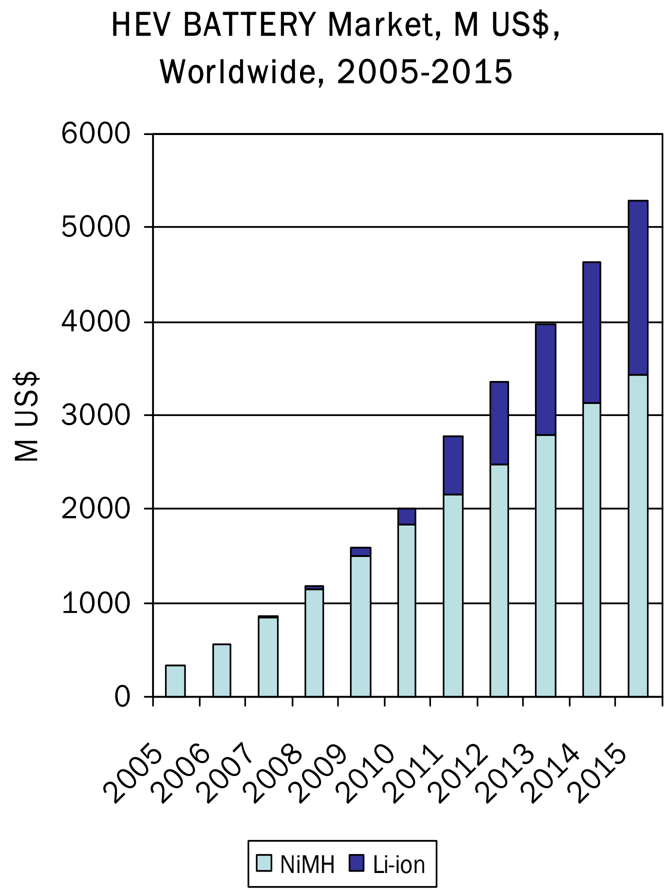


However, lithium batteries fall short of satisfying needs for high energy for application in more demanding markets, such as efficient use of renewable energy and hybrid vehicles.

If improvements in energy density and safety are obtained, the lithium ion battery can enter in the HEV market!

Long Term HEV Battery forecast





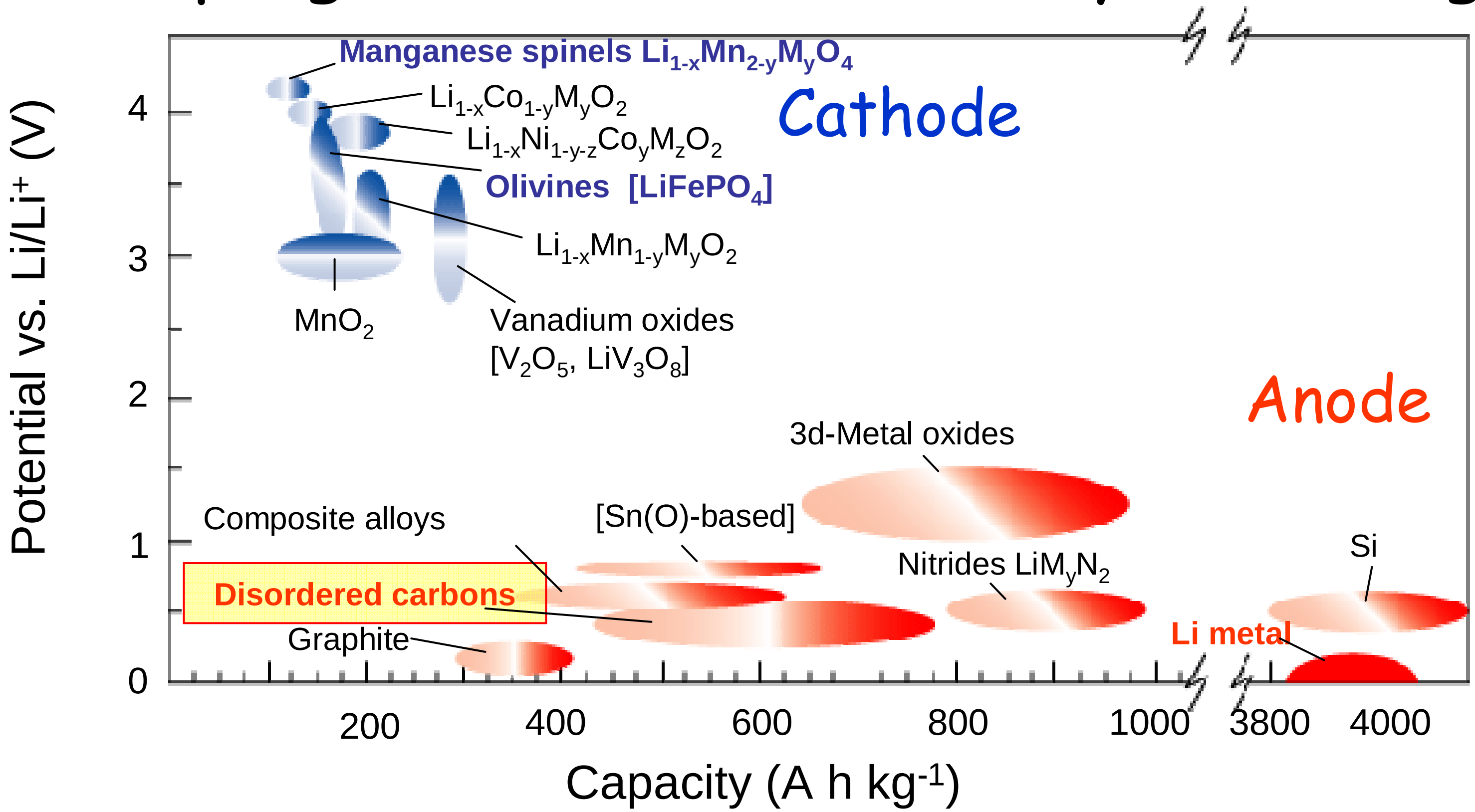
From A. Madani, BATTERIES 2006, Paris, June 2006

ENERGY DENSITY

So far, the energy density of lithium ion batteries has been improved by engineering cell optimization, however, still keeping the original chemistry.

The limit has been now reached and jumps in energy density can only be obtained by renewing the overall cell chemistry.

Various electrode materials are suitable for progress in lithium battery technology



Anodes: lithium metal alloys and lithium titanium oxides

Cathodes: Lithium manganese spinels and lithium iron phosphate phospholivines, lithium manganese layered.

Courtesy of Prof. K. Kanamura, Tokyo Metropolitan University

SAFETY

In addition to energy density, also safety is a key parameter for batteris designed for HEV applications

Safety is still an issue for conventional C/ $LiPF_6$-EC-DMC/ $LiCoO_2$ lithium-ion batteries.

Dell computer burnt in the conference in Osaka in June 2006

Approaches to improve safety:

Replacement of liquid electrolytes with lithium conducting polymer electrolytes.

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

Polymer electrolytes

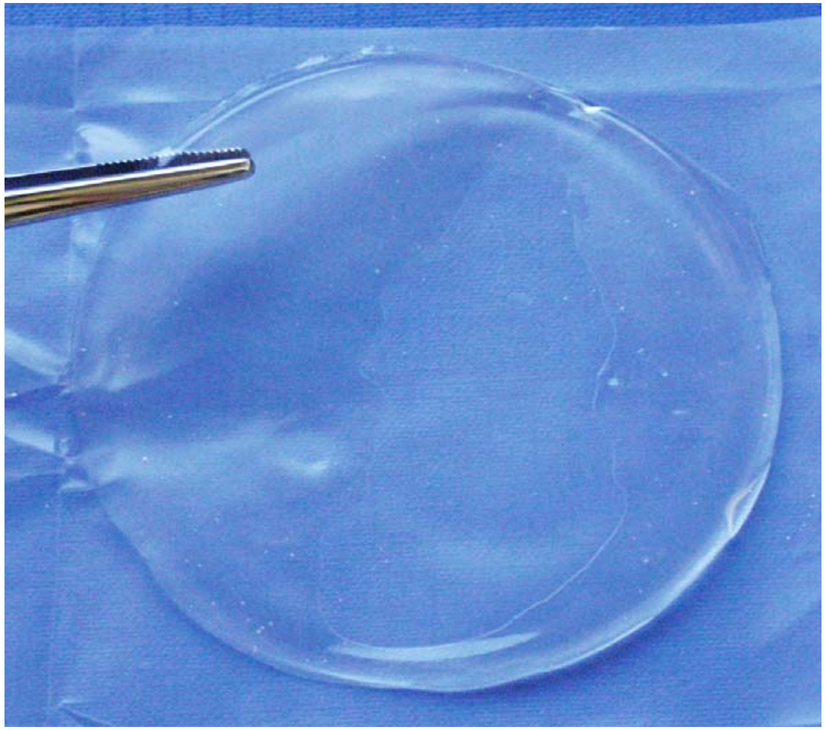
Two main types

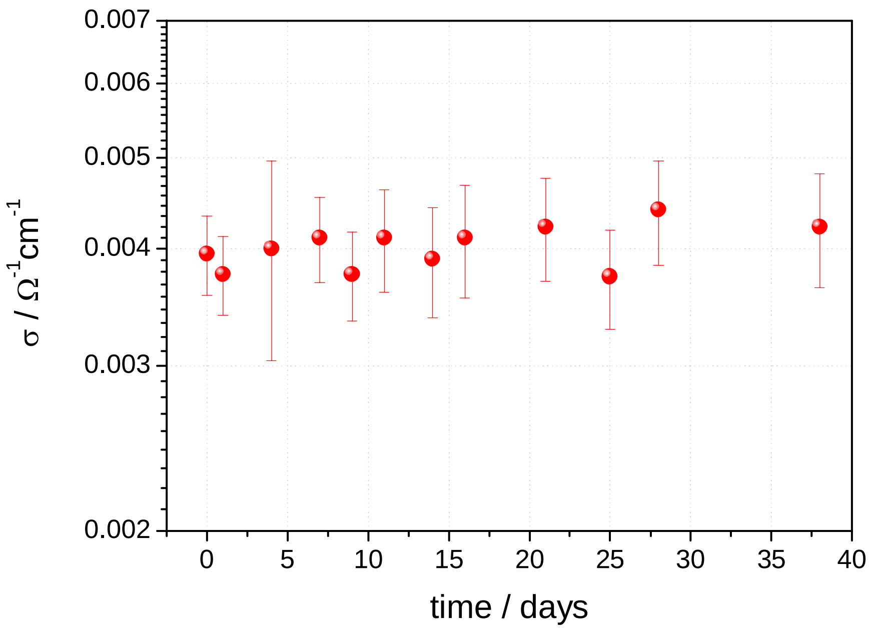
Solvent-free membranes, formed by blending , poly(ethylene oxide), PEO, with a lithium salt, LiX (*SPEs*)

Liquid-polymer hybrid membranes, formed by formed by trapping liquid solutions (e.g., a $LiPF_6$-PC-EC solution) in a polymer matrix (*GPEs*).

POLYMER ELECTROLYTES

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*).

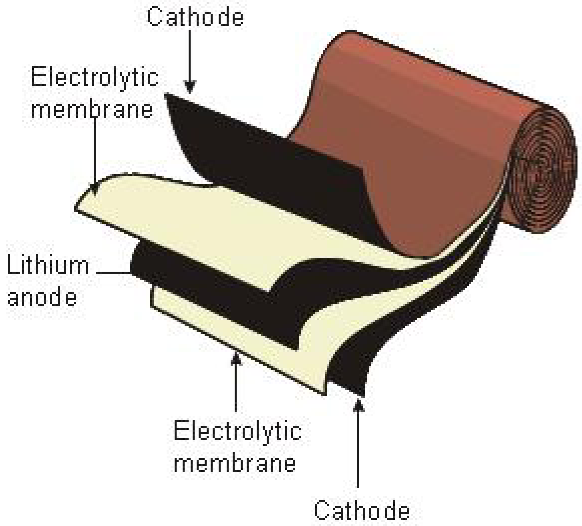




High conductivity

L. Persi, F. Croce and B. Scrosati; *Electrochem. Comm.* 4 (2002) 92

$Li_4Ti_5O_{12}$ / GPE/ $LiFePO_4$ lithium ion polymer cell



A 2V lithium-ion polymer battery!

P.Reale, S. Panero, B. Scrosati,J. Garche, M. Wohlfahrt-Mehrens, M.Wachtler,

J.Electrochem.Soc, 151 (2004) A2138

The $Li_4Ti_5O_{12}$ / GPE/ $LiFePO_4$ battery is characterized by reliability, long life an a high degree of safety.

However, this battery does not entirely meet the requirements for use in HEV where, in addition to safety and stability, also high rate is a key parameter.

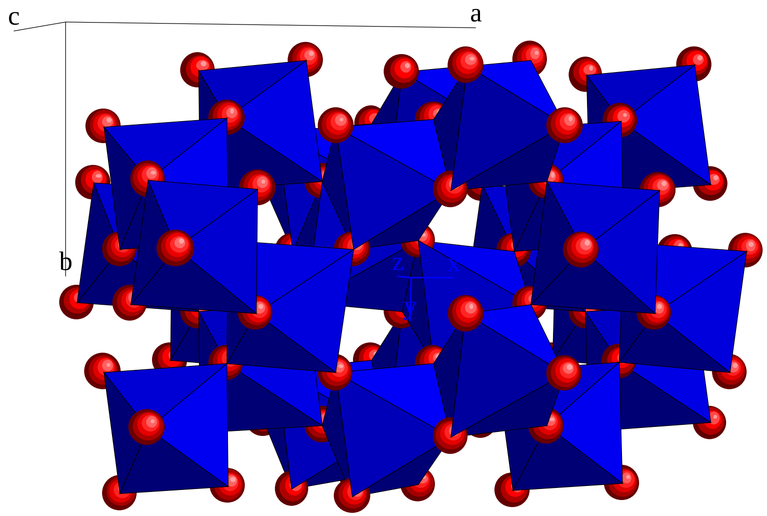
Nanotechnology is a popular path to improve the rate capability of solid-state electrodes because of the reduced lithium diffusion length.

Examples are the nano-structured nano-modified titanium oxide and the Ni-substituted manganese spinel.

A.S. Aricò, P. Bruce, B. Scrosati, J-M.Tarascon, W. van Schalkwijk
Nature Materials, 4 (2005) 366

New type of high rate anode: nanstructured TiO_2 *

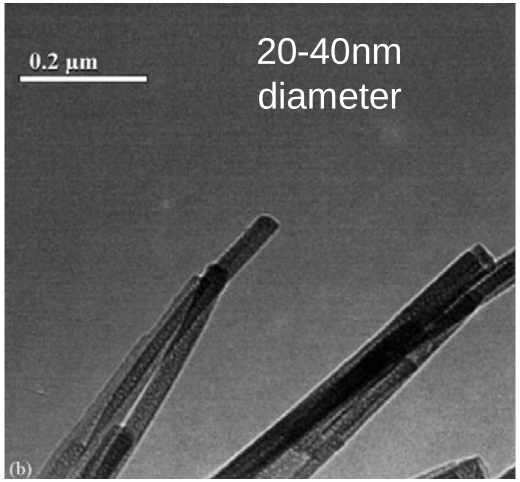
Brookite structure Pbca



*In collaboration with Prof P.Bruce of University of St.Andrews, UK

$TiO_2 + xLi^+ + xe^- \leftrightarrows Li_xTiO_2$ 1.5V

Theoretical specific capacity: 335 $mAhg^{-1}$



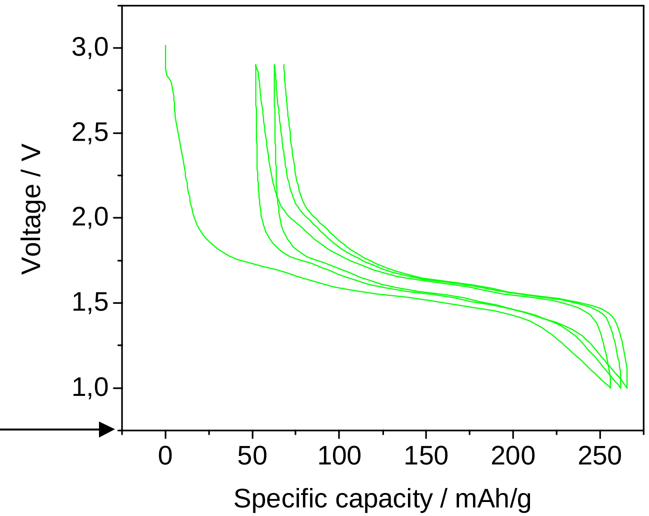
Hydreothermal synthesis:

TiO_2 in NaOH

400°C 4h in air

← morphology

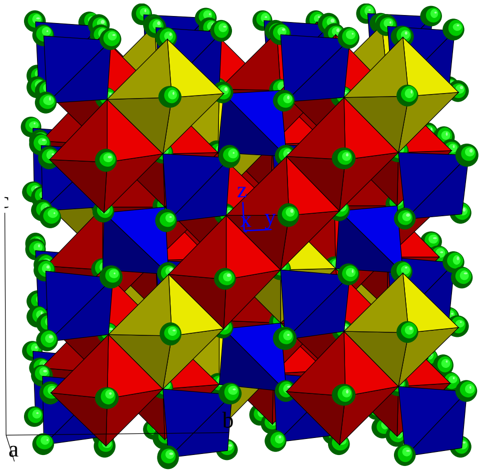
Voltage profile →

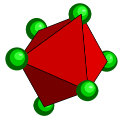
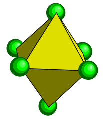
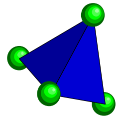


A.R.Armstrong, G.Armstrong, J.Canales, P.G.Bruce, *Journal of Power Sources* 146 (2005) 501
A.R.Armstrong, G.Armstrong, J.Canales, P.G.Bruce, *Electrochemical and Solid-State Letters,* 9(2006) A139

Ni-substituted $LiNi_{0.5}Mn_{1.5}O_4$ spinel

Spinel structure $P4_332$

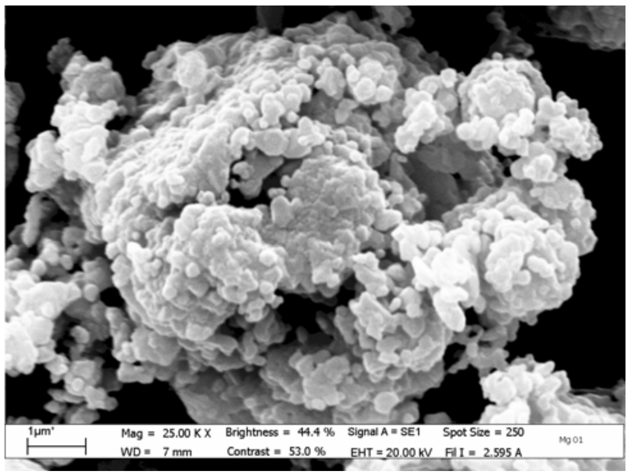


 12d MnO_6  4b NiO_6  8c LiO_4

$$LiNi_{0.5}Mn_{1.5}O_4 \leftrightarrows Li_{0.5}Ni_{0.5}Mn_{1.5}O_4 + 0.5Li^+ + 0.5e^-$$

$$Li_{0.5}Ni_{0.5}Mn_{1.5}O_4 \leftrightarrows Ni_{0.5}Mn_{1.5}O_4 + 0.5Li^+ + 0.5e^-.\quad 4.5\ V$$

Theoretical specific capacity: 146 $mAhg^{-1}$



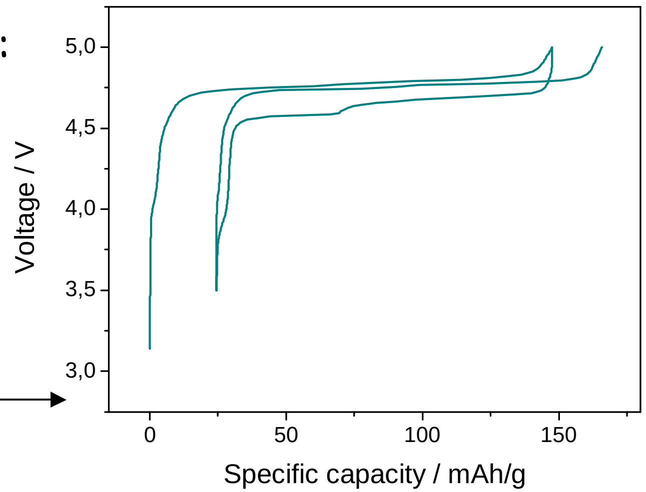
Wet chemistry synthesis:

Li^+, Ni^{2+} and Mn^{2+} nitrides in water

800°C 16h in air

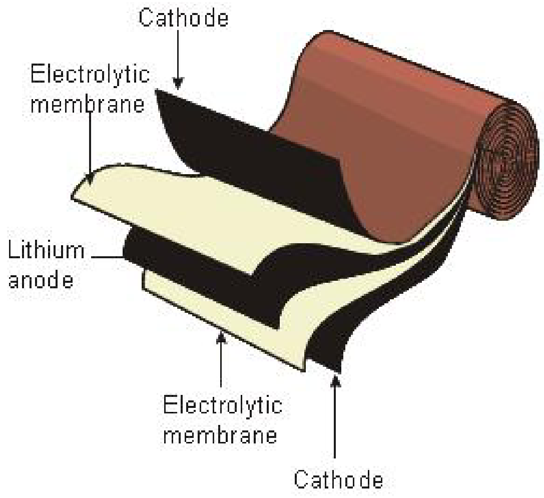
← morphology

Voltage profile →



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

TiO_2 / GPE / $LiNi_{0.5}Mn_{1.5}O_4$ lithium ion polymer cell



A 3V Lithium-ion Polymer Battery!

G. Armstrong, A.R. Armstrong, P.G. Bruce, P. Reale, B. Scrosati
Adv. Mater., 18 (2006) 2597

Lithium ion polymer battery

Future research trends for HEV lithium battery R&D progress

Replace conventional anode and cathode with higher capacity electrode materials(energy density).

Replace liquid with polymer electrolytes (safety).

Develop proper electrode nanostructures (rate).

Zero emission hydrogen fuel cell vehicles

Environmentally Clean

On-Board Power

High Performance

Design Freedom

Low Maintenance

High Efficiency

Reliability

Low Noise

Comfort (no vibration)

General Motor's ELECTROVAN (1967)

(with 400V, 160 kW UCC Alkaline FC System, liquid H_2 und O_2)


fuel cell vehicle
zero emissions
www.fuelcelltoday.com

FC Cars Today

Ford

Fuel: CH2
Veh.basis: Focus
Stack: Ballard

GM/Opel

Fuel: CH2
Veh.basis: Zafira
Stack: GM/Opel

Hyundai

Fuel: CH2
Veh.basis: Santa Fé
Stack: IFC

Honda

Fuel: CH2
Veh.basis: EV Plus
Stack: Ballard / Honda

Nissan

Fuel: CH2
Veh.basis: XTerra
Stack: Ballard / IFC

Toyota

Fuel: CH2
Veh.basis: Kluger V
Stack: Toyota

VW

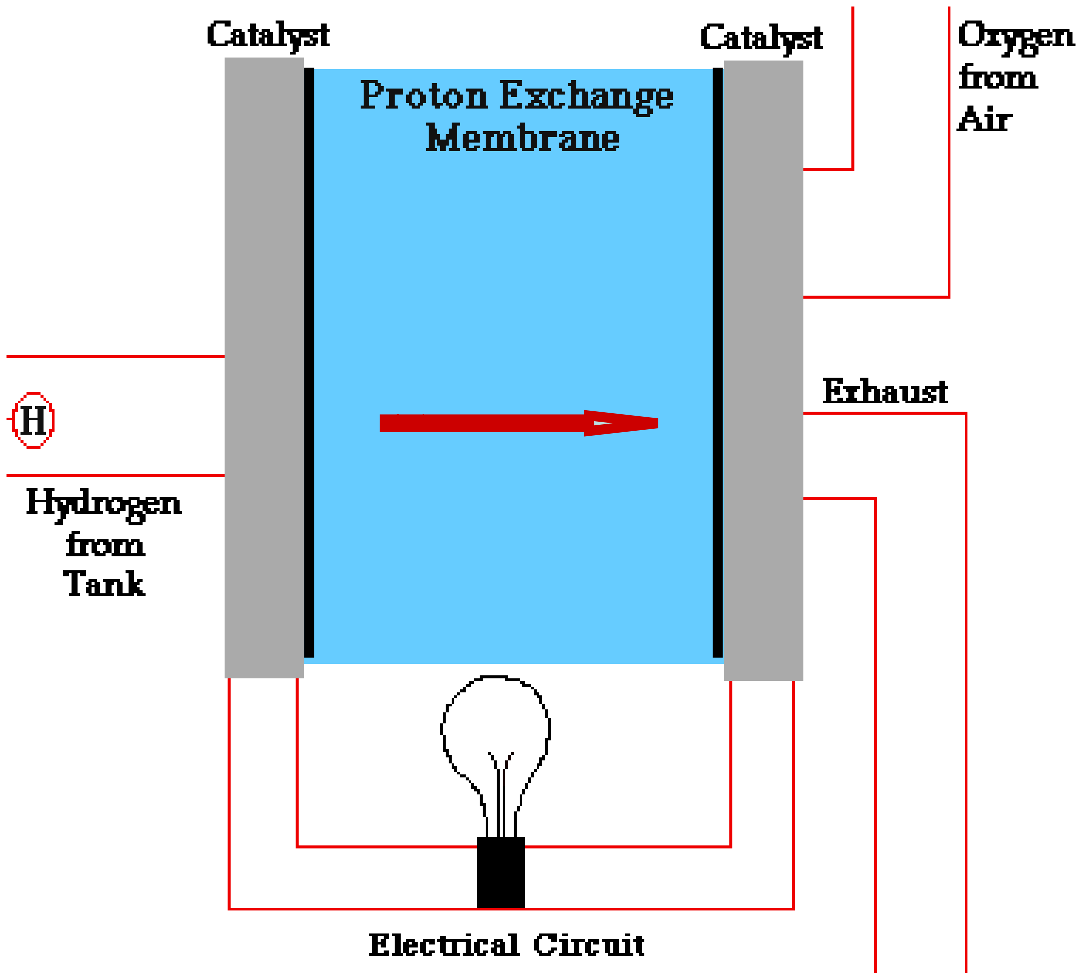
Fuel: CH2
Veh.basis: Bora
Stack: Ballard / PSI

PEUGEOT / CITROËN
+ RENAULT

Source: Prof. Panik, DC


driving the future
uel
F-Cell

Fuel cell operation



anode

$$H_2 \rightarrow 2H^+ + 2e^-$$

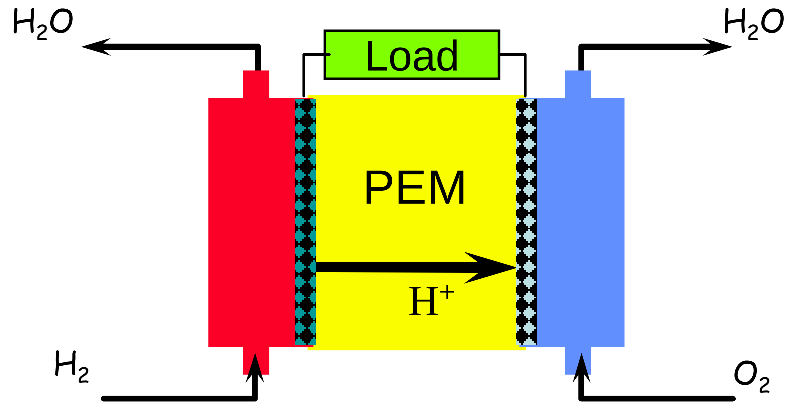
cathode

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

The most promising for electric vehicle applications the
Polymer **E**lectrolyte **M**embrane **F**uel **C**ell, **PEMFC**

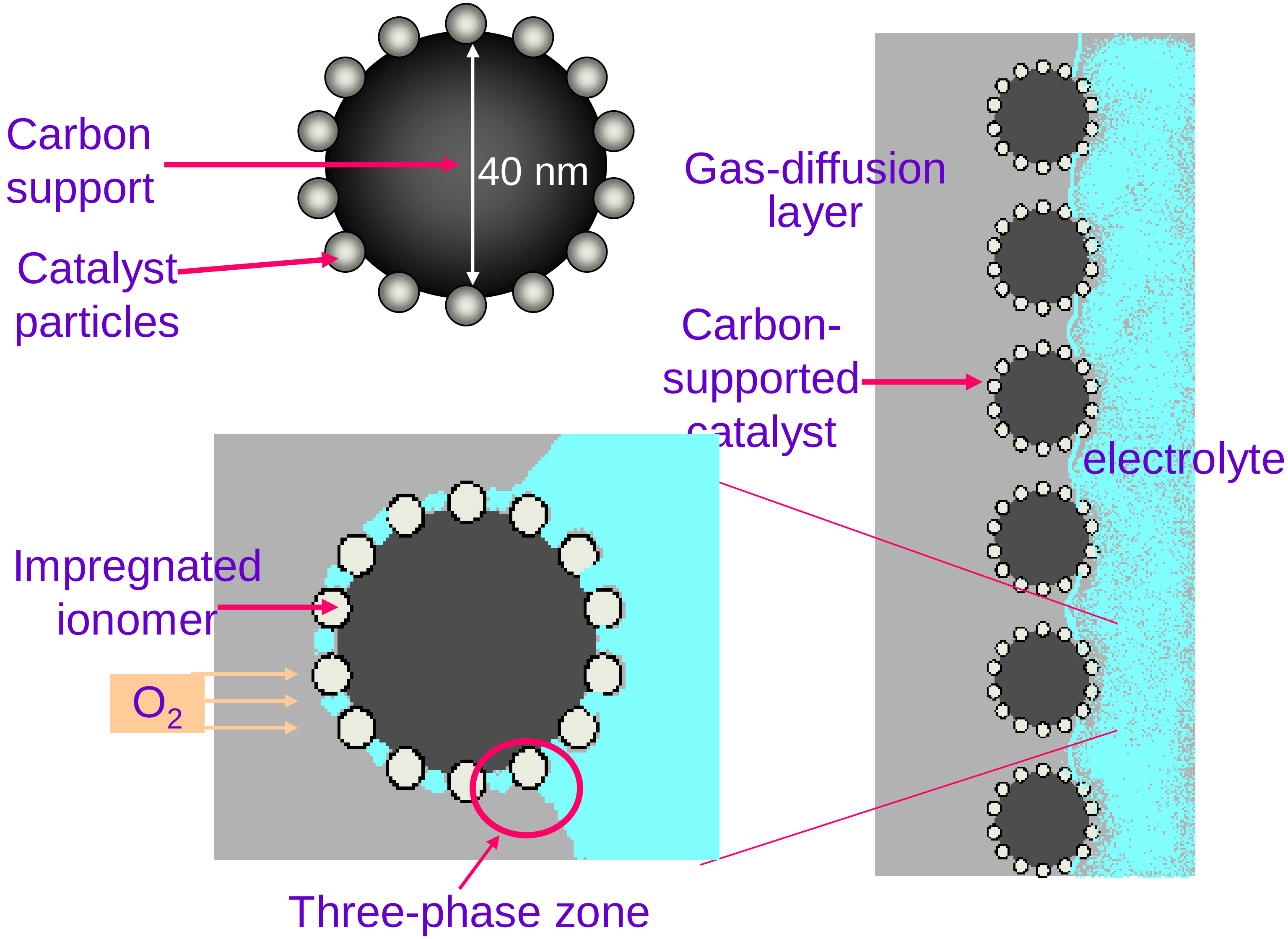
Energy renewal
(*hydrogen-economy*)

Environmental control
(*No-emission vehicles*)



Major drawback: cost
the catalyst (noble metals)
the polymer electrolyte
membrane (Nafion™ -type)

Fuel cell electrode structure

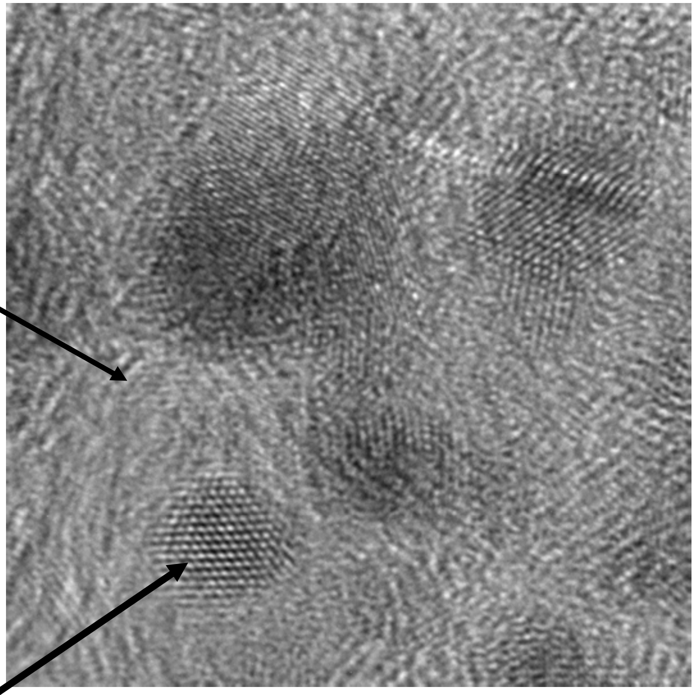


Courtesy of Professor E.Peled, Tel Aviv University

Fuel cell electrode structure

The cost of the electrode structure may be controlled by using high surface area substrates on which nanoscale catalyst (Pt, Pt-Rh) particles may be dispersed.

High surface area carbon substrate



Catalyst (Pt) particle

With this approach, the precious metal loading may be reduced to very low levels, e.g few mg/cm^2 and, with the new technologies, to 0,5 mg/cm^2.

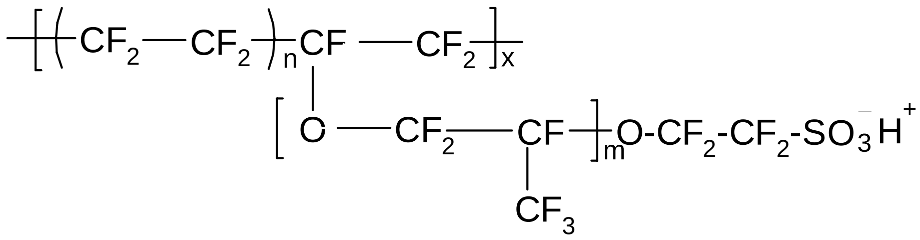
The goal of the car companies is to reach Pt loadings even lower than this limit.

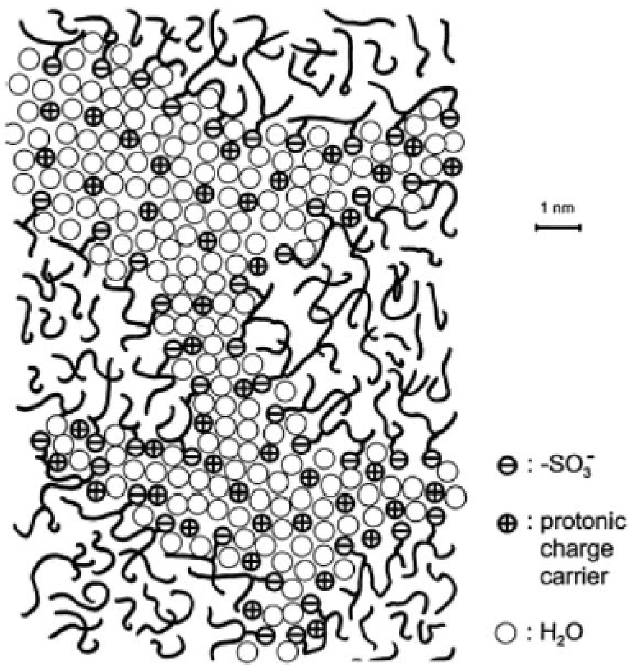
Courtesy of Prof. Tom Zavodinski, Case Western University, Cleveland, USA

Successful R&D Work
Pt-Catalyst Content

Time	Pt content [mg/cm²]
1997	4
2002	0.1
Today (labotatory results)	0.007

Common electrolytes for PEMFCs: perfluorosulphonic membranes, e.g., *NAFION®*

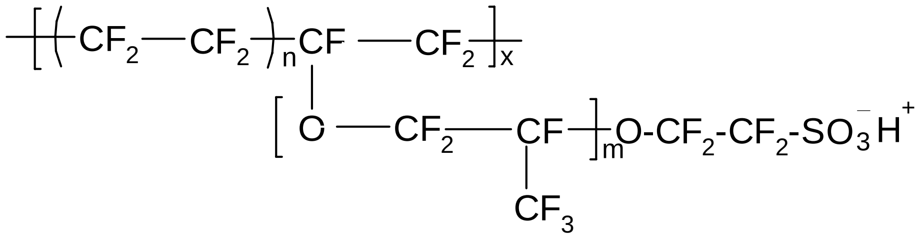




Nanoscale phase separated microstructure as determined by SAXS (small angle X-ray scattering)

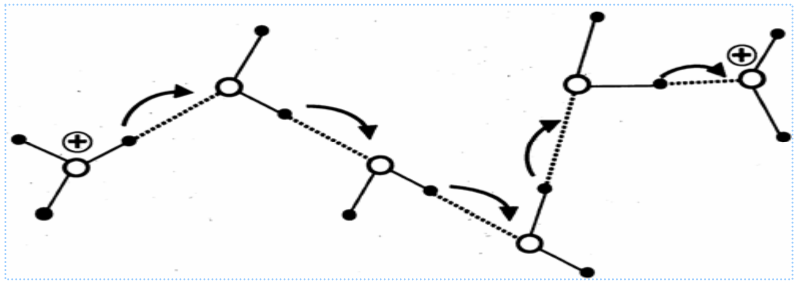
K. D. Kreuer, J. Membr. Sci., 185 (2001) 2

Common electrolyte membrane: *NAFION*®

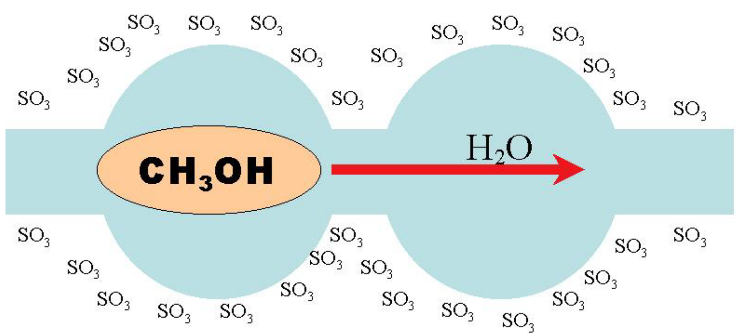


- ☺high chemical stability
- ☺ good conductivity
- ☹ high cost
- ☹ transport dependent on hydration state
- ☹ methanol crossover

✓ Assisted protonic transport:Grotthuss mechanism



✓Methanol crossover



New types of proton membranes, having lower cost, higher thermal stability and higher selectivity than Nafion, are urgently required!

Strategy

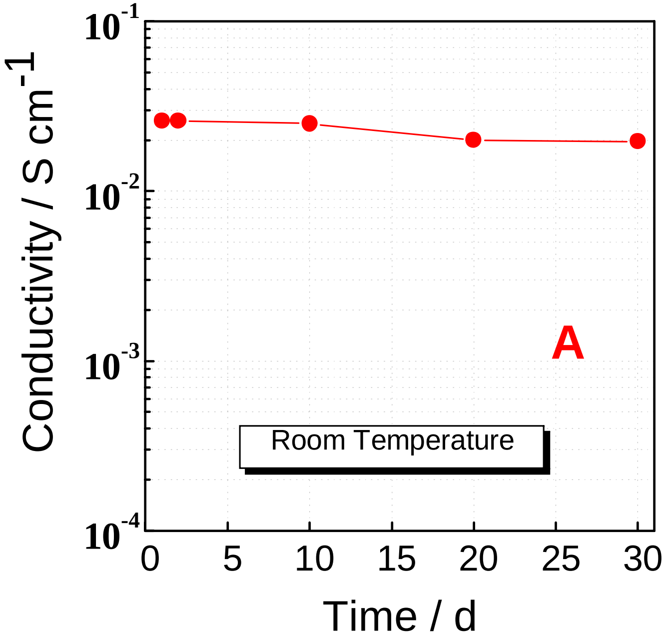
***In lithium battery technology*:**
lithium conducting membranes formed by trapping liquid solutions (e.g., a LiPF6-PC-EC solution) in a suitable polymer matrix (e.g. a poly(vinylidene fluoride), PVdF matrix)
***Gel polymer electrolytes*.**

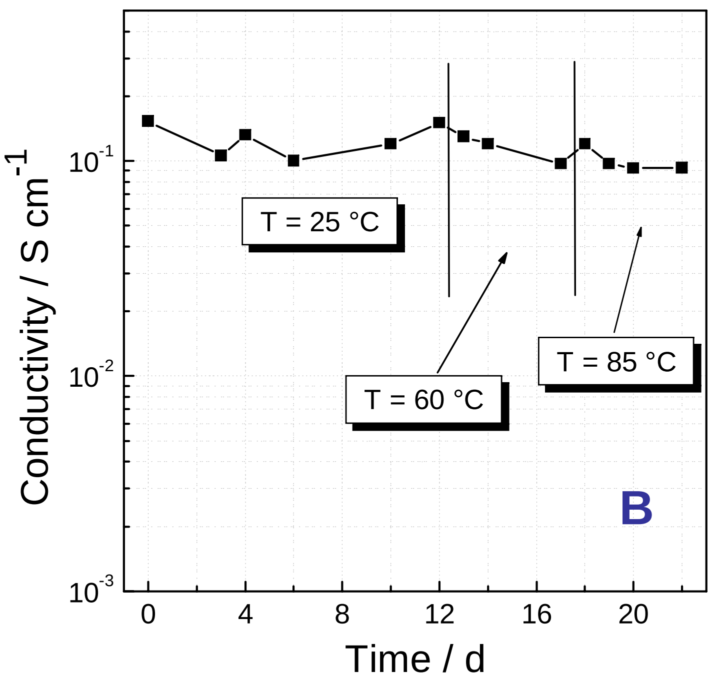
↓

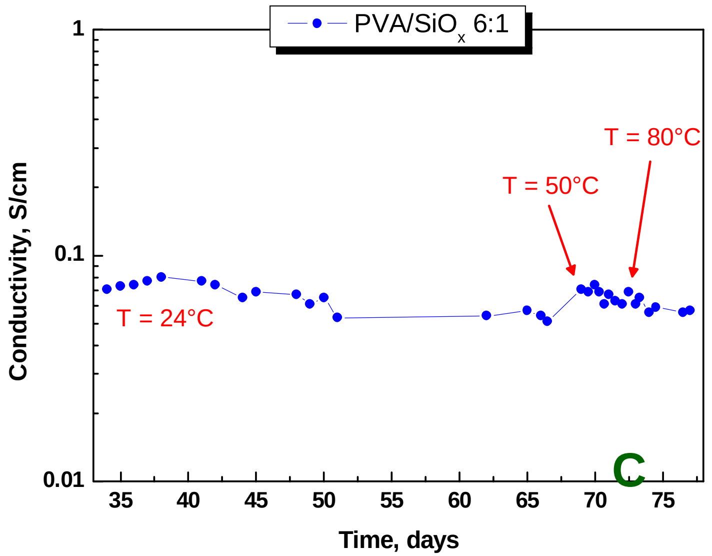
***Extension to fuel cell technology*:**
proton conducting membranes formed by trapping acid solutions (e.g., H_2SO_4 solutions) in suitable composite (polymer + ceramic filler) matrices.
***Composite gel electrolyte membranes*.**

The main goal is to develop low-cost, low-methanol-permeability, temperature-resistant membranes for PEMFCs (DMFCs).

Conductivity







Time evolution of the conductivity of composite gel-type membranes at various temperatures.

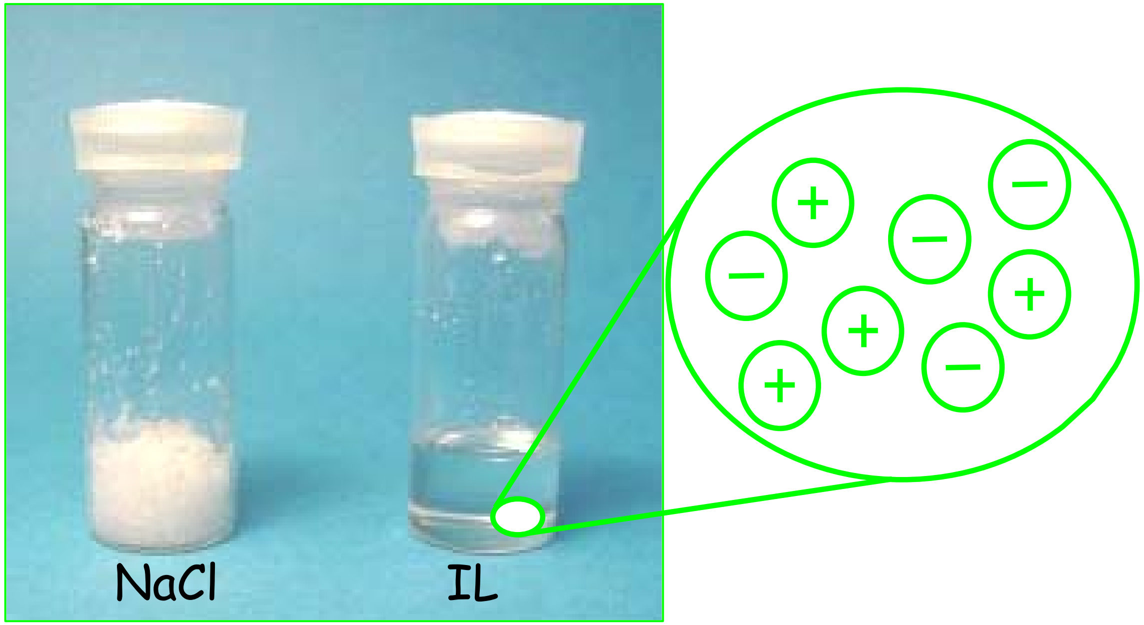
A) Al_2O_3-added PVdF-based membrane;

B) Al_2O_3-added PVdF-PAN-based membrane;

C) SiOx-added crosslinked PVA-based membrane.

M.A. Navarra, S. Panero, B.Scrosati, *J.Electrochem.Soc.*, 2006

Ionic Liquids, ILs



Sodium chloride melts at 800 °C (Hot solution).
Ionic liquids melts at much lower temp (Cool solution).

Liquids composed of only ions!!

Ionic liquids

They may have …

Thermal/chemical stability

Moderate polarity

Low melting point

+ —

Non-volatility

Non-flammability

Low viscosity

Solubility (affinity) with several compounds

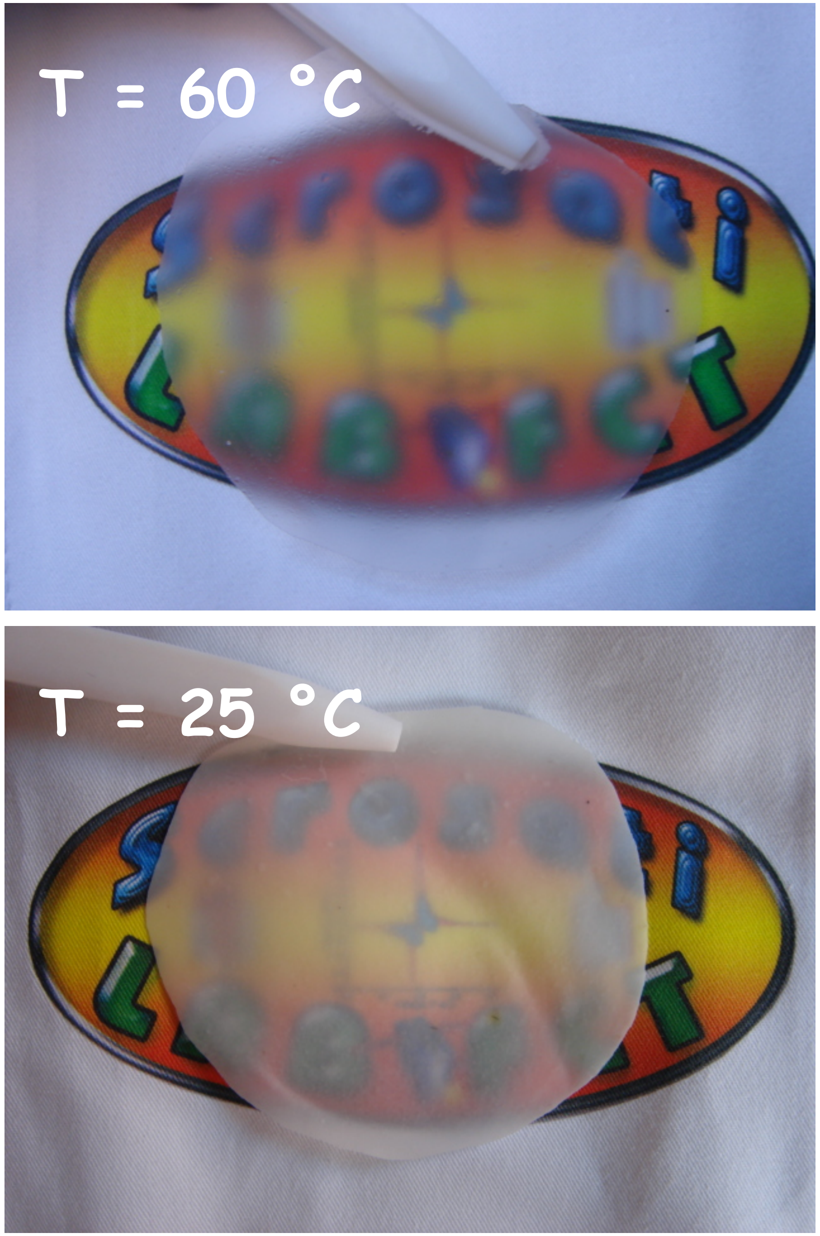
High ionic conductivity

Variation of ion structure

Ion conductive materials for Electrochemical devices

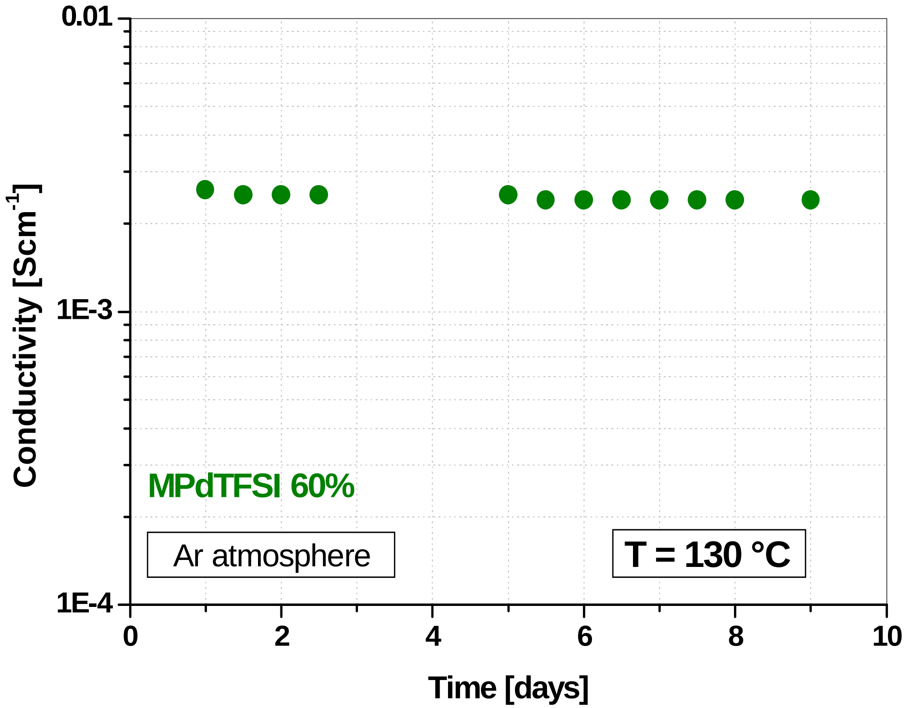
Solvents for Chemical reaction

Appearance of protic IL-based membranes



A. Fernicola, S. Panero, B.Scrosati, M.Tamada, H. Ohno, *PhysChemChemPhys*, submitted

IL-based membranes have a significant ionic conductivity. The conductivity increases with temperature, reaching at 130 °C high and stable values.



Conductivity of IL 60%-PVdF 40% membrane at 130 °C.

A. Fernicola, S. Panero, B.Scrosati, M.Tamada, H. Ohno, *PhysChemChemPhys*, submitted

Future research trends for fuel cell R&D progress

Develop adequate electrode nanostructure (Pt loading).

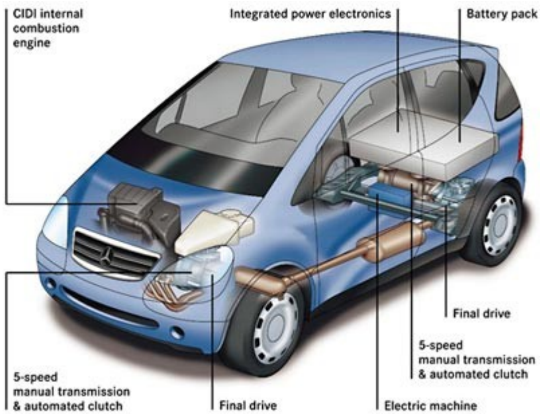
Search of alternate, not-precious metal catalysts (Cost).

Replace conventional Nafion-based membranes (Cost, crossover).

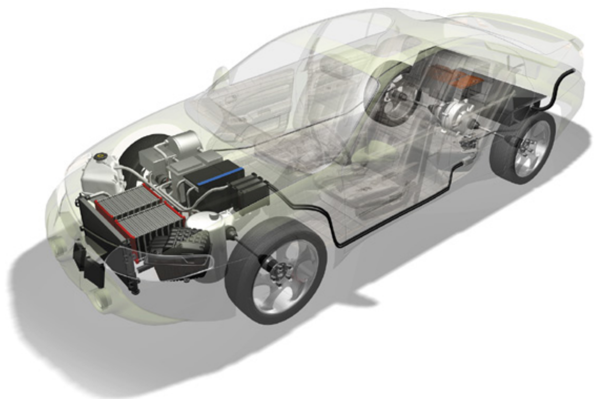
Develop ionis-liquid- based membranes (thermal stability).

Ecologic car
Prospective

Electric car: prototypes
Zero emission



Hybrid car: in the market
Controlled emission



Hydrogen car: in the market by 2010 (prevision)
Zero emission?


UN GIORNO LE MACCHINE ANDRANNO A ACQUA
E L'ACQUA COSTERÀ IL DOPPIO DELLA BENZINA
2004 GIULIANO