Novel Efficient Solid Storage for Hydrogen

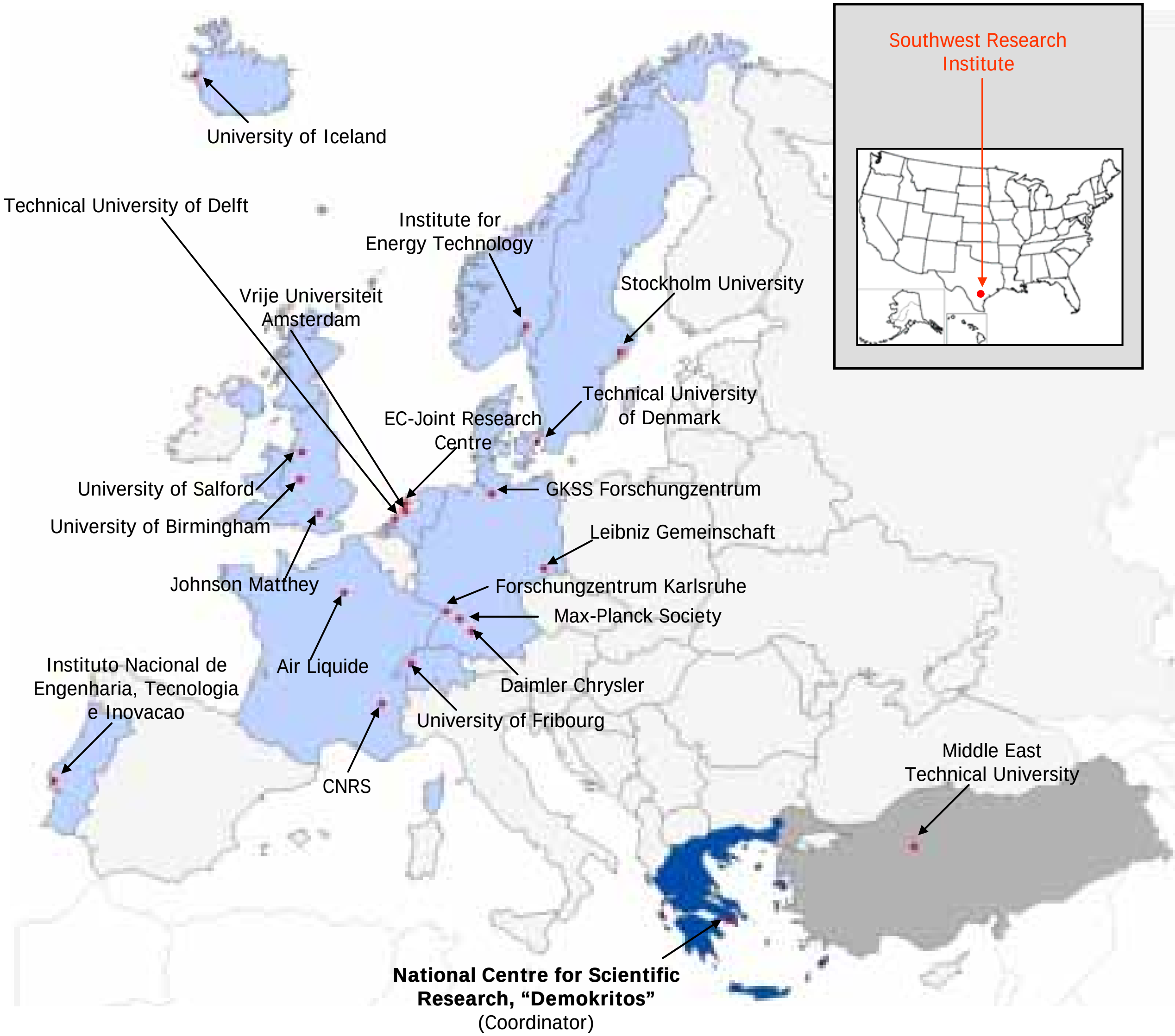
The NESSHY Integrated Project: An Overview

NESSHY
Novel Efficient Solid Storage for H_2

Thanos Stubos
National Center of Scientific Research « Demokritos »
Athens – Greece

NESSHY General facts

- Co-ordinator: NCSR Demokritos (Greece)
- Duration:1.1.2006 – 31.12.2010 (5 years)
- Budget: M€ 11.3
- EC contr.: M€ 7.5
- 22 partners from 12 European countries and USA (1 OEM, 19 research institutes, 2 industrial companies)

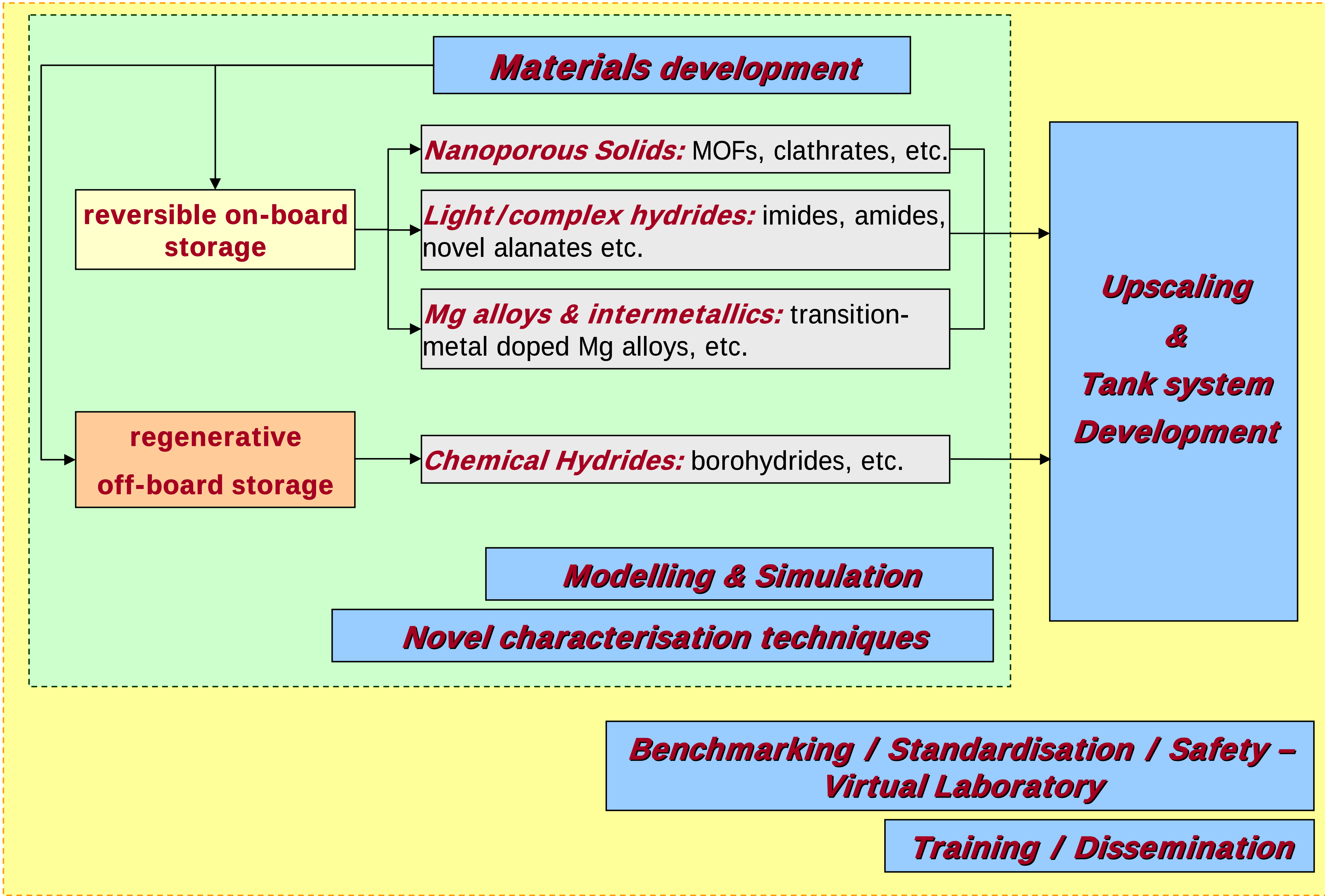


NESSHY key objectives

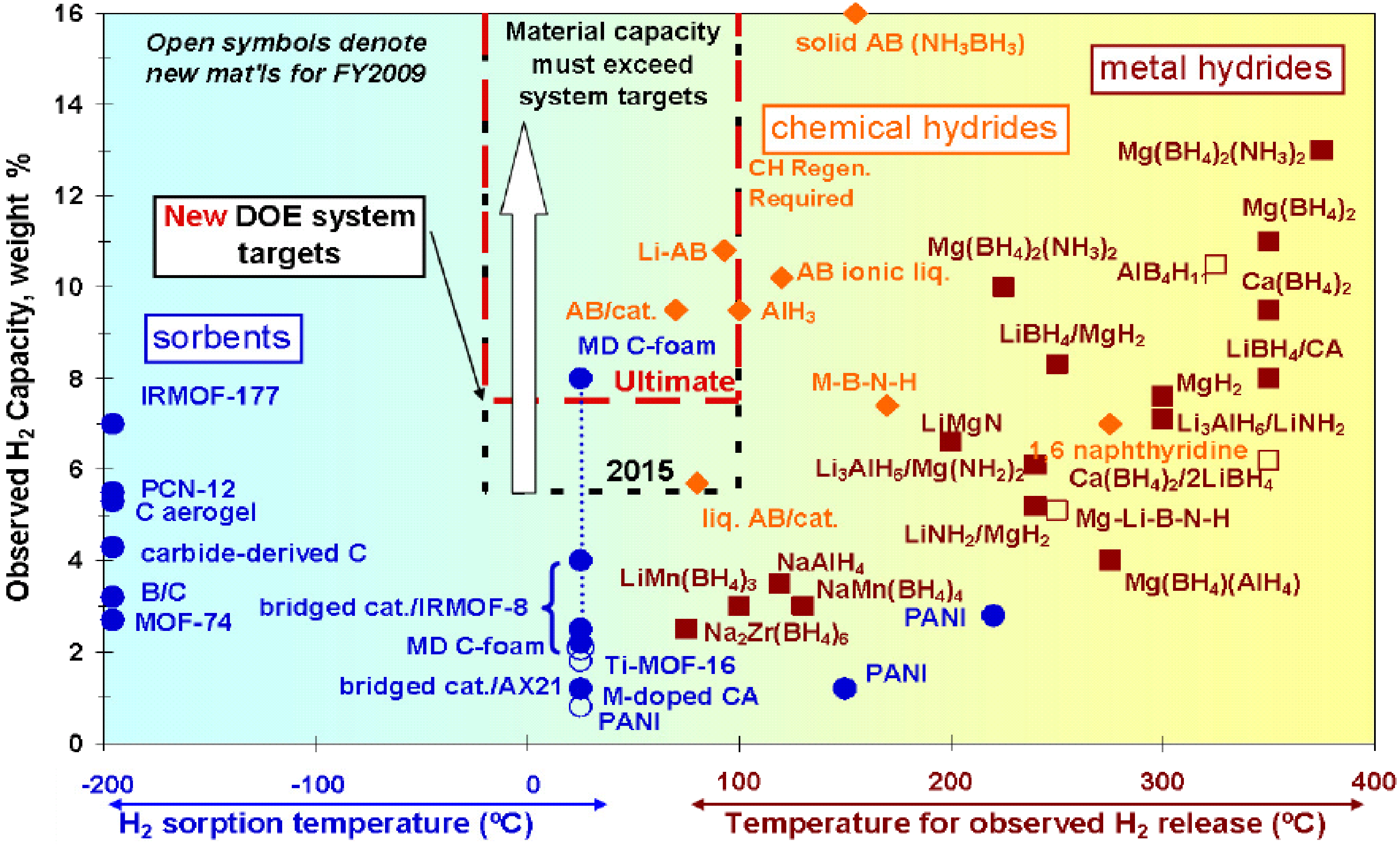
.... *NESSHY is a European endeavour aspiring to adopt a <u>holistic multidisciplinary approach,</u> aiming at advancing the current state of hydrogen storage in solid materials, with respect to ......*

- novel materials
- enhanced understanding of the physical mechanisms involved
- novel analytical characterisation tools and measurement techniques
- standardisation, testing protocols
- ab initio and phenomenological modelling using advanced numerical methods for optimal storage design
- upscaling the production processes of promising materials
- design and testing of storage tank systems

Overall approach



Materials state-of-the-art



DOE: G. Thomas (2007), G. Sandrock (2008), B. Bowman (2009)

NESSHY

Major Achievements

Porous Solids

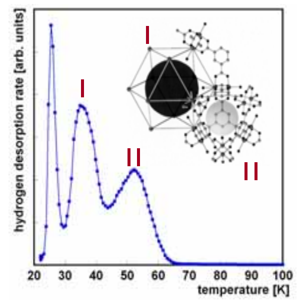
Framework materials

- Assessment of H_2 storage capacity on a range of MOF materials (from BASF)

  → 5 wt% H_2 (77 K, 60 bar)

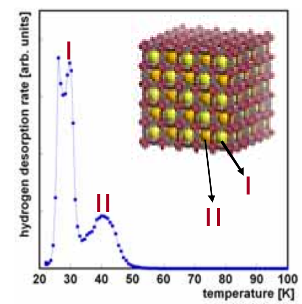
- Investigation of the effect of pore size/metal centers on H_2 sorption

Cu-BTC



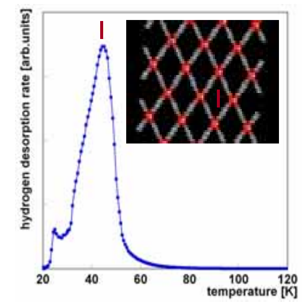
Picture from Krawiec et al. *Adv. Eng. Mater*. **8** (2006) 293

MOF-5

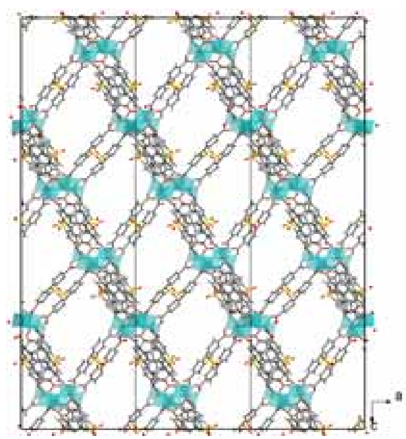


Picture kindly provided by J. Rowsell

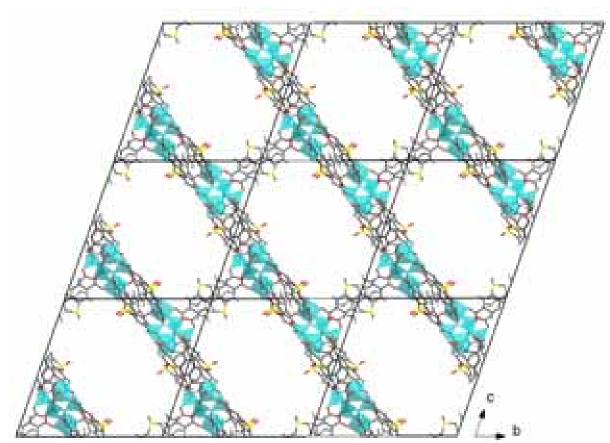
MIL-53



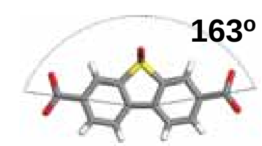
- New MOF structures (e.g. Zn-based Sulfone Functionalized MOFs)



UoC-1



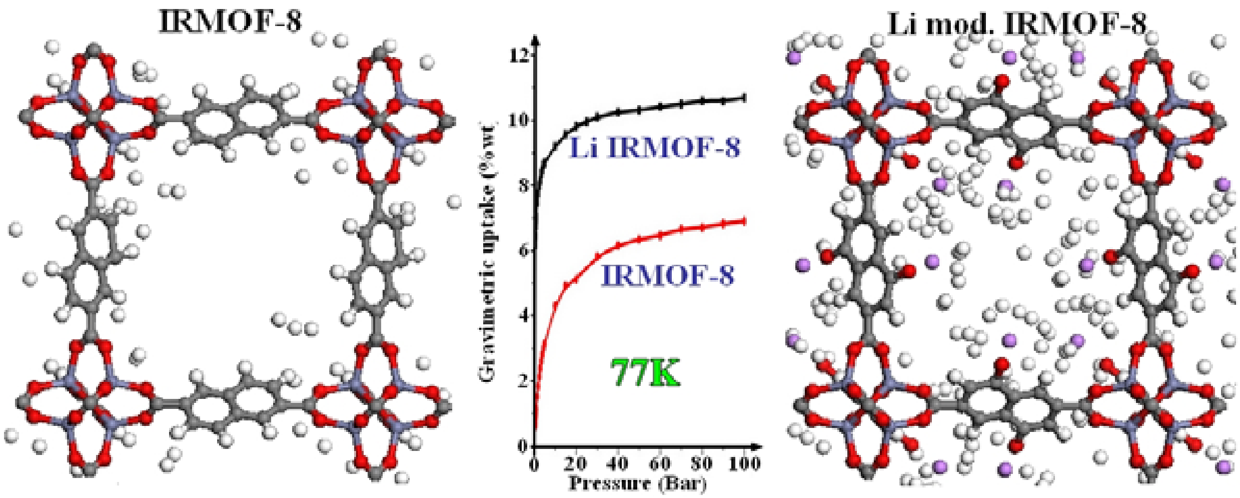
UoC-2



4,4'-bibenzoic acid-2,2'-sulfone (ligand)

Metal doping

Improvement of MOFs H_2 storage capacity by functionalizing the organic linker with Li



E. Klontzas, A. Mavrandonakis, E. Tylianakis, G. E. Froudakis, *Nano Letters,* 8 (2008) 1572

Improving the Hydrogen-Adsorption Properties of a Hydroxy-Modified MIL-53(Al) Structural Analogue by Lithium Doping**

Angewandte Chemie

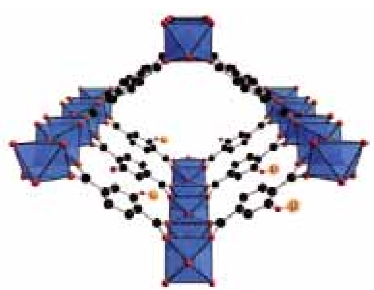
Communications

Angew. Chem. Int. Ed. 2009, *48*, 1–5

Metal–Organic Frameworks

D. Himsl, D. Wallacher, M. Hartmann* ———— ▮▮▮▮–▮▮▮▮

Improving the Hydrogen-Adsorption Properties of a Hydroxy-Modified MIL-53(Al) Structural Analogue by Lithium Doping

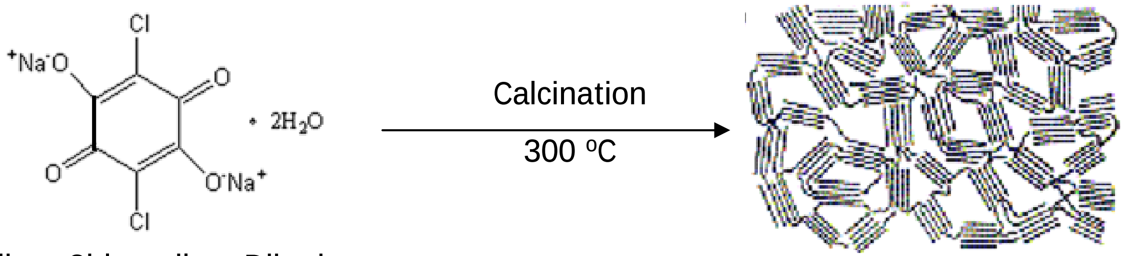


Lithium makes the difference: A simple strategy for the synthesis of lithium-doped porous metal-organic frameworks (MOFs) is developed (see structure C black, O red, AlO_6 blue octahedra) thus, paving the way for the facile preparation of lithium-doped MOFs. Moreover, the significant increase in hydrogen adsorption predicted by theoretical calculations is observed.

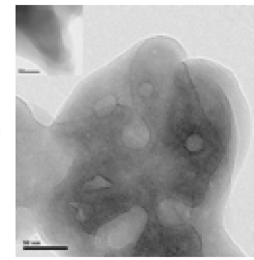
Nanoporous materials

Enhanced H_2 / porous solid interaction via metal doping

- Synthesis of novel carbogenic foam with high surface spin concentration



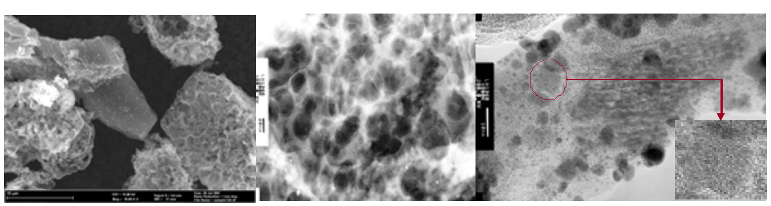
Sodium Chloranilate Dihydrate

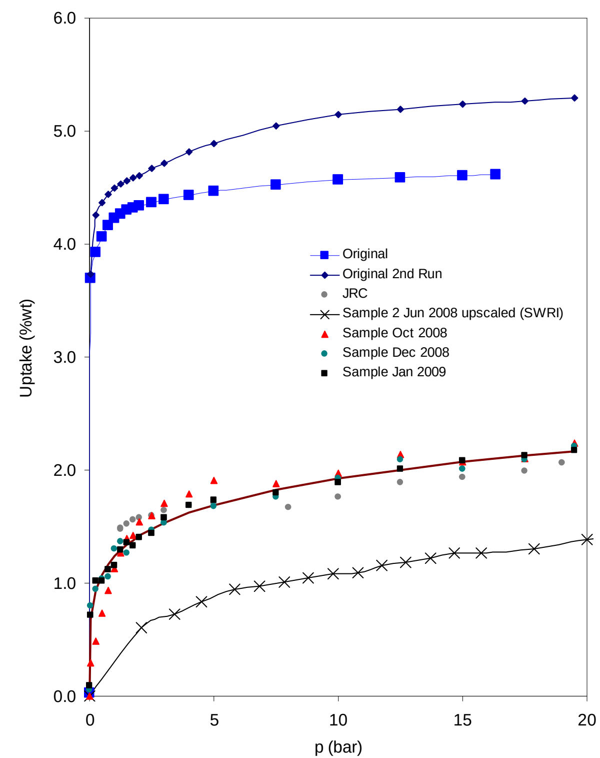


C_2OH

d~ 0.030 g cm^{-3}
500 m^2 g^{-1}
67 % porosity

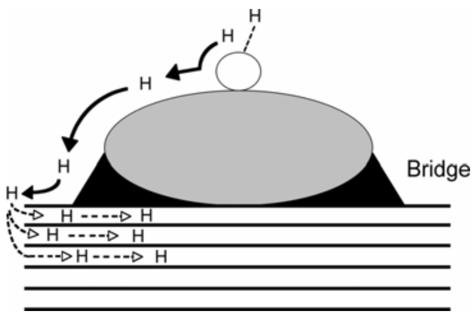
Synthesis of metal/carbon foam nanocomposites to exploit the "**spillover effect**" →
Pd: 2.1 wt% H_2 uptake at 300 K, 3 bar ; Mixed metals: 2.5 - 5 wt% at 300 K, 80 bar

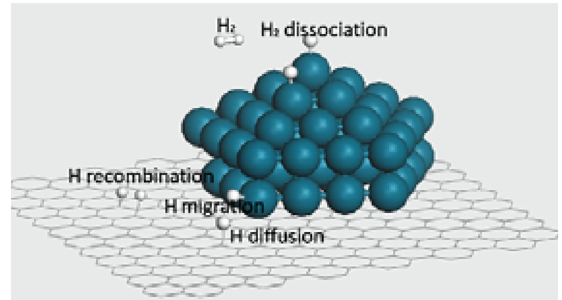




The spillover mechanism

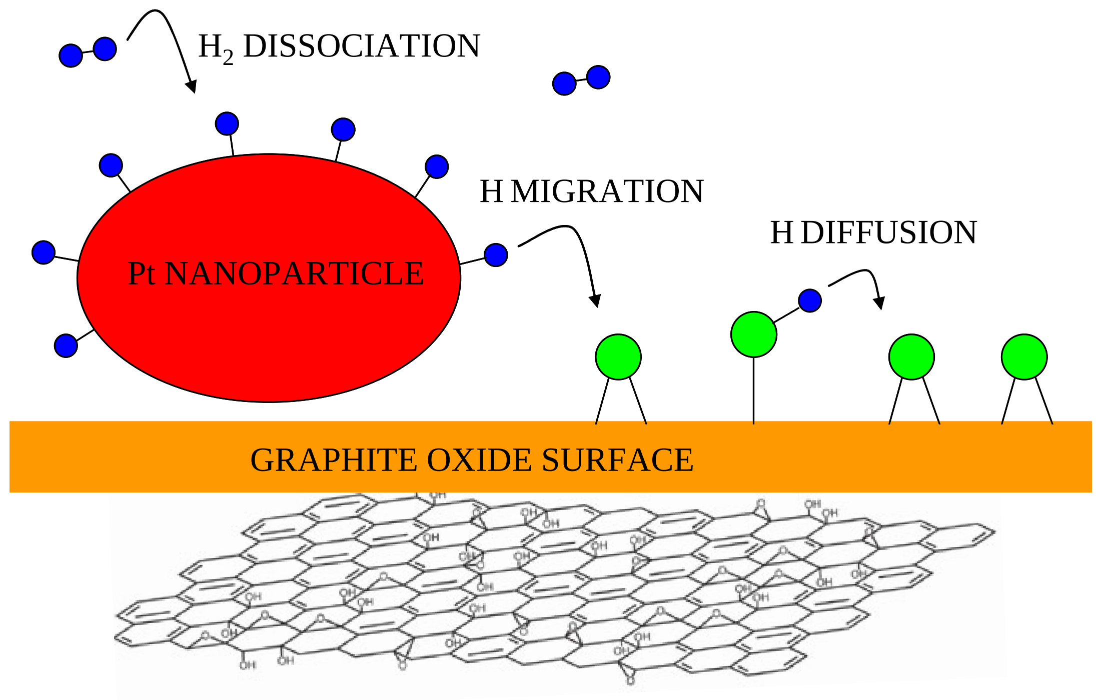
Theoretical evidence





"Spillover" is favourable in carbon materials with oxygen functional groups

- Barrierless dissociation of H_2 molecules on Pt (or Pd) cluster
- H – migration to graphite oxide: energy barrier = 9.2 kcal/mol (vs. 60 Kcal/mol in graphene)
- Diffusion of chemisorbed H requires ~ 7.6 kcal/mol (vs. 31 kcal/mol in graphene)
- H_2O formation also probable (energy barrier = 9.5 kcal/mol)

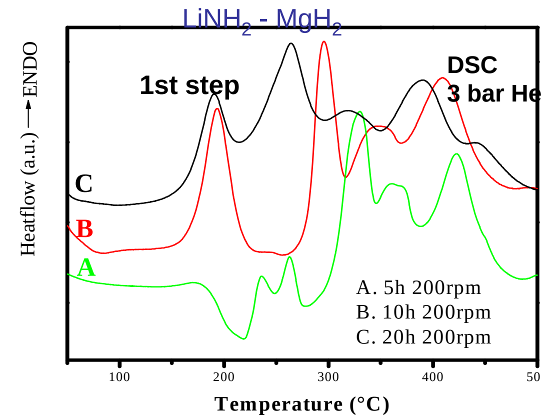


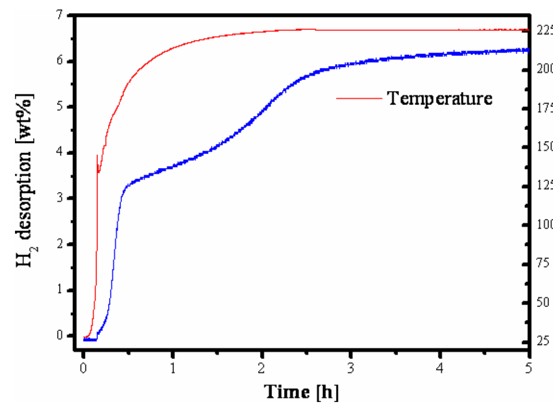
G. Psofogiannakis, G. Froudakis , *J. Phys. Chem. C*, 113 (33) (2009) 14908
G. Psofogiannakis, G. Froudakis, *J. Am. Chem. Soc.*, ASAP (2009)

Light/Complex Hydrides

Amides/imides systems

- Mg- and Li-amides and imides structure determination
- Produced Mg-Li-NH systems in Mg by ball milling : Li ratios 1:2, 3:8 and 1:1
- 3Mg – 8LiNH$_2$ system reversible at 200 ºC/100 bar H$_2$. For 1:1 system: need >300°C for desorption, practically reversible
- Improved understanding of the reaction mechanisms for 1:2 & 3:8 systems (FZK, IFE)
  - Reaction mechanism mediated by ammonia (FZK)
  - Intermediate phase for the 3:8 system: Li$_{2.6}$MgN$_2$D$_{1.4}$ (IFE)
- 1:1 system: 6-6.5wt% (225°C), possible candidate for small tank (FZK, collaboration with Univ. Utah)

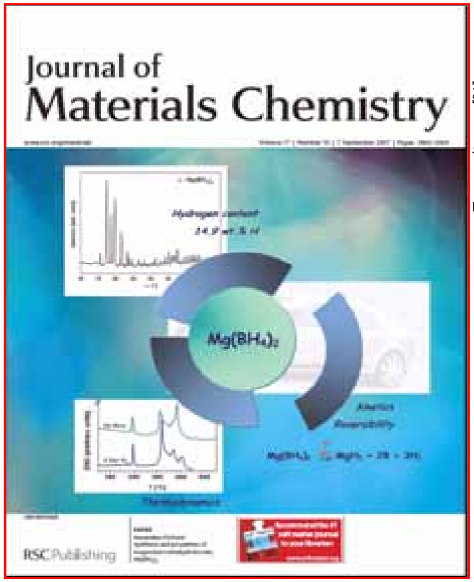


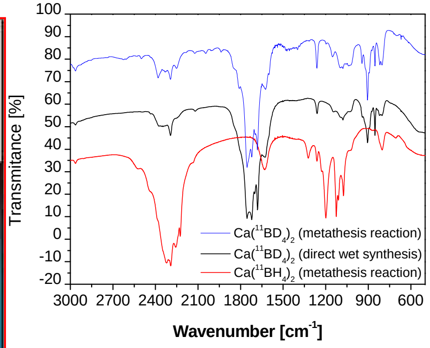


Light / Complex Hydrides

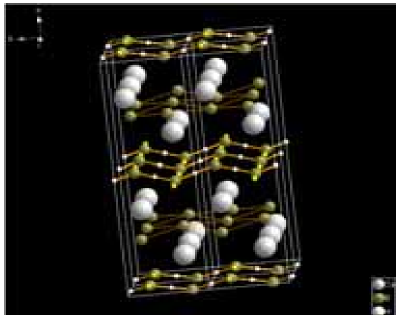
Borohydrides

- Synthesis of $Mg(BH_4)_2$, $Ca(BH_4)_2$, $LiBH_4$ by different methods – Structural & decomposition investigations (incl. determination of intermediate phases)





CaB_2H_2

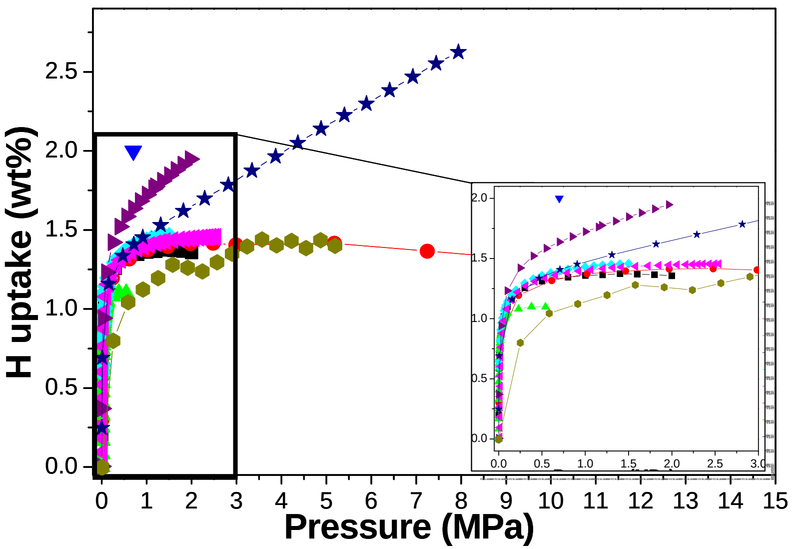


Mixed alanates

- Changed thermodynamics by substitution with fluorine in $NaAlH_4$ → launch of FP7 project FLYHY

Virtual Laboratory

- **Organisation of the first Round Robin Test in Europe:**
  - Physisorption @ 77K (commercial Carbon Molecular Sieve) – Completed
  - Complex hydride (already started) & Mg-based materials (starting soon)
  - In collaboration with SwRI/DoE and external (EU & non EU) organisations



- **Accuracy and source of errors** of hydrogen capacity measurements report*

*D.P. Broom, "The accuracy of hydrogen sorption measurements on potential storage materials", *International Journal of Hydrogen Energy*, **32** (2007) 4871– 4888)

An Integration paradigm

Solid hydrogen storage based on MgH_2 : from nano-structured powders to pilot tank development

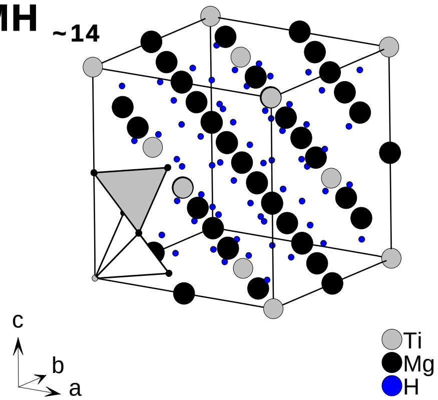
Mg Alloys and Intermetallics (film vs bulk)

$Mg_7TMH_{\sim 14}$

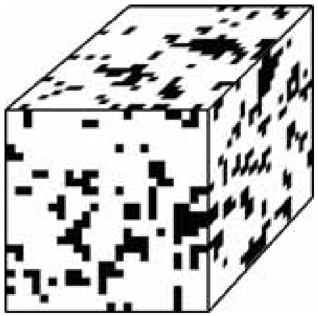
- Reversibility - understanding why both film and bulk hydrides can be cycled reversibly (stop the TM-H building blocks from dehydriding and dehydride the Mg-H part)

- DFT calculations indicate stable Mg_3TM tetrahedral sites in bulk hydrides. If they are not fully emptied, the FCC structure is maintained, and the hydrides are reversible. In film hydrides, dispersed TiH_2 clusters, with a size smaller than 20 nm, keep the structure from collapsing during cycling. Strong TM-H bonds form building blocks responsible for preventing the more open FCC structure from collapsing into more stable hydrides. Both systems show significantly more rapid diffusion than rutile MgH_2.

Bulk $Mg_7TMH_{\sim 14}$



Cluster size < 20 nm in film $Mg_7TMH_{\sim 14}$



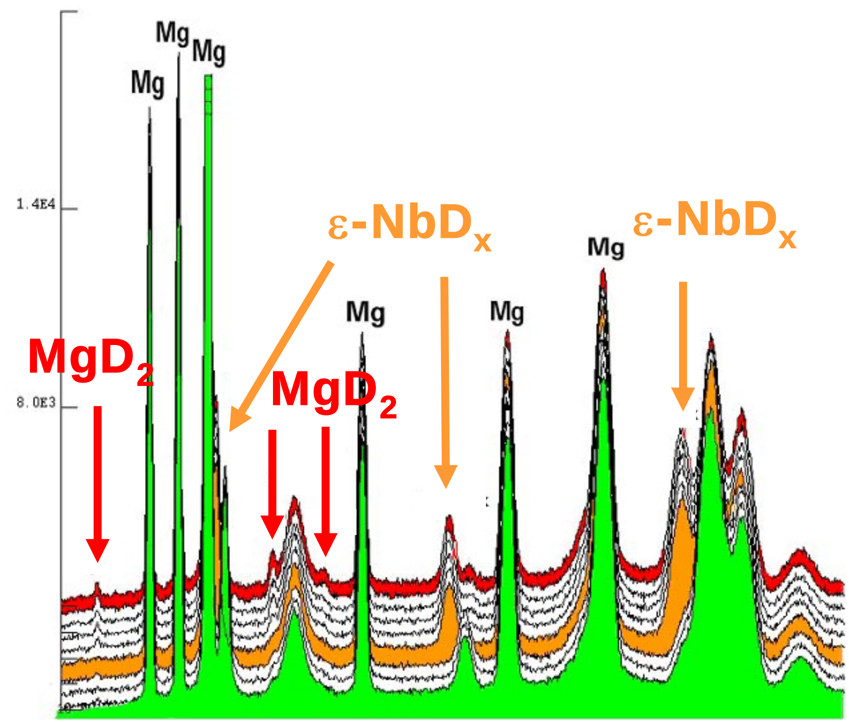
Ball-milling from MgH_2

- Optimization of the Ball-milling process
- Impact of transition element additions

In-situ neutron diffraction study (ILL - D20)

ε - $NbD_{0.75}$ rapid formation prior to the MgD_2 formation

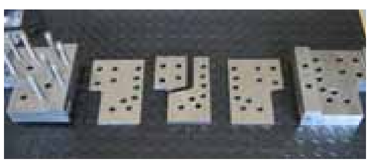
Initiating role of the transition metal Additives = "gates" that favour the hydrogen dissociation, then the hydrogen diffusion

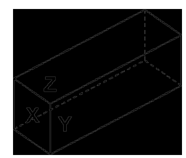


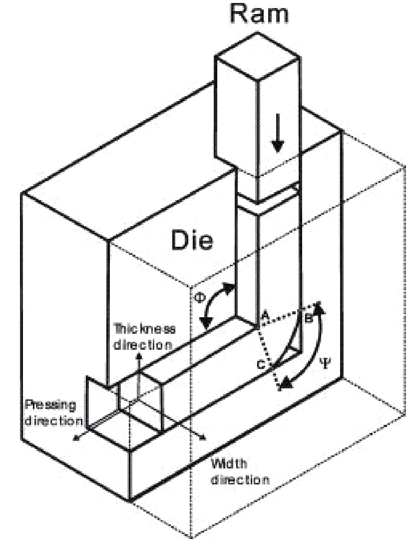
In-situ hydrogenation
(5 at.% Nb, T ~ 280 ° C, P = 20 bars)

Alternative route for Mg processing: ECAP

- Production of nanostructured Mg at lower cost
- Enhanced sorption kinetics

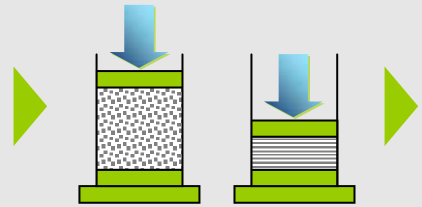






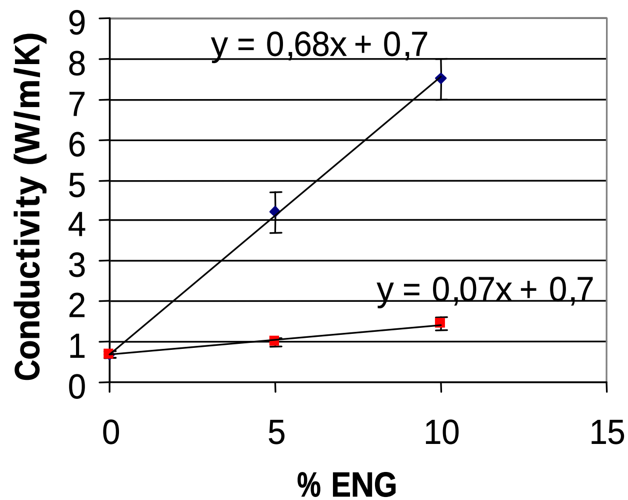
MgH_2 + ENG compacts

Compaction of MgH_2 + Expanded Natural Graphite



The benefits of composite material:

- **Solid and fully machinable**
- **High thermal conductivity**
  (x 30 vs. ball-milled powders)
- **Safe and inert in air**
- **Density of MgH_2 x3**

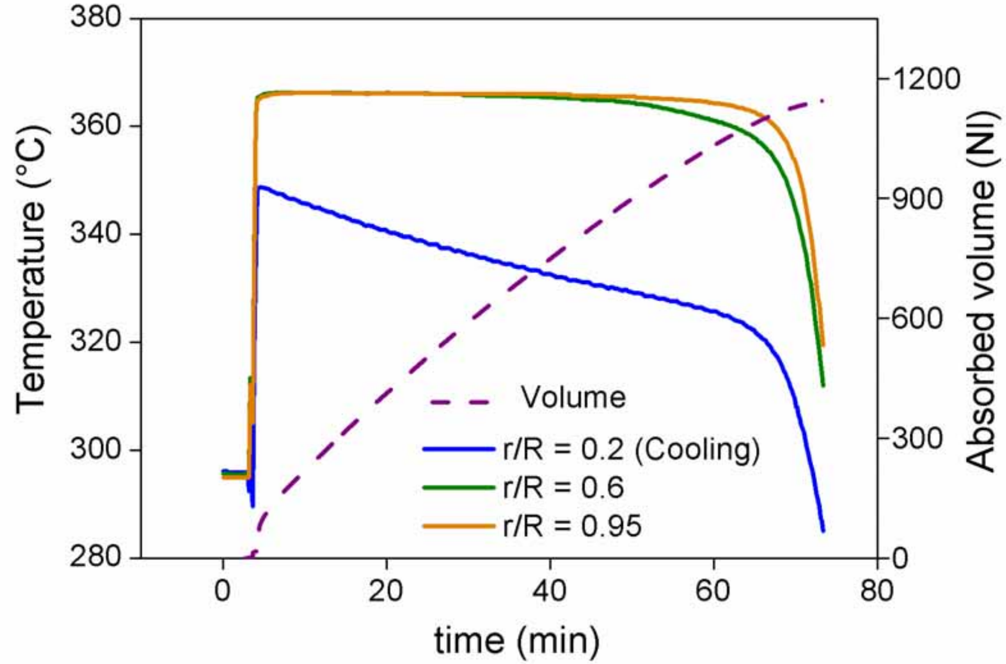


CNRS patents:
WO2009080986
WO2009080975

Intermediate scale tank (1.8 kg MgH_2)

1170 NL H_2 - 104.5 gr H_2 (6,07 wt %)

Absorption test (10 bar)



System capacities :
42 g/l - 0.85 wt %

Connection to a Fuel Cell*

2kW_e for 45 min

* designed by CEA – Grenoble

Auto-adaptive system :

No need to adapt hydrogen pressure or mass flow

Up-scaling of the production

McPhy energy

- Ball milling of MgH_2
- Specific additives (Ti-Cr-V), CNRS patent WO 2007125253
- Compaction with ENG
- Large scale tanks design & manufacture (10-20 kg MgH_2)

↓

Stationary applications

- Storage of sustainable energy forms
  - Balancing energy peaks

Low to medium temperature pilot scale tank

– design and build a complex hydride tank with improved characteristics with respect to the sodium alanate STORHY tank (0.865 wt %, 21 kg H_2/m^3)

Integration, Training, Dissemination

- **www.nesshy.net**
- **Interaction with other hydrogen related projects (IP-STORHY, PICS, COSY, HYDROGEN RTNs, SURMOF, MOFCAT, HYCONES, NANOHY, FLYHY) – Joint workshops**
- **Three training and dissemination events with wide multi-national participation have been supported up to now by NESSHY**
  - Hydrogen Summer School, University of Iceland - Reykjavik (June 2006, June 2008)
  - Magnesium Titanium Hydride workshop, Vrije Universiteit - Amsterdam (August 10, 2006)
- **NESSHY Newsletters**
- **Establishment of collaboration with Chinese and Russian organisations → SSA HYSIC** (also participation to Round Robin Test)
- **More than 340 publications/presentations in journals/conferences**
- **8 patent applications**

Enhancing Cooperation

Collaboration with other FP6 & FP7 projects

	Project	Coordinator	Topic
Energy Priority	**STORHY** www.storhy.net **2004-2008**	**Magna Steyr** ***Austria***	Next generation H_2 storage technologies (compressed gas, cryogenic liquid and solid materials*) with a focus on automotive applications * Na-alanate, mixed alanates, alane
	NANOHY www.nanohy.eu **2008-2011**	**Forschungszentrum Karlsruhe** ***Germany***	Nanocomposites consisting of hydride particle sizes in the lower nm range protected by a nanocarbon template or by self-assembled polymer layers in order to prevent agglomeration
	FLYHY www.flyhy.eu **2009-2011**	**GKSS Research Centre Geesthacht GmbH** ***Germany***	Materials destabilisation / stabilisation by halogen substitution for alane, borohydrides and reactive hydride composites , in order to achieve a breakthrough in the thermodynamic properties of these materials
NMP Priority	**HYCONES** www.hycones.eu **2006-2009**	**NCSR Demokritos** ***Greece***	Hydrogen storage in carbon cones
	SURMOF www.rhur-uni-bochum.de/pc1/SURMOF **2006-2009**	**Rhur University** ***Austria***	Anchoring of MOFs to surfaces
	MOFCAT www.sintef.no **2006-2011**	**SINTEF** ***Norway***	Functional MOFs as heterogeneous catalysts and adsorbents
Marie Curie Research Training Networks (RTN)	**COSY** www.cosy-net.eu **2006-2009**	**GKSS** ***Germany***	Fundamental understanding of the sorption kinetics in reactive hydride composites
	HYDROGEN www.theorchem.leidenuniv.nl **2006-2009**	**Leiden University** ***The Netherlands***	Hydrogen storage in alanates, borohydrides and a new class of materials to store it in form of ammonia

Workshop on

Solid Storage of Hydrogen - International Perspectives

co-organized by NESSHY, HYCONES, and NANOHY EC projects

Fodele Beach Hotel – Crete, Greece

10 - 11 June 2009

Wednesday, June 10

09:15-09:30	Welcome - Introduction	NESSHY, HYCONES, NANOHY Coordinators
09:30-10:00	Novel Efficient Solid Storage for Hydrogen – the NESSHY Project	Thanos Stubos NCSR "Demokritos"
10:00-10:30	Hydrogen Storage in Carbon Cones – the HYCONES Project	Theodore Steriotis NCSR "Demokritos"
10:30-11:00	Embedding Hydrides in Nanoscale Matrices – the NANOHY Project	Max Fichtner FZK
11:00-11:15	*Coffee break*	
11:15-11:45	Metal-Organic Frameworks for Hydrogen Storage	Jeffrey Long U. Berkeley
11:45-12:15	SW Carbon Nanohorns for Hydrogen Storage	David Geohegan ORNL
12:15-12:45	On Nanoscaffolding and Nanostructures Impact on Metal Hydride Materials Performance: On-going Efforts in USA	Ewa Rönnebro PNNL
12:45-14:00	*Lunch break*	
14:00-14:30	Developments on Nanostructured Materials / Carbons	Gavin Walker U. Nottingham
14:30-15:00	Novel Functionalized Metal-Organic Frameworks and High Surface Area Carbon-based Materials for Hydrogen Storage	Pantelis Trikalitis U. Crete
15:00-15:30	Complex Hydrides for Hydrogen Storage	Max Fichtner FZK
15:30-16:00	Borohydrides for Hydrogen Storage	Andreas Züttel EMPA
16:00-16:20	*Coffee break*	
16:20-16:50	Improving Hydrogen Storage Properties of Mg-based Hydrides by Limiting Metal Atom Diffusion	Dag Noreus U. Stockholm
16:50-17:20	Tanks for Complex Hydrides	Jose Bellosta von Colbe GKSS
17:20-17:40	JTI Prospects/Opportunities for Hydrogen Storage	Marcello Baricco U. Torino
17:40-18:00	Discussion – Closing of Day I	ALL
18:00 -19:00	Poster session	

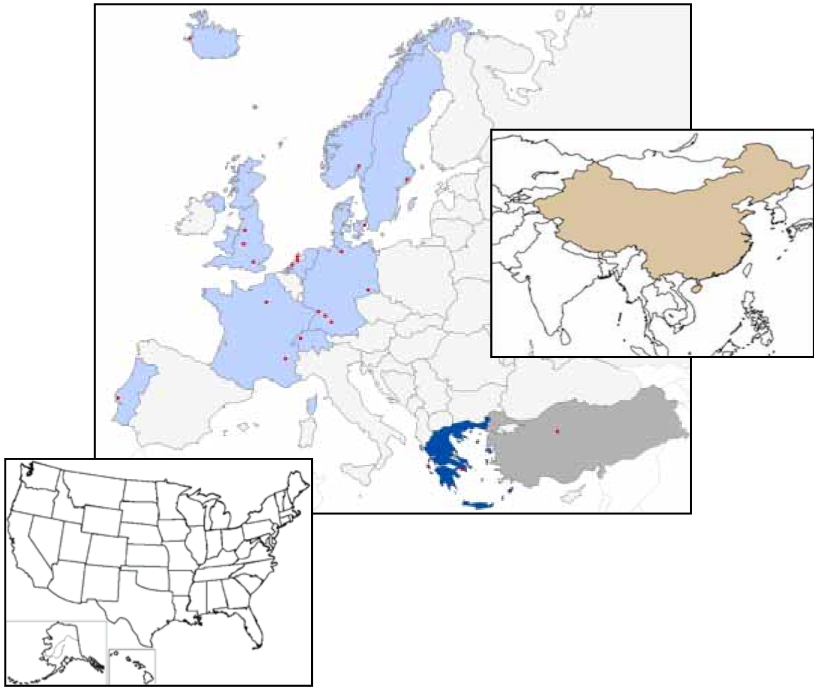
Thursday, June 11

09:30-10:00	From Optimised MgH_2 based Composites to Efficient Storage Tanks	Patricia de Rango CNRS
10:00-10:30	Design of Nanoporous Materials for Hydrogen Storage	George Froudakis U. Crete
10:30-11:00	Computer Modelling of Release Temperature in Hydrogen Storage Materials	Ian Morisson U. Salford
11:00-11:20	*Coffee break*	
11:20-11:50	Hydrogen Storage: Car Industry Perspective	Katsuhiko Hirose Toyota
11:50-12:10	IEA – HIA Task 22 Activities	Bjorn Hauback IFE
12:10-13:00	Discussion - Closing Remarks	ALL
13:00	End of Workshop	

Enhancing Cooperation

International Collaborations

- IPHE label (September 2006)
- Participation of SwRI, the American institute officially appointed by DoE for standardisation in H_2 solid storage measurements
- HySIC: <u>"Enhancing International Cooperation in running FP6 Hydrogen Solid Storage Activities"</u> Specific Support Action linked to NESSHy (2007-2008)
  - 8 partners from EU, Russian Federation, P. R. China
  - Key Objectives:
    - *Performance of studies enhancing international cooperation (sample preparation and characterisation, benchmarking, round-robin testing, testing protocol standardization)*
    - *Joint dissemination actions (workshops and integration activities)*



The HySIC SSA Experience

- Staff exchanges for training and R&D
- Sample synthesis and exchanges
- Participation to NESSHY Round Robin Tests
- Joint publications
- Joint experimental campaigns :

(USAL/Nankai: Neutron Scattering on Mg-nanowires)

- Joint HySIC-NESSHY dissemination actions in China

Workshop September 2008

- Wide participation of Chinese groups
- Visits to GRINM, LN-Power Sources Co.
- Opportunities for further collaboration

NESSHY
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