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International Atomic Energy Agency

2245-18

Joint ICTP-IAEA Advanced School on the Role of Nuclear Technology in Hydrogen-Based Energy Systems

13 - 18 June 2011

Large Scale Development for Stationary & Nomad Hydrogen Storage Units Metal Hydrides: the Unique Solution for Intermediate and Mass Energy Storage

Daniel Fruchart
Institut Neel, CNRS
Genoble
France

LARGE SCALE DEVELOPMENT FOR STATIONNARY & NOMAD HYDROGEN STORAGE UNITS

METAL HYDRIDES : THE UNIQUE SOLUTION FOR INTERMEDIATE AND MASS ENERGY STORAGE

Daniel FRUCHART

Expert IEA – Observer IAEA

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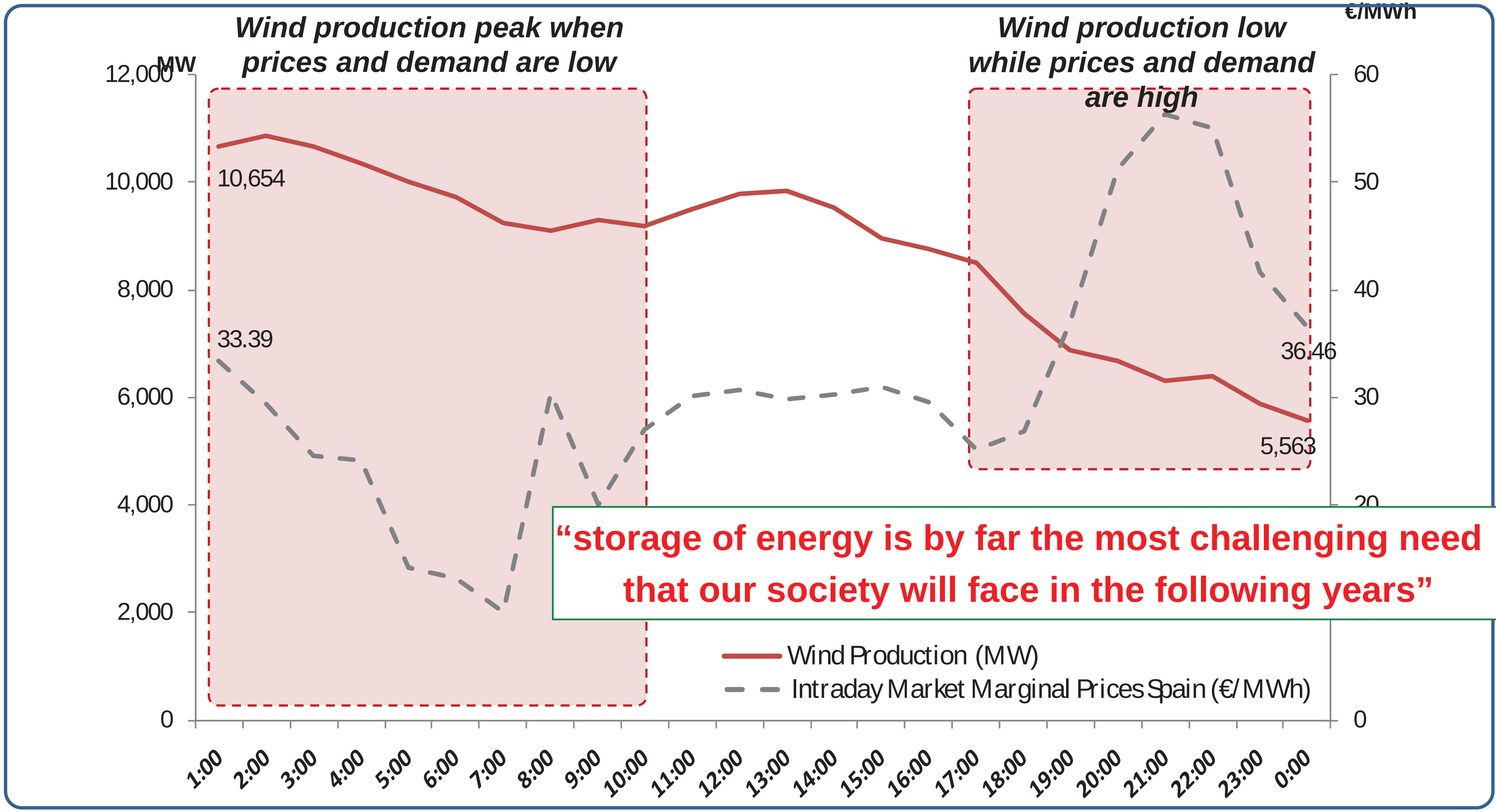
Research Manager
McPhy Energy - 26190 La Motte Fanjas, France - www.mcphy.com

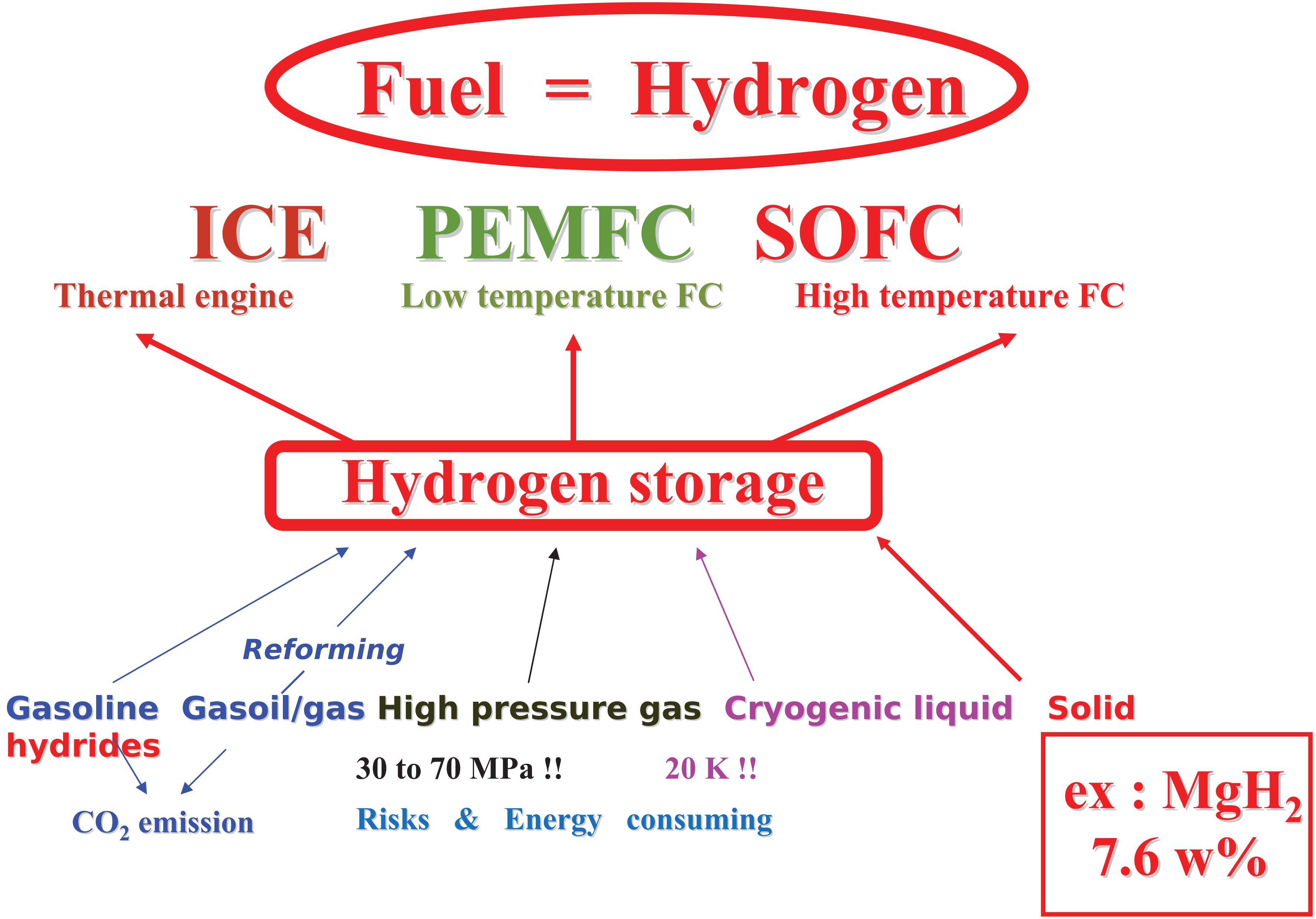
Where the error is ?…

Variable electricity production from Wind Power does not allow electricity to be produced when it is most needed, ie when demand is highest

Evolution of Spanish Wind Energy Production on 6/02/2010

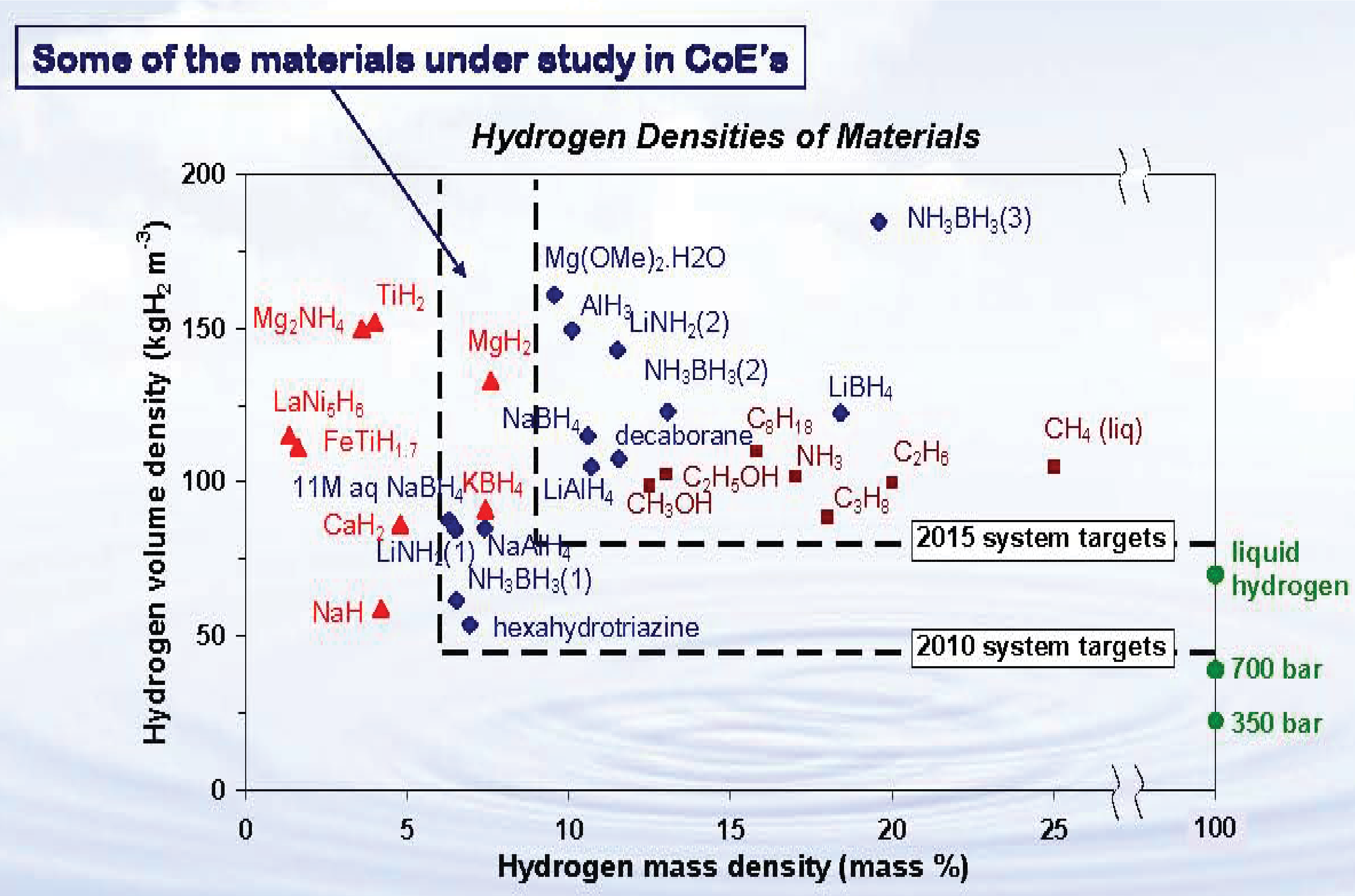


"storage of energy is by far the most challenging need that our society will face in the following years"



Fuel = Hydrogen
ICE
PEMFC
SOFC
Thermal engine
Low temperature FC
High temperature FC
Hydrogen storage
Reforming
Gasoline
Gasoil/gas
High pressure gas
Cryogenic liquid
Solid
hydrides
30 to 70 MPa !!
20 K !!
CO2 emission
Risks & Energy consuming
ex : MgH2
7.6 w%

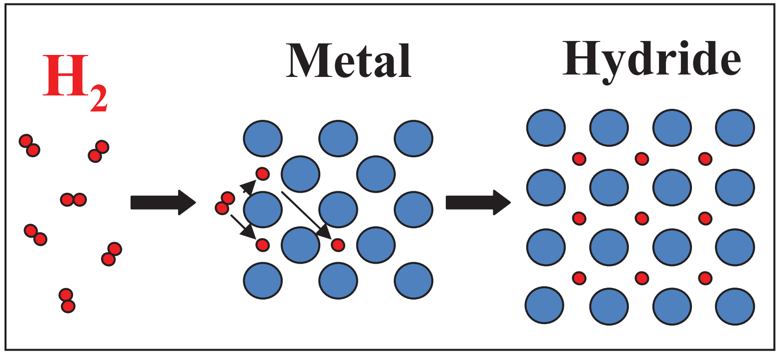
Mass and Volume Densities



Reversible Metal Hydrides

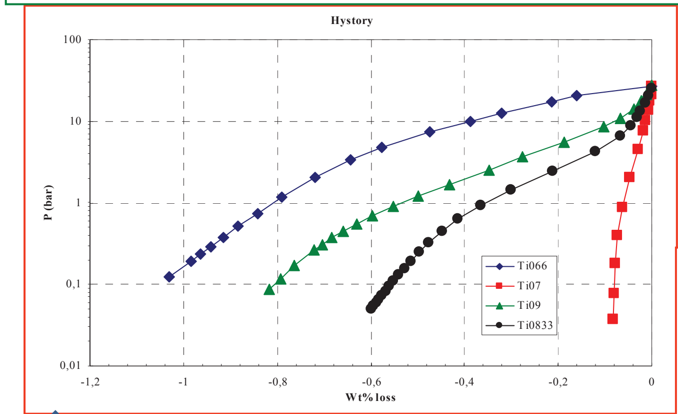
- – Safe storage

  Low pressure + endothermal desorption
- – High volume density
- – High purity hydrogen
- –Poor mass density… but

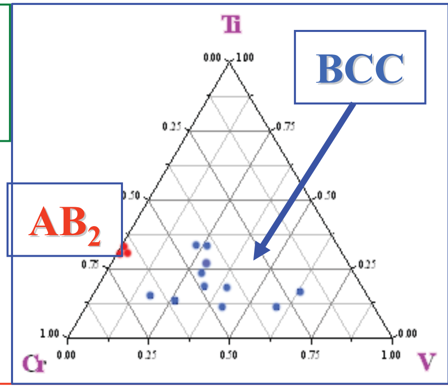


	kg H_2 / m^3	weight %
H_2 gas (700 b)	62	100
H_2 liq. (20 K)	70	100
$LaNi_5H_6$	123	1.4
Ti-V-Cr	205	3.7
$AlNaH_4$	96	7.5
MgH_2	106	7.6

BCC type alloys

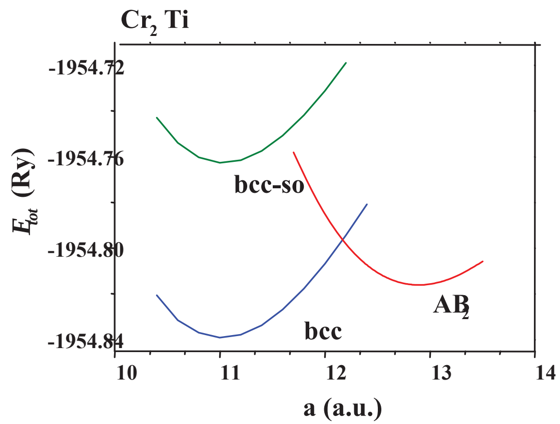


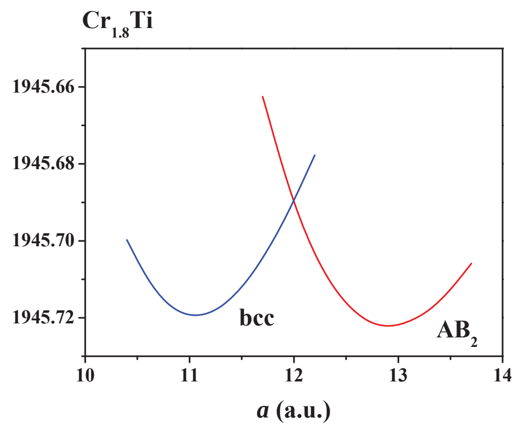
PCT (H/M vs pressure)



Relative stability : Experimental & Theoretical Approaches

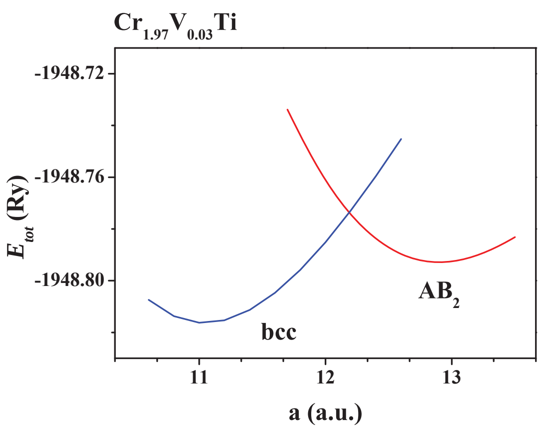
BCC alloys form FCC hydrides !

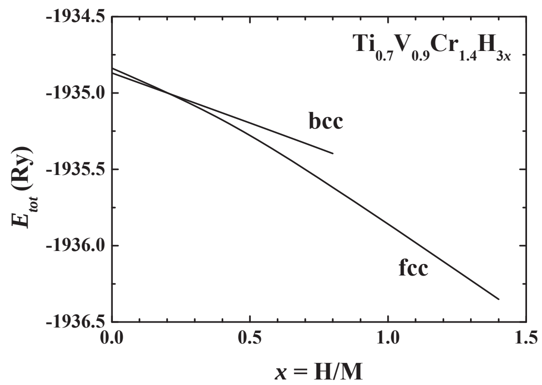


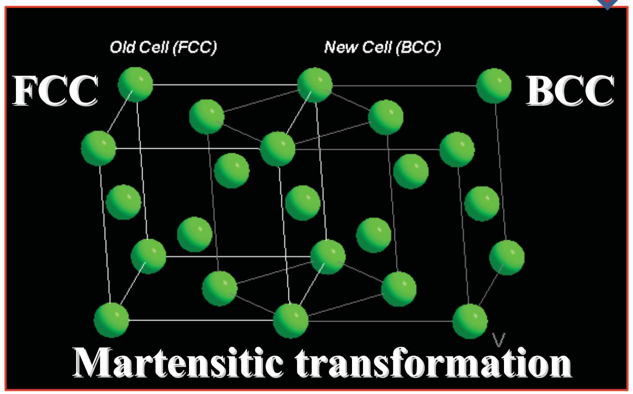


FLAPW & KKR-CPA band structure calculations

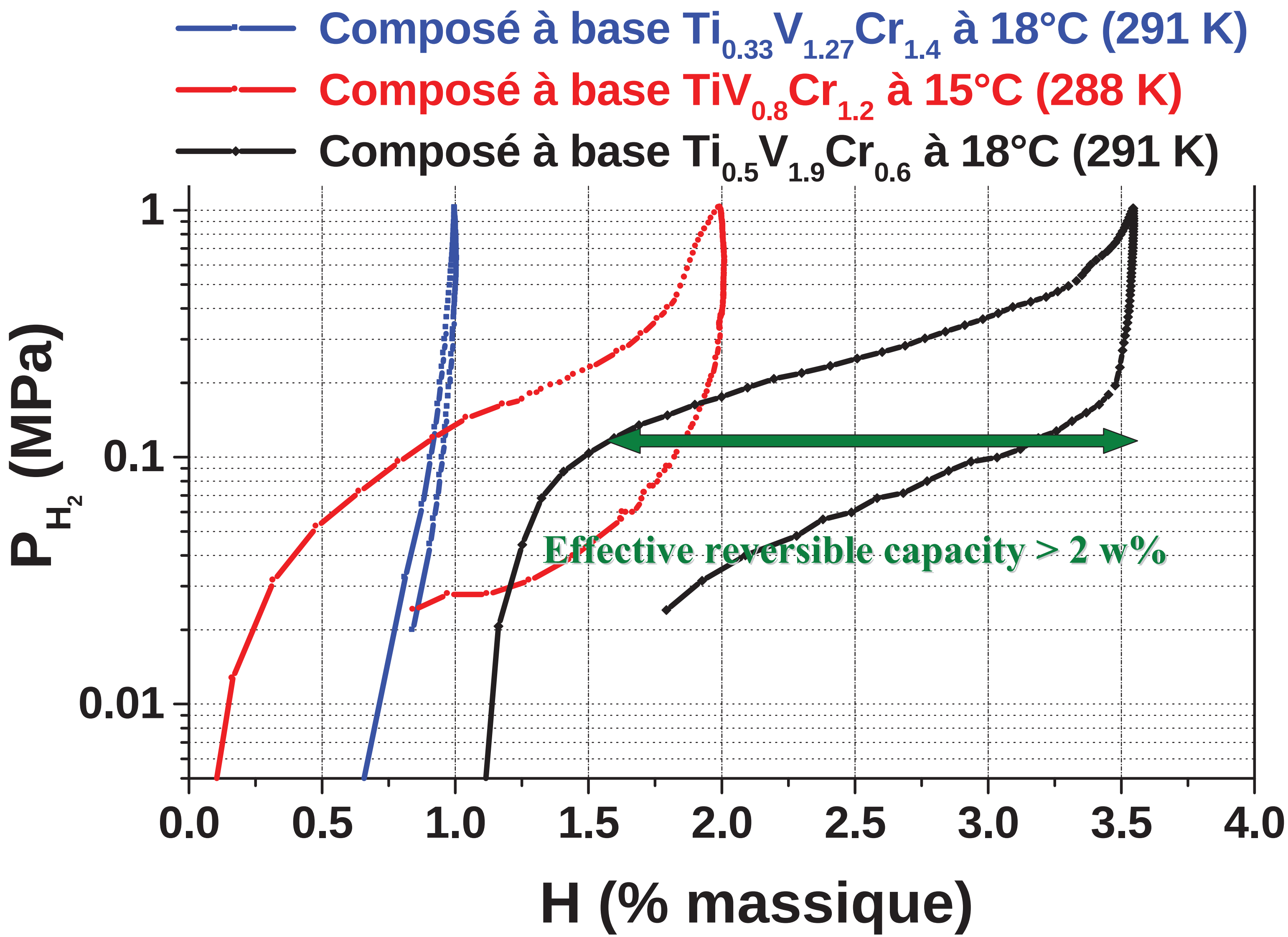
Martensitic transformation







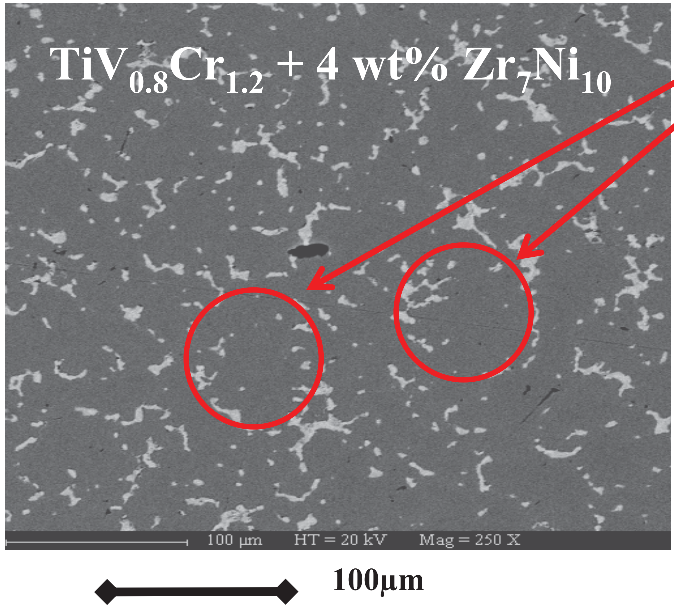
BCC based alloys : $Ti_xV_yCr_{1-x-y}$

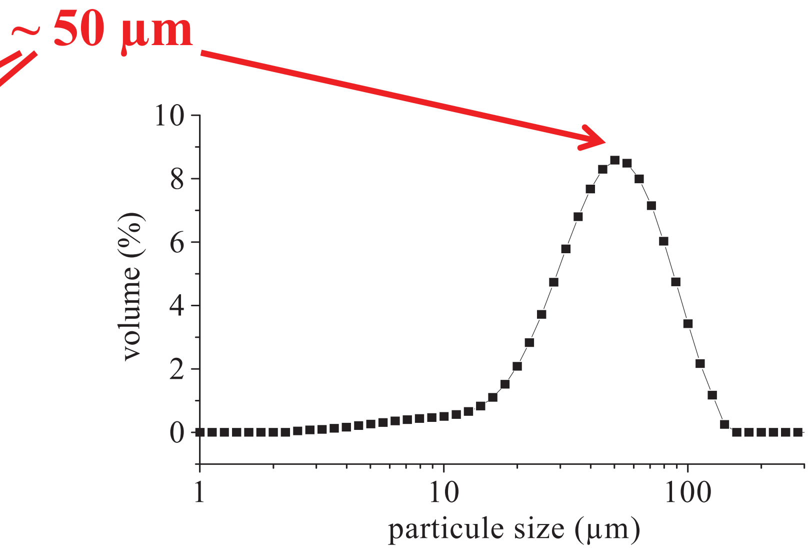


Fast reactivity of $Ti_xV_yCr_{1-x-y}$ alloys to hydrogen when composited with x% of Zr_7Ni_{10} additives

Reactive bulk microstructure

Decrepited powders





Specific process : Patent W0 2007096527

Pseudo-cellular microstructure for a fast intergranular hydrogen diffusion and homogeneous powder size decrepitation

Targets : nomad and mobile applications

HyCan (= CNRS – McPHy – PaxiTech – Boxal - AdVAnta)

Development of small cans to H-supply micro fuel cells

FUI

(P_{eq} < 13 bars at 50°C)

Hycan SA

McPhy Energy
Boxal
Paxitech
Ad'Venta

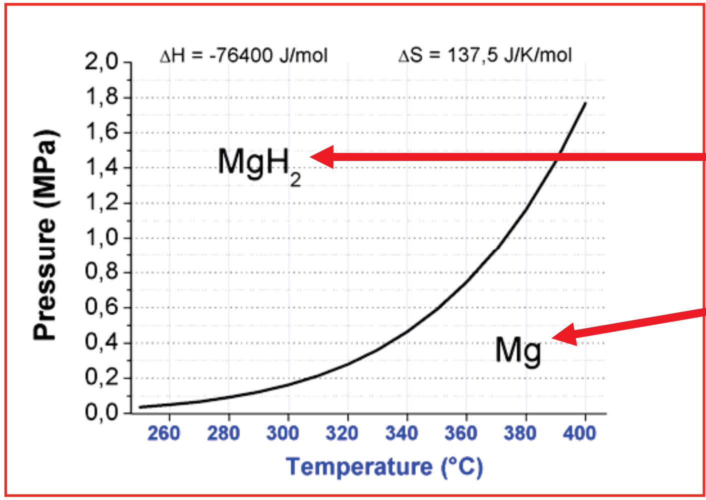
MODERNHy'T (CNRS - CEA-Liten - G-INP – SNCF - PSA)

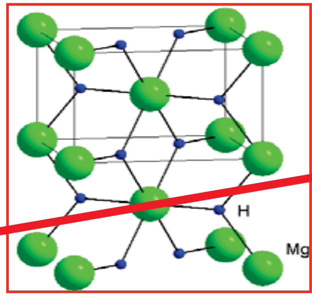
Hybride storage for automotive applications

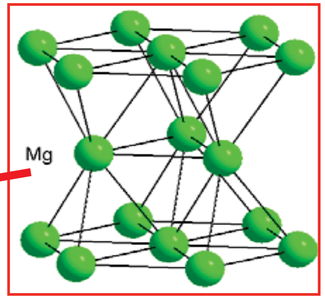
(P_{eq} > 100 bars : gas + metal hydride)

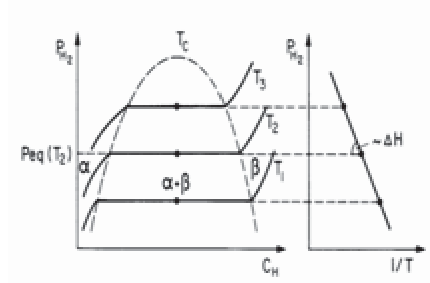
Agence Nationale de la Recherche GIP
ANR

Mg vs MgH_2









<u>So called difficulties with Mg</u>

H-reaction kinetic are said low, but…

Temperature of reaction is high, but…

<u>Mg is the best ?</u>

Mg is the 7th most abundant element on earth

Mg has ~ same cost as Al

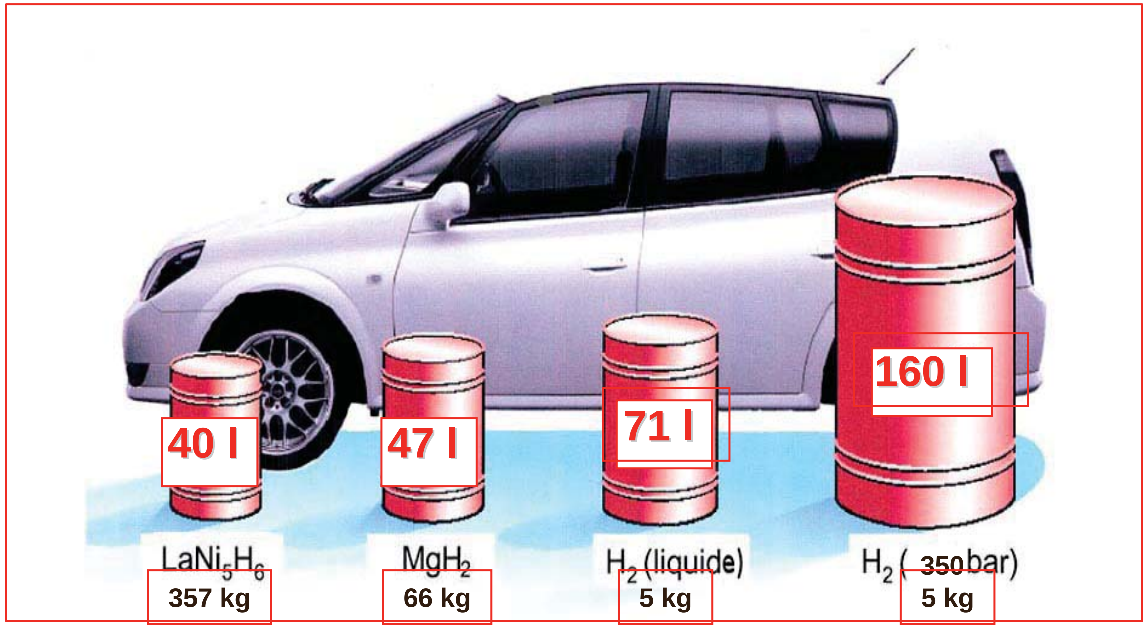
Mg metallurgy is easy

Mg is bio-compatible

Mg is re-cyclable

MgH_2 is monometal hydride system: no demixtion

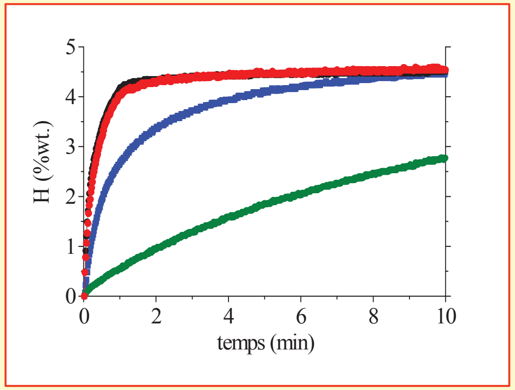
MgH_2 uptake is 7.6 w%

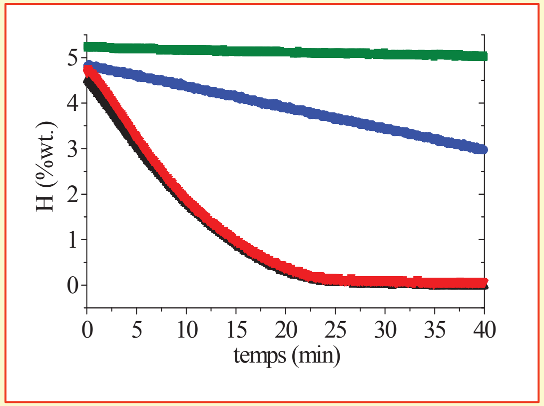


Tank : 5 kg H_2 = 300 km

Metal «catalyst» deposits on BM MgH_2 particules

- 1 h
- 5 h
- 10 h
- 20 h

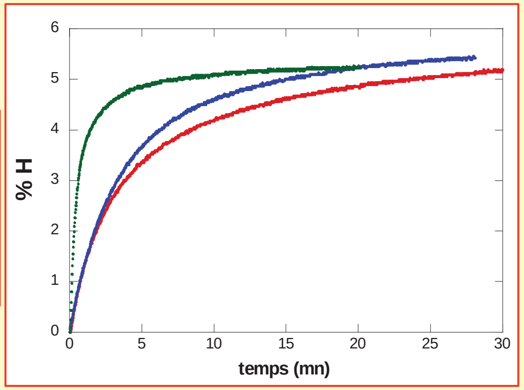


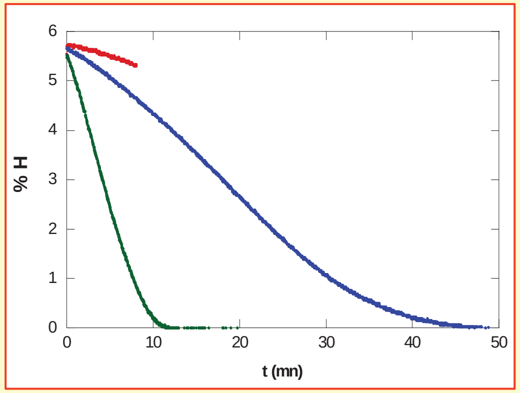


Energetic Ball-Milling is a common method used to prepare reactive powders : homogeneous nano-crystallites, high density of defects, doping with metal type catalysts®

Absorption 240°C – 1 MPa **Desorption 300°C – 10 kPa**

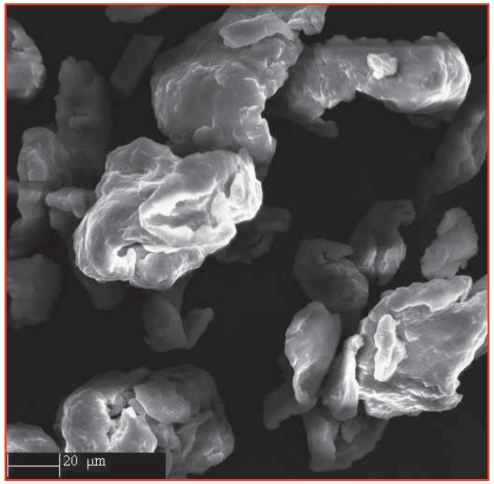
- 1 % at V
- 3 % at V
- 5 % at V

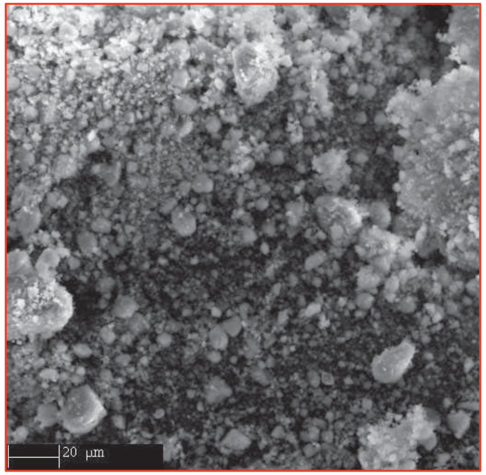




@ McPhy Energy SA France

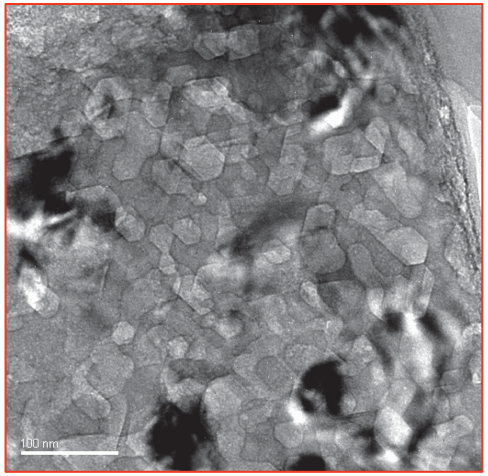
Micro- to Nano-structure + high density defects

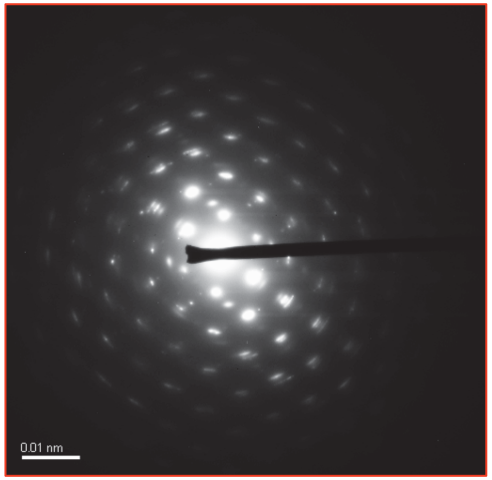




a - SEM picture of as received MgH_2, the mean grain size is about 40 µm

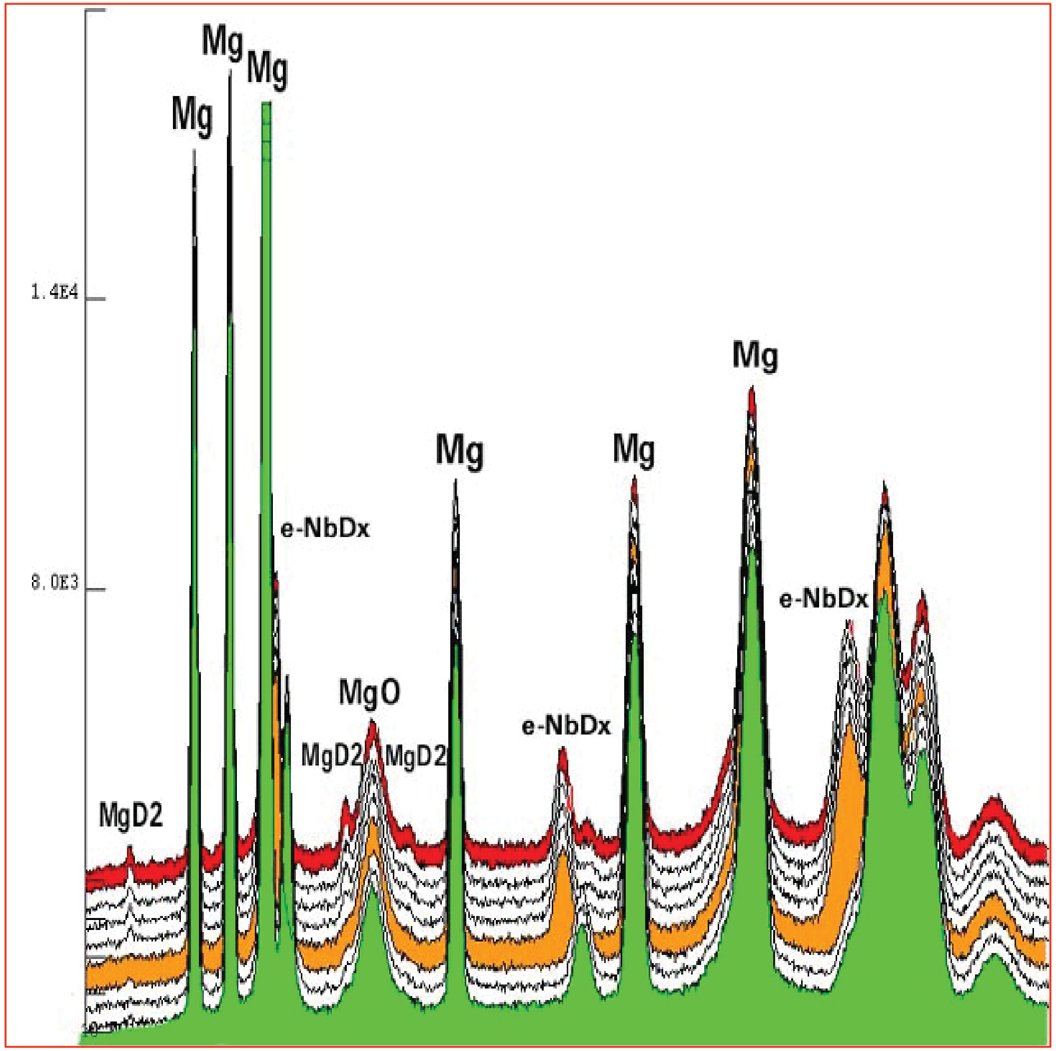
b – SEM picture of a 10 hour ball-milled MgH_2, the mean size distribution ranges from 0.2 to 10 µm





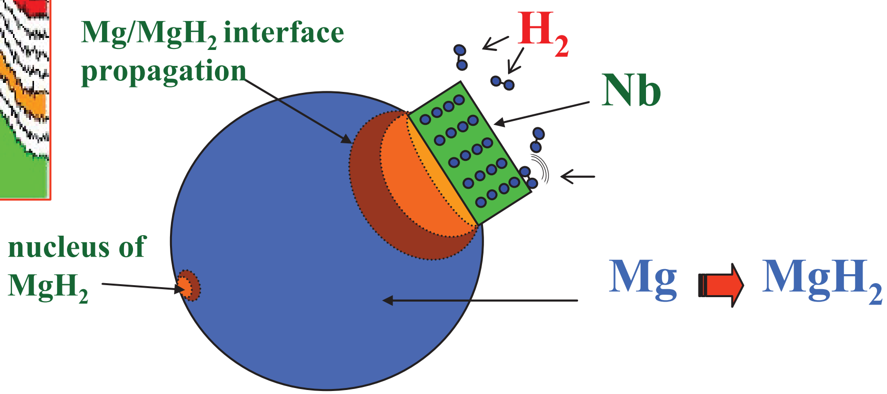
a - HREM picture of a 6 hour ball-milled MgH_2, defects and nanocrystalline state transform to well shaped homogeneous sized crystals after evacuation under the e^- beam; mean grain size ~ 20 nm

b – Electron diffraction picture of in-situ well recrystallised Mg from the MgH_2 precursor

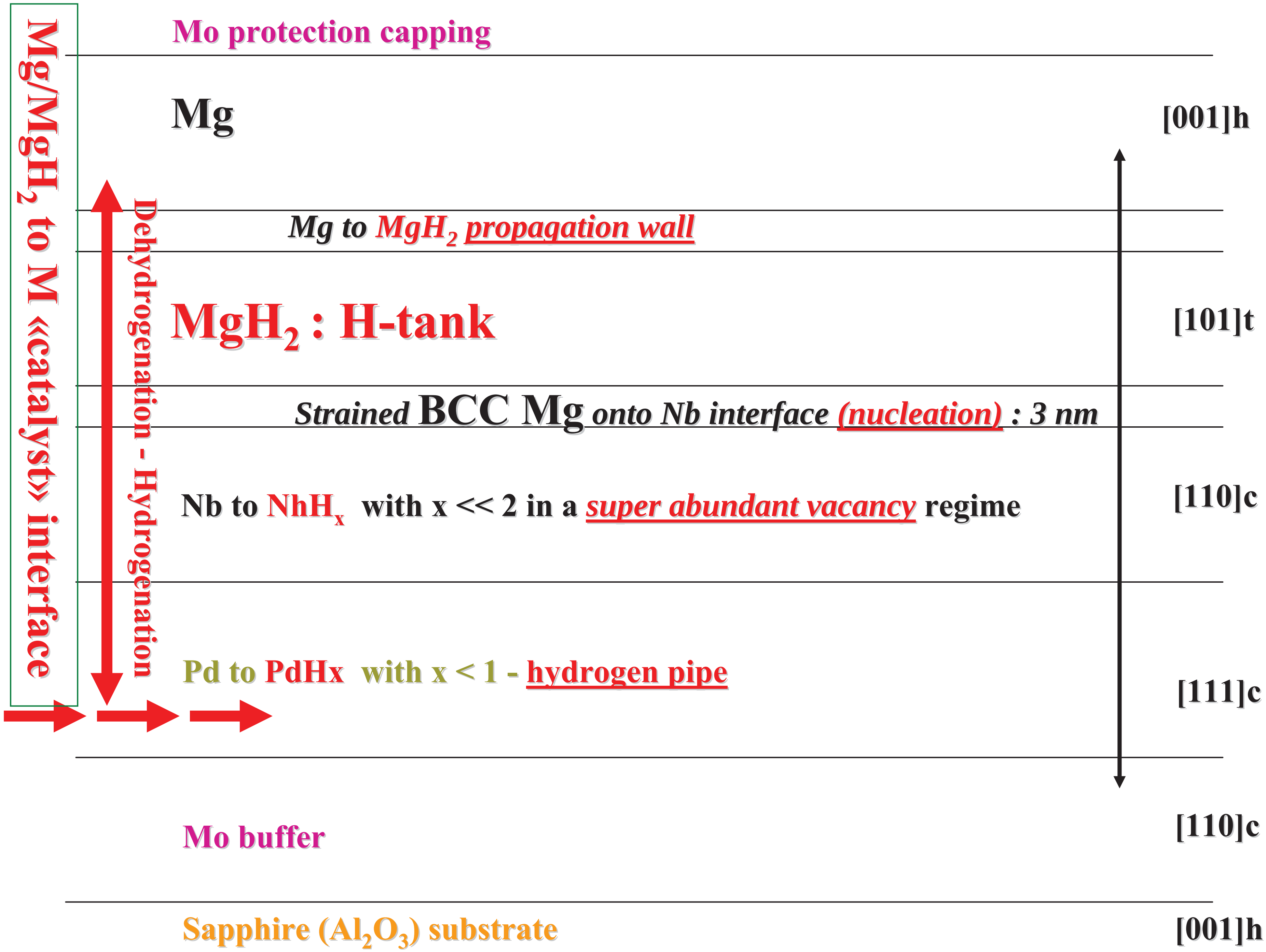


So-called «Catalytic» Effect ?

In-situ neutron diffraction hydrogenation of Mg via Nb/NbH_x as « catalyst »



Scheme : a Nb nano-particle interfacing a micrometric Mg grain


Mo protection capping
Mg
[001]h
Mg to MgH_2 propagation wall
MgH_2 : H-tank
[101]t
Strained BCC Mg onto Nb interface (nucleation) : 3 nm
Nb to NhH_x with x << 2 in a super abundant vacancy regime
[110]c
Pd to PdHx with x < 1 - hydrogen pipe
[111]c
Mo buffer
[110]c
Sapphire (Al_2O_3) substrate
[001]h
Mg/MgH_2 to M «catalyst» interface
Dehydrogenation - Hydrogenation

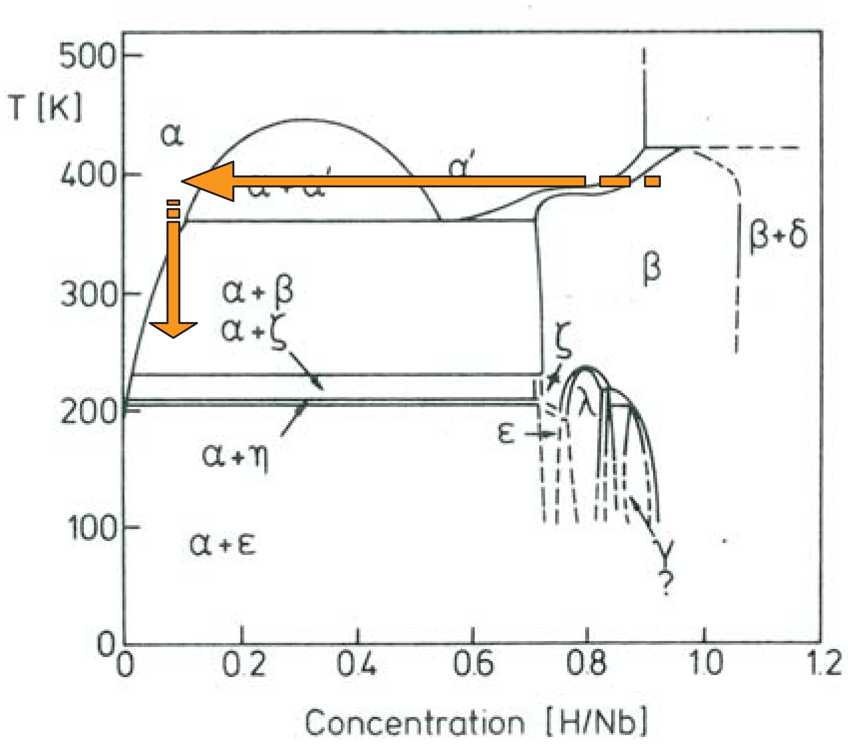
Interface M «catalyst» - Mg/MgH_2

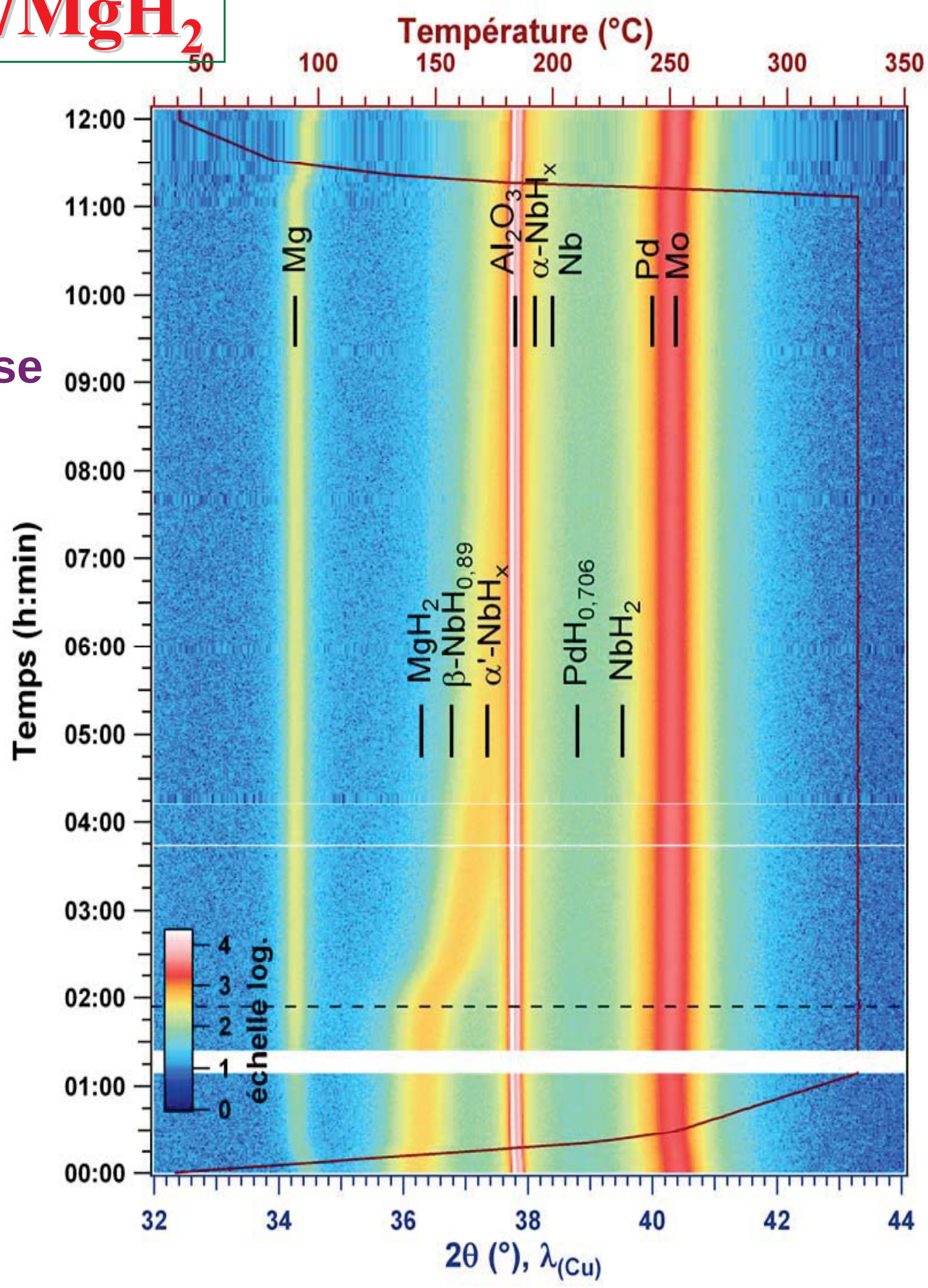
Formation of β-$NbH_{0,89}$

β-$NbH_{0,89}$ → α'-$NbH_{<0,89}$ → α-$NbH_{\sim 0,2}$

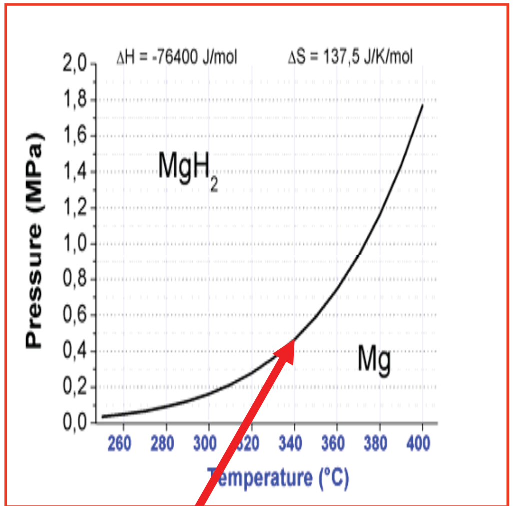
Orthorhombic Superstructure
Non mobile H

Disordered Cubic Phase
Mobile H (vacancies)



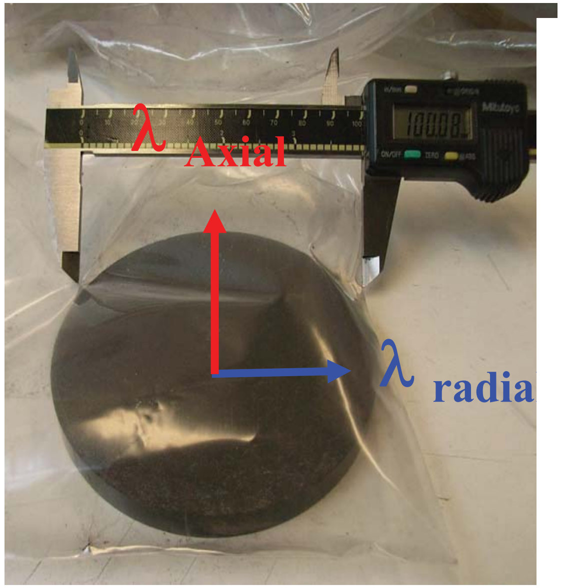


Heat of Reaction Management
Compacts MgH_2 + Expanded Natural Graphite

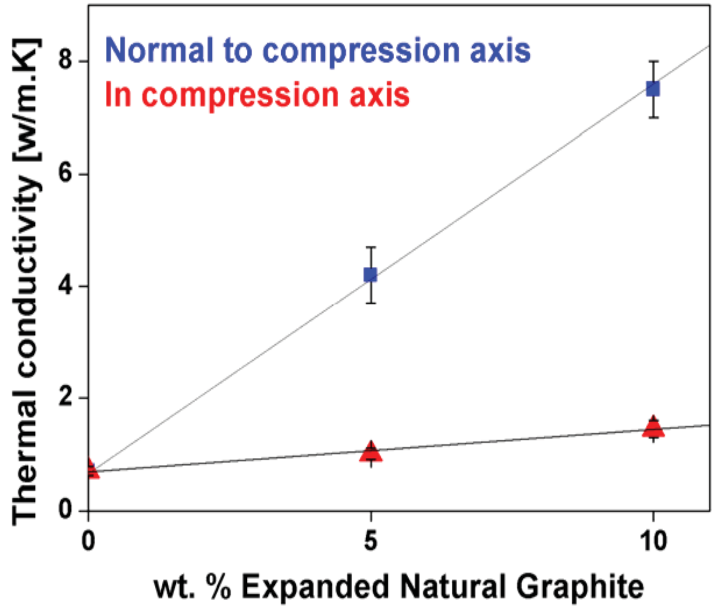


Heat of Formation !

~ 1/3 H_2 Combustion



Compact Φ 10 cm
60 Nl H_2



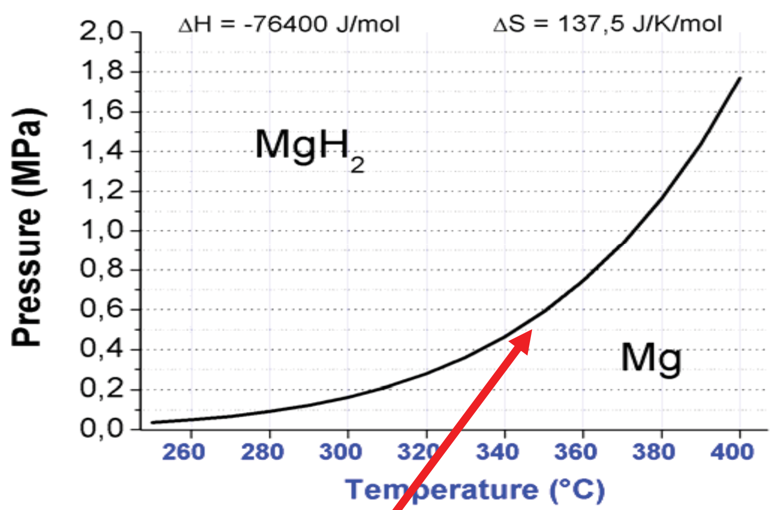
Improve radial thermal conductivity (x 30 / free powder)

Homogeneous, mechanically stable on H_2 cycling

Improvement of H_2 volumetric capacity (x 3)

Very safe storage

Adiabatic tank concept



Stack : 73 disks / 13 cm

10 kg MgH_2 + 5 %wt ENG

126 kg CPM (Mg-Zn-Al)

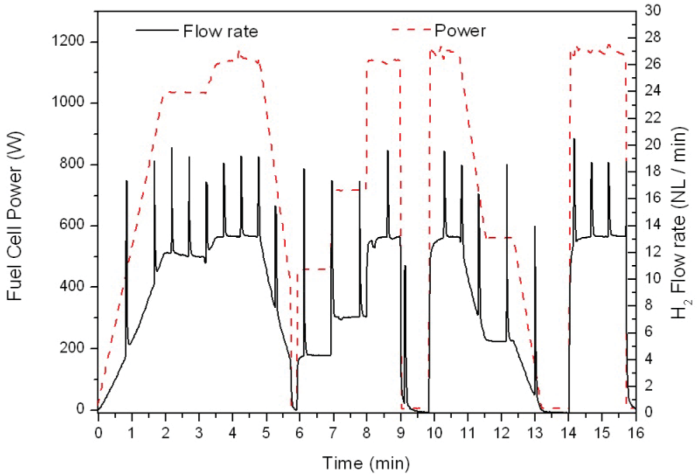
Electrical power : 1.2 kW

Direct connexion between tank and FC

No H_2 buffer, no mass flow regulation

FC H_2 pressure limitation : 0.12 MPa

Autonomy > 10 h. at max. FC power



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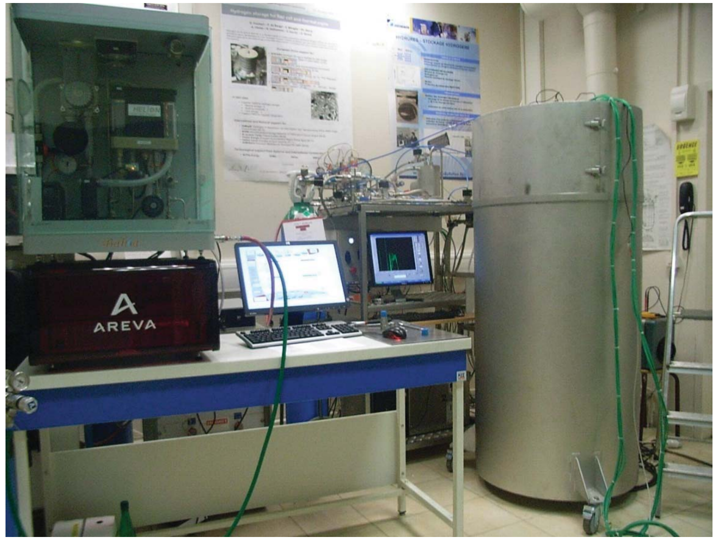
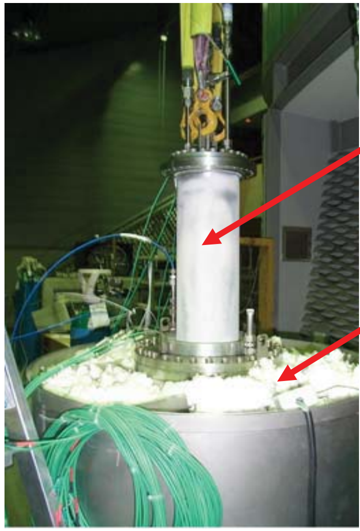


LARGE REVERSIBLE SAVING ENERGY = STORE REVERSIBLY HEAT WITH A CPM

Adiabatic tank concept



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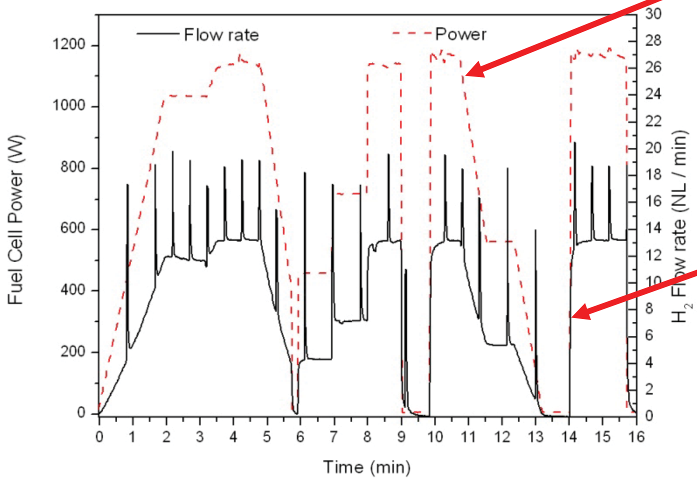
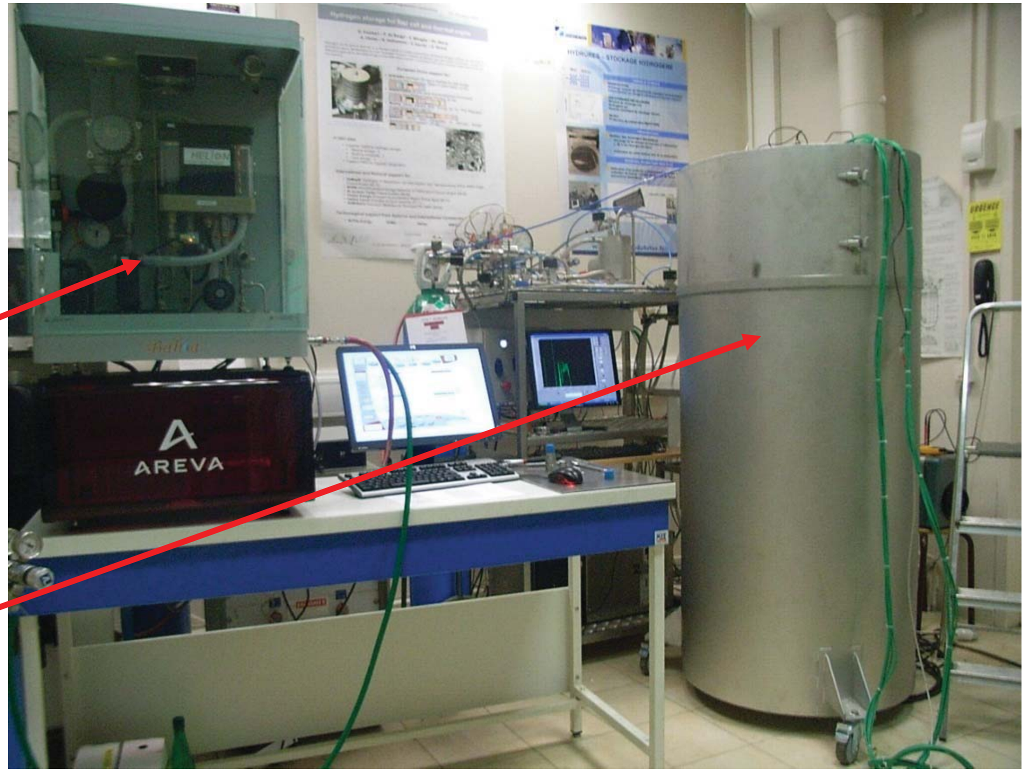




Opening new routes for a mass production

Nanostructuration, high density of defects

CNRS & UQTR

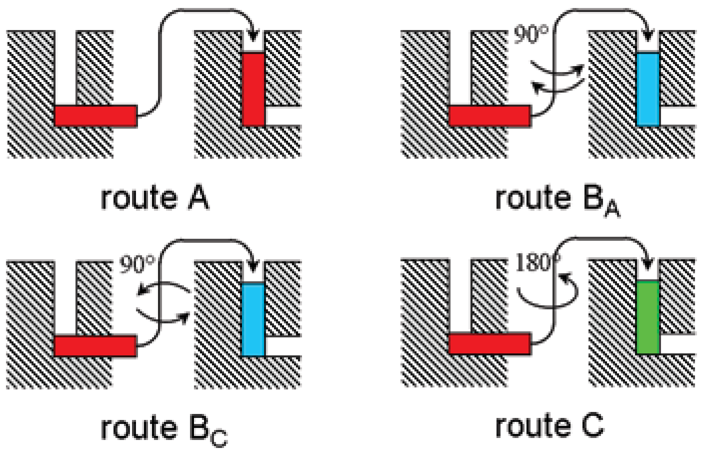
Ball Milling is a traditionnal and very effective process, but very expensive for a mass production in terms of time, energy, manpower….
Unsafe since powder pyrophoricity

ECAP (as e.g. Cold Rolling, Fast Forging) allows better understanding of metallurgy parameters than Ball Milling

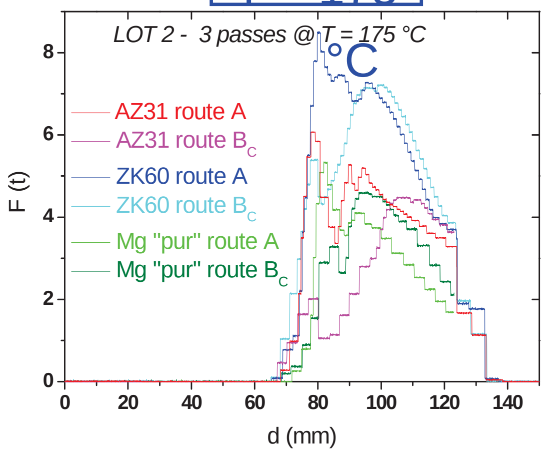
No «catalyst» additive => towards 7.6 w% !

Manufacture Mg-rich composites : temp., route, activation

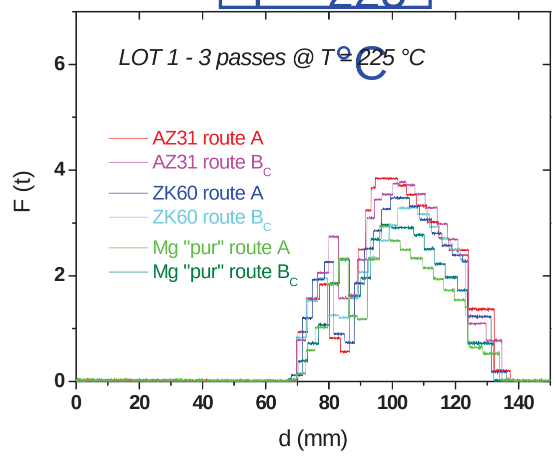
ECAP process

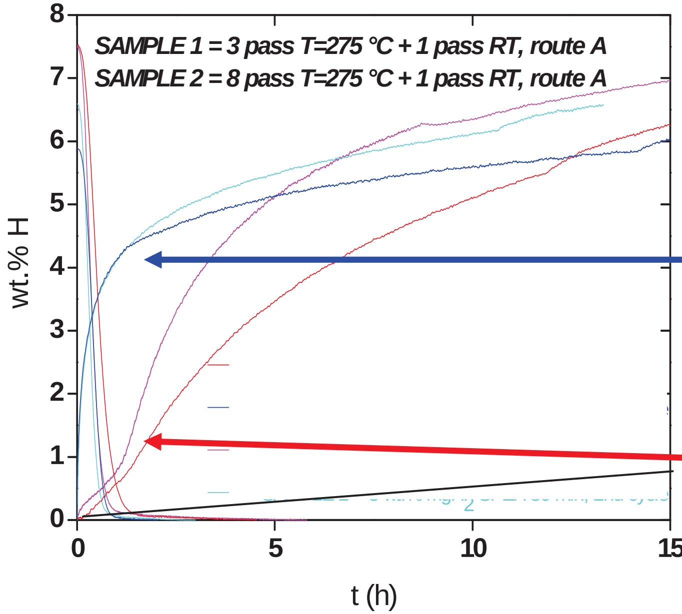


T = 175 °C

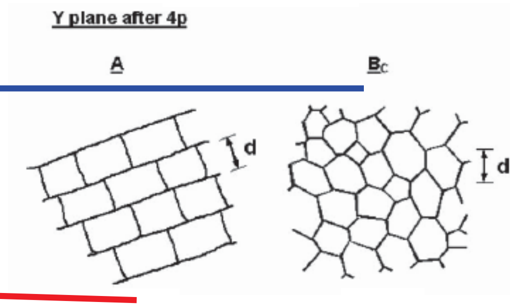


T = 225 °C





After
4 passes

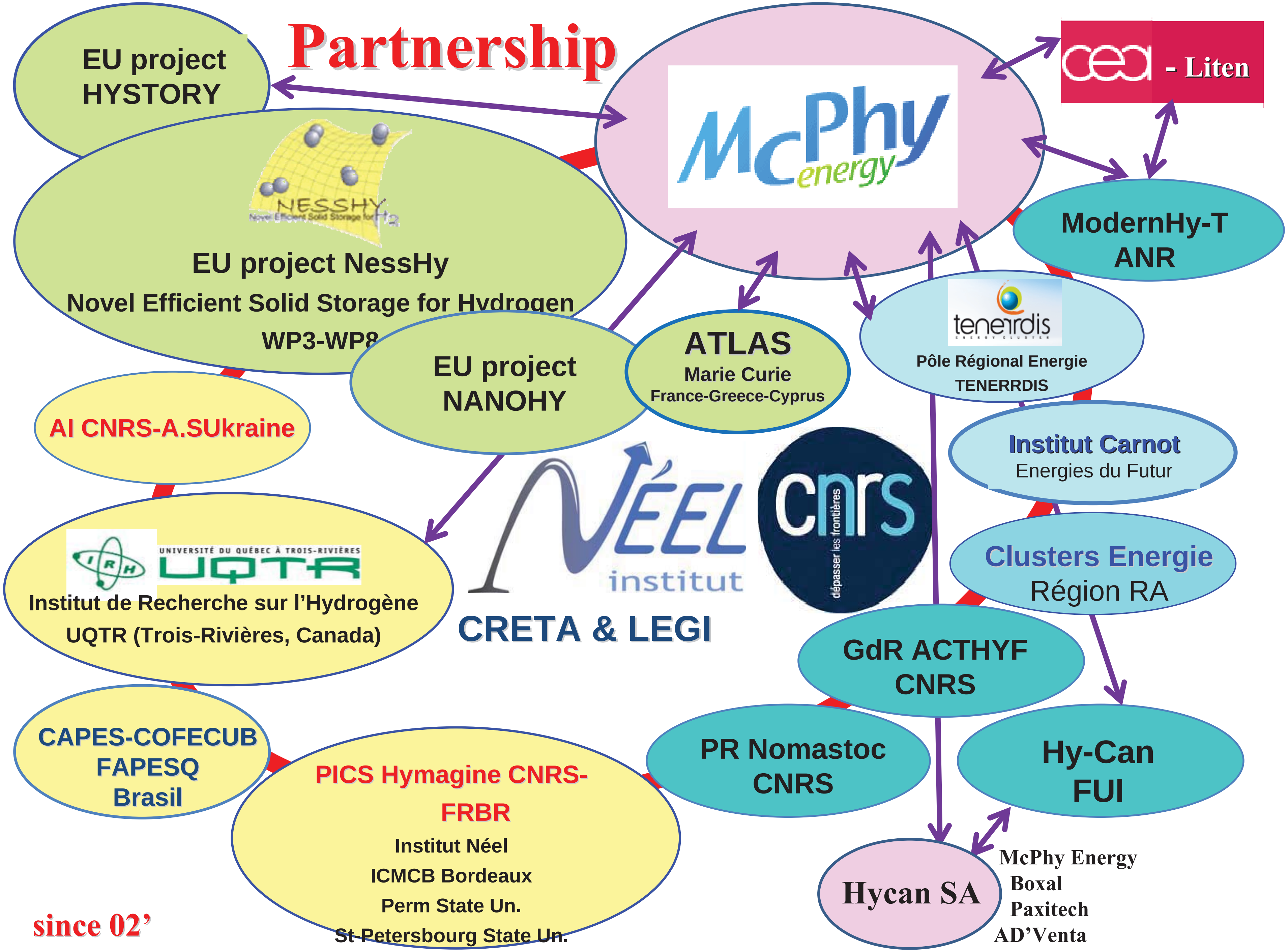


A B_C

[T.G. Langdon, Mat. Sci. Eng. A 462 (2007)]

Port-folio of Patents

- CNRS WO2007096527 : Pulverulent intermetallic material for the reversible storage of hydrogen - Charbonnier-J, de Rango-P, Fruchart-D, Miraglia-S, Rivoirard-S
- CNRS WO2007125253 : Nanocrystalline composite for storage of hydrogen- Fruchart-D, de Rango-P, Charbonnier-J, Miraglia-S, Rivoirard-S, Skryabina-N, Jehan-M
- CNRS WO2009080986 : Hydrogen storage material made of magnesium hydride - de Rango-P, Chaise-A, Fruchart-D, Miraglia-S, Olivès-R
- CNRS WO2009080975 : Hydrogen storage tank - de Rango-P, Chaise-A, Fruchart-D, Marty-P, Miraglia-S
- CNRS /McPhY Energy F08 07087: Réservoir adiabatique d’hydrure métallique - de Rango-P, Fruchart-D, Jehan-M, Miraglia-S, Marty-P, Chaise-A, Garrier-S, Bienvenu-G
- MCPhy /CNRS FR0904442 : Réservoir de stockage et de déstockage d’hydrogène et chaleur - Jehan-M, Peyraut-L, Bienvenu-G, de Rango-P, Marty-Ph
- CNRS/UQTR/McPHy Energy FR1002928 : Matériaux déformés plastiquement pour le stockage de l'hydrogène - Fruchart D., Miraglia S., de Rango P., Skryabina N. Jehan M., Huot J., Lang J., Pednault S.



Partnership
EU project HYSTORY
McPhy energy
cea - Liten
NESSHY
Novel Efficient Solid Storage for H2
EU project NessHy
Novel Efficient Solid Storage for Hydrogen
WP3-WP8
ModernHy-T ANR
EU project NANOHY
ATLAS
Marie Curie
France-Greece-Cyprus
tenerrdis
Pôle Régional Energie
TENERRDIS
AI CNRS-A.SUkraine
Institut Carnot
Energies du Futur
NÉEL institut
cnrs
dépasser les frontières
CRETA & LEGI
Clusters Energie
Région RA
UNIVERSITÉ DU QUÉBEC À TROIS-RIVIÈRES
UQTR
IRH
Institut de Recherche sur l'Hydrogène
UQTR (Trois-Rivières, Canada)
GdR ACTHYF
CNRS
CAPES-COFECUB
FAPESQ
Brasil
PICS Hymagine CNRS-FRBR
Institut Néel
ICMCB Bordeaux
Perm State Un.
St-Petersbourg State Un.
PR Nomastoc
CNRS
Hy-Can
FUI
Hycan SA
McPhy Energy
Boxal
Paxitech
AD'Venta
since 02'

McPhy energy

3 sites (factory, office, design)

starts Feb. 2008

Metal Hydrides & Tank Systems

30 employees June 2011

McPhy Energy

Société anonyme à Directoire et à Conseil de Surveillance
au capital de 129.136,60 euros
Siège social : La Riétière, 26190 La Motte Fanjas
502 205 917 RCS Romans

Representatives

McPhy-Italy

McPHy-Spain

McPhy-Japan

McPhy-India

McPhy GmbH Germany

Directory :

P. Mauberger: COE, M. Jehan: Director, D. Fruchart: Sc. Manager, A. Screnzi: Business

H_2 pressure ≈ 0.12 MPa

Electrical power : 1.2 kW

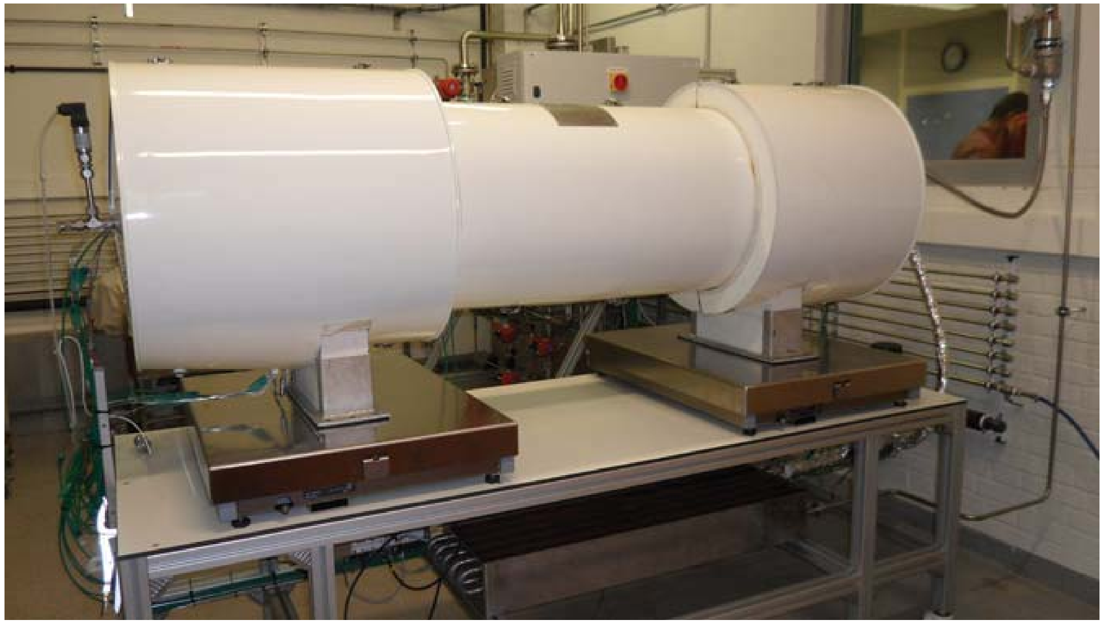
NÉEL institut

Direct connexion between tank and FC

No H_2 buffer or mass flow regulation

McPhy energy

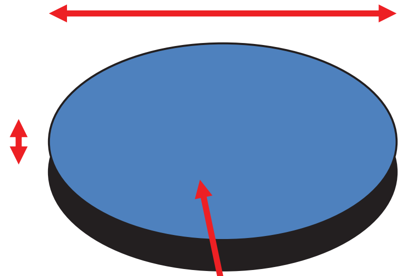
cea -Liten



~ 100 kg MgH_2 precursor / day

First-Hydrogenation Reactor

30 cm



1 cm

MgH_2 composite

density ~ 1

~ 0.45 Nm^3 H_2 - eq. pressure ~ 500 b

Milling capacity of nanostructured and activated <u>reactive MgH_2</u>

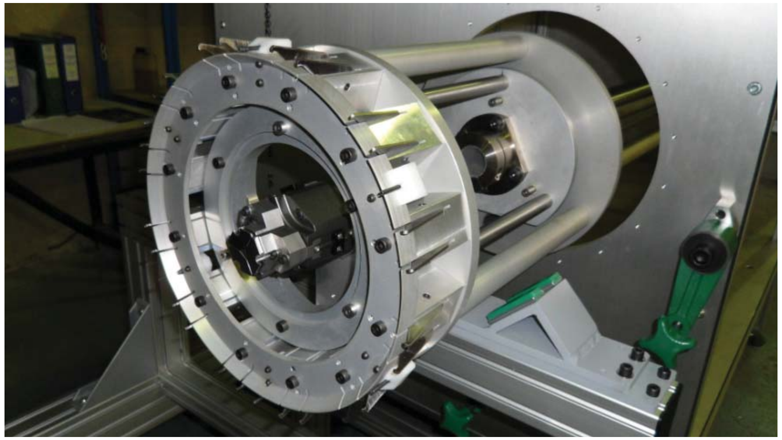
100 kg / day

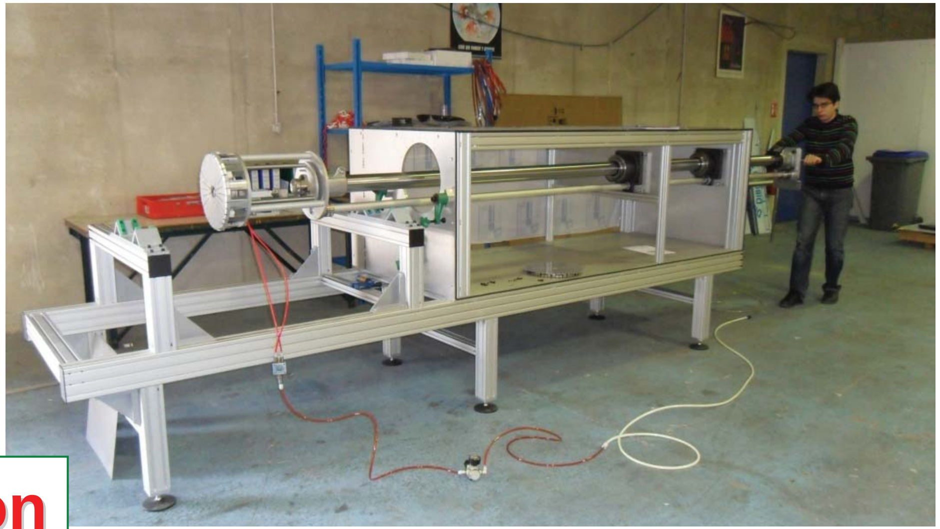
reactive MgH_2

NGE

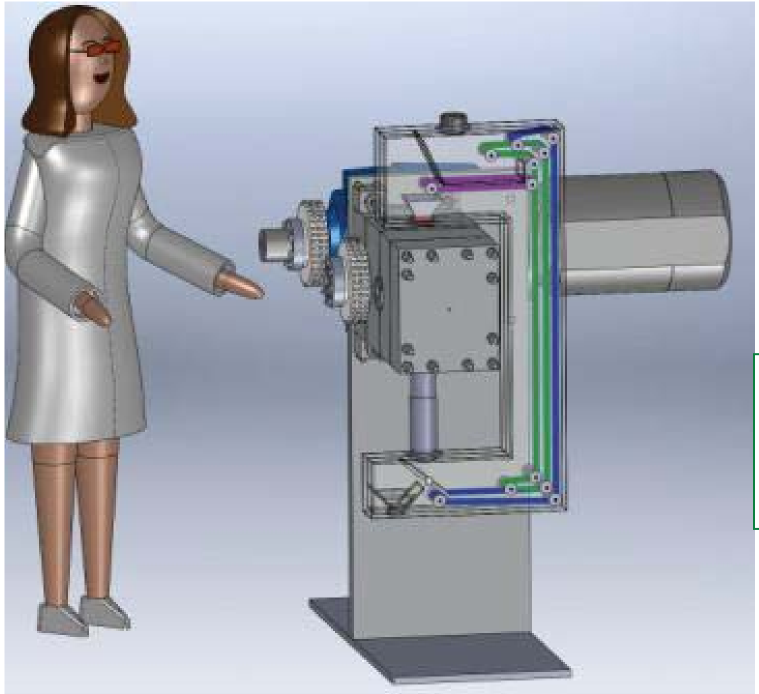
HF synthesis of $TiVCr^{®}$ additives

CPM® melter and doser to fill the heat storage tank





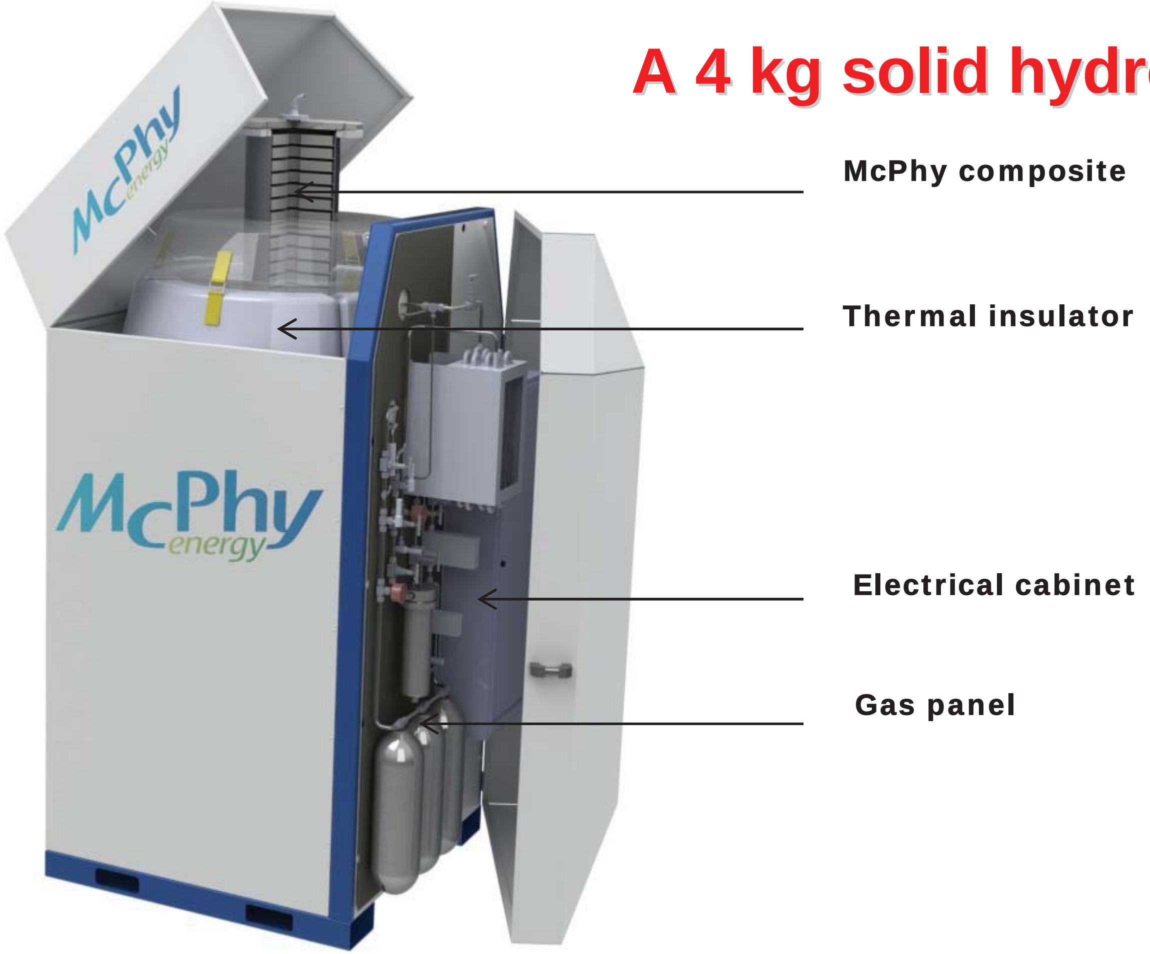
Automatic loading tank station



Severe Plastic Deformation Station (under development)

Almost a realty…

A 4 kg solid hydrogen unit



Design approved by ENEL: Feb. 7th & 8th , 2011

Design approved by Iwatani: March 1st , 2011

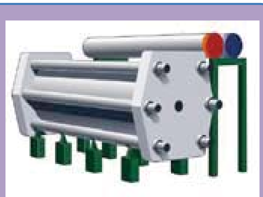
+ UK Clean Village + Hymage II + MYRTHE…

BACKUP POWER SUPPLY APPLICATION

Electrolyser

300 Nm_3 /h

60 bara



CPM storage system

50 kg @ 2 bar

equivalent to 555 Nm^3 (1665 kWh)

10 bara
$40Nm^3/h$

2 bara
$42{,}7Nm^3/h$

Power Generator

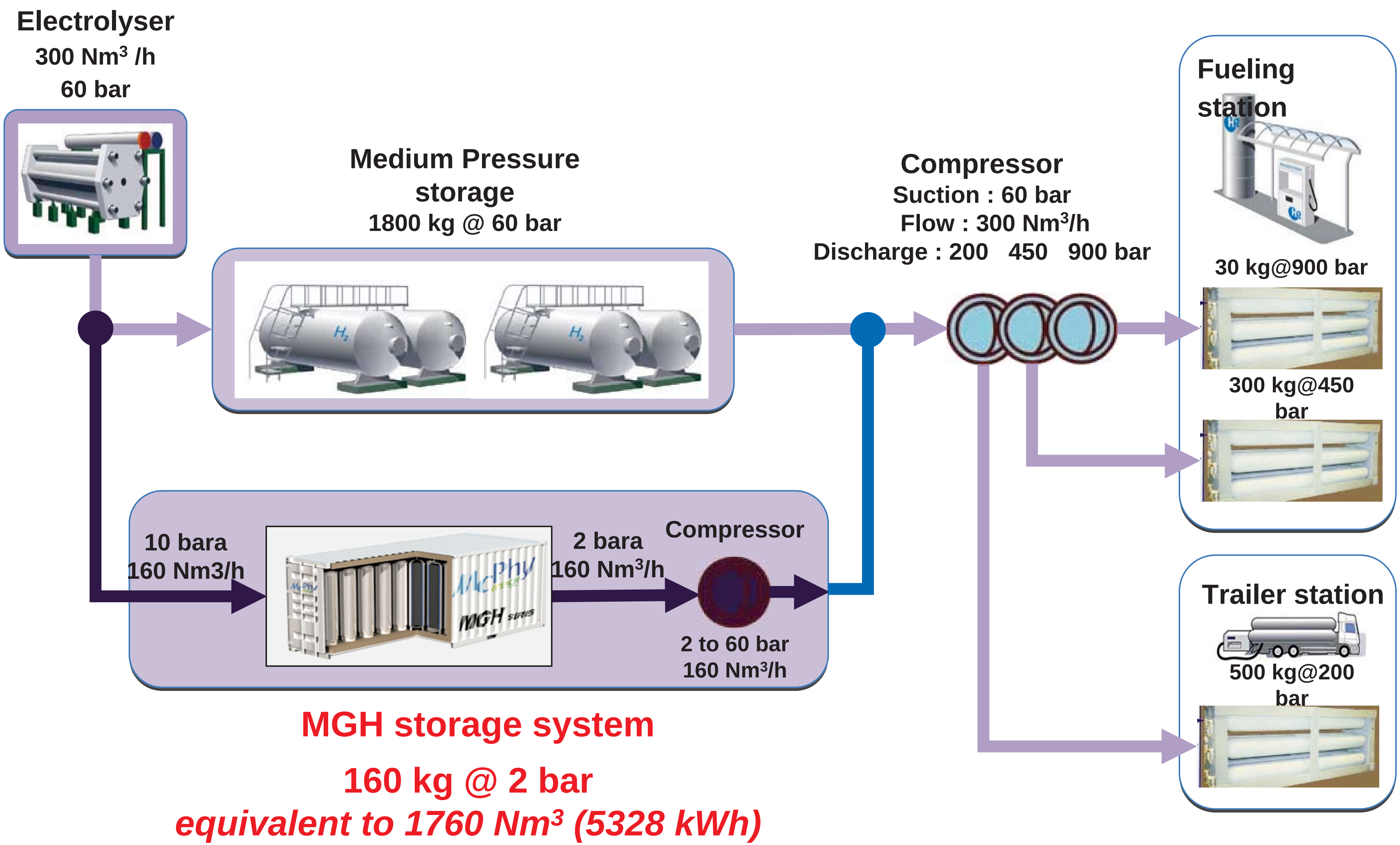
50 kW/h during at least 12h

Hydrogen turbine

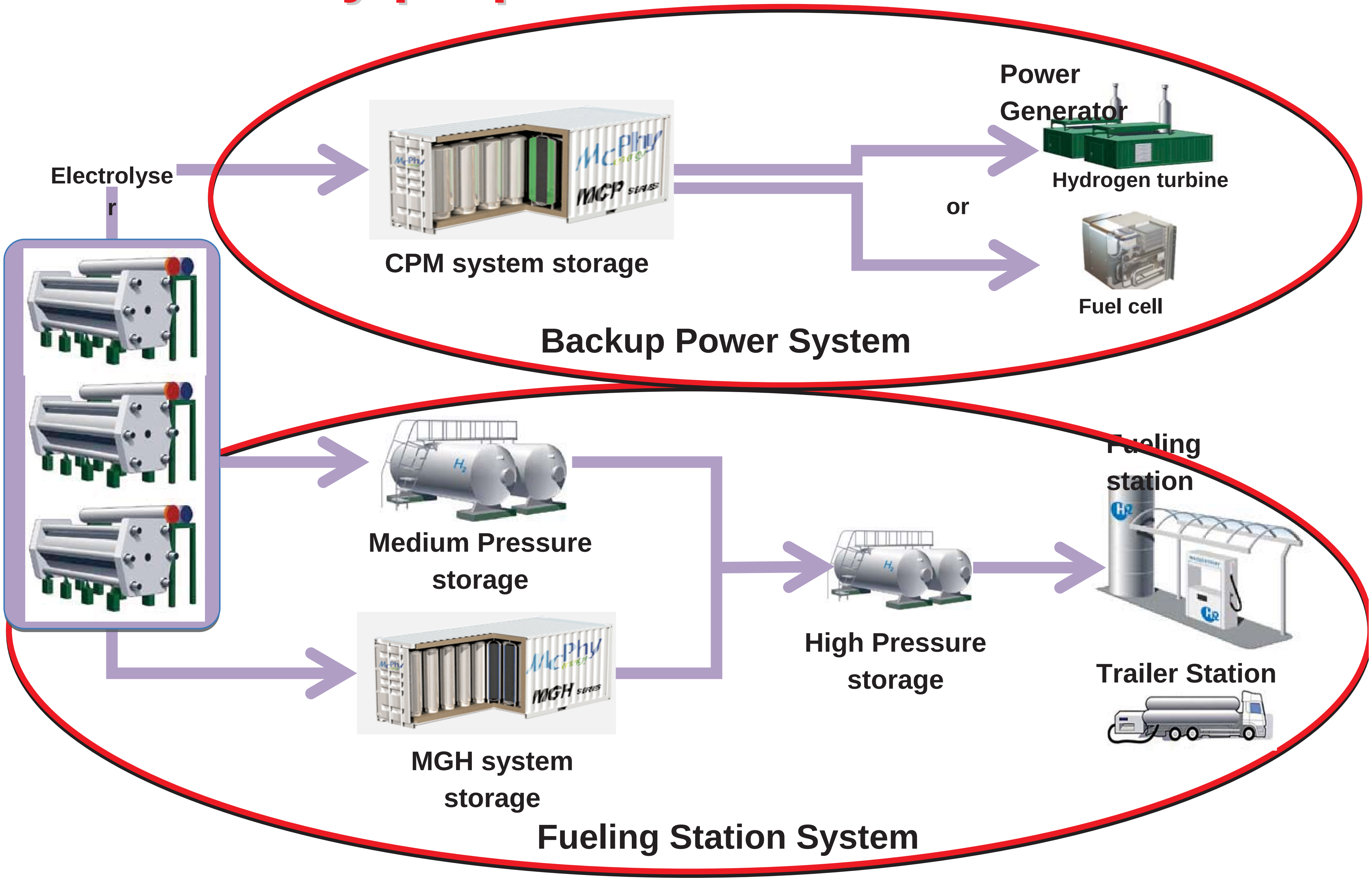
or

Fuel cell

HYDROGEN FUELING STATION



INTEGRATED PROJECT
McPhy proposal



H_2 REFUELING STATION

Process and logistic complexity

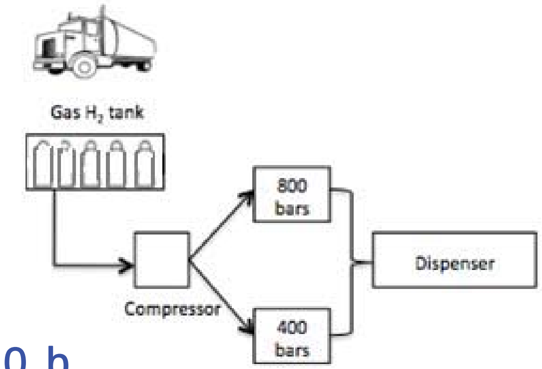
Currently in refueling station

Liquid storage

- 253°C

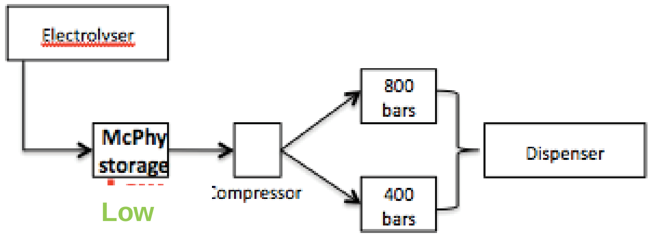
Gas storage

Logistic complexity



300 b

McPhy solution



Low pressure < 10 bar

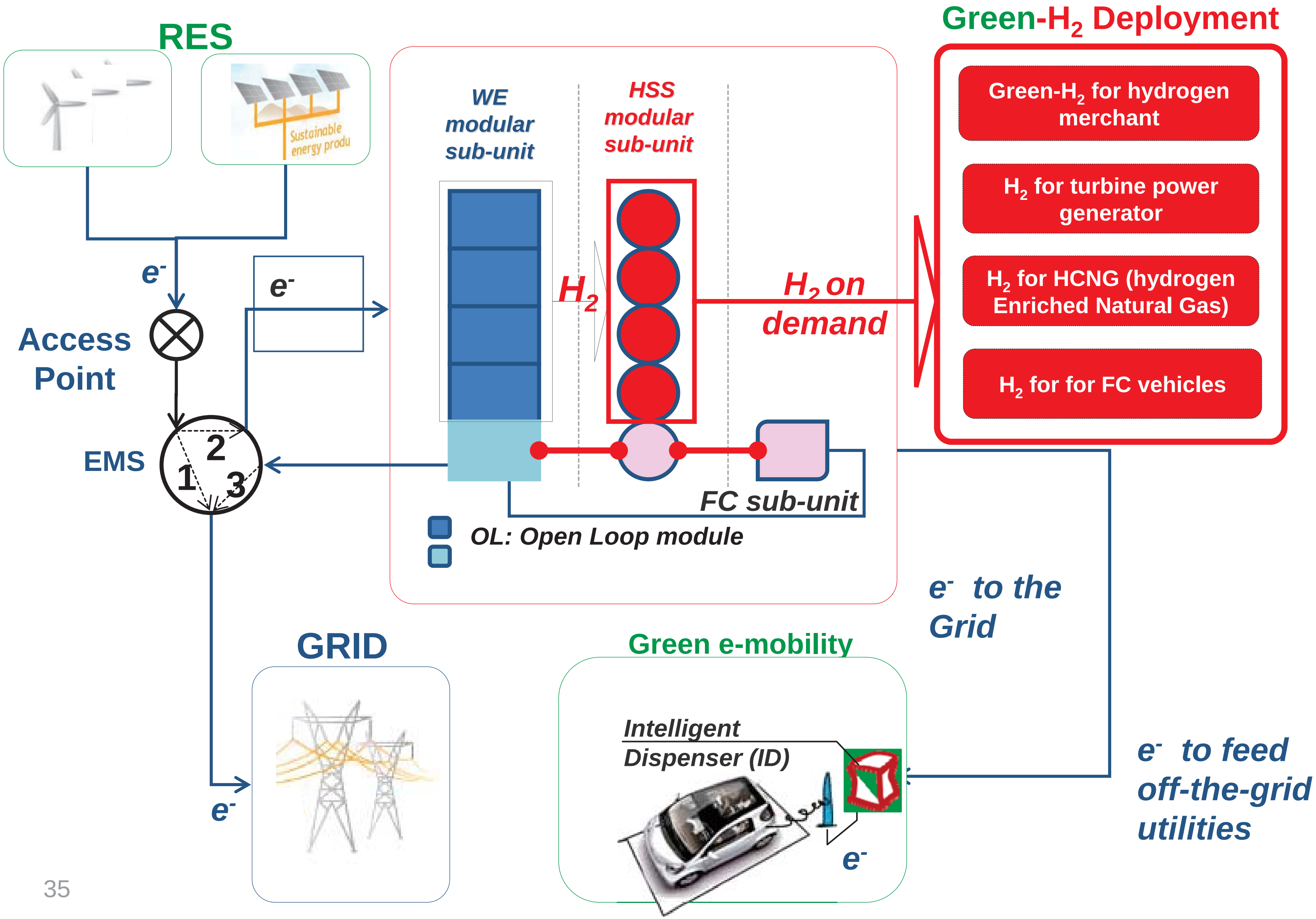
solid ~ RT < 10 b

No logistic / Easy to use

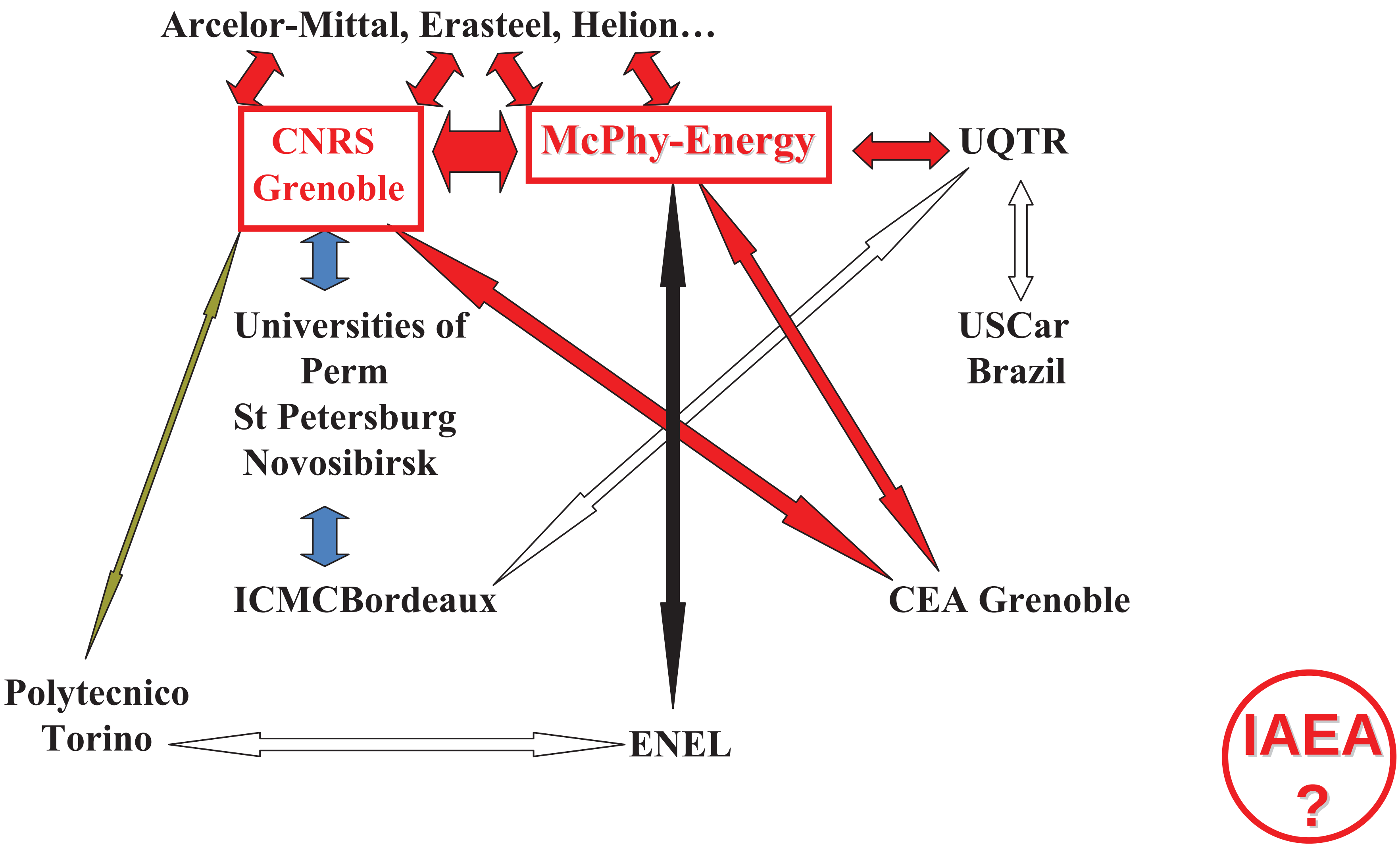
Safety / Minimize regulation issues

«Green» PROJECT

GES - Green Energy Storage System



SOME R & D COLLABORATIONS



OUR VISION

Stationnary Applications (heat management)

Mass storage and transportation (up to GW)
FC or turbine to grid - regulation of RE
Refilling station (e.g. on site)
On site industry applications
Merchant hydrogen

Mobile applications (heat management)

ICE fuelling
Hybride ICE/FC/Electric

Nomad applications

All type hydrides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