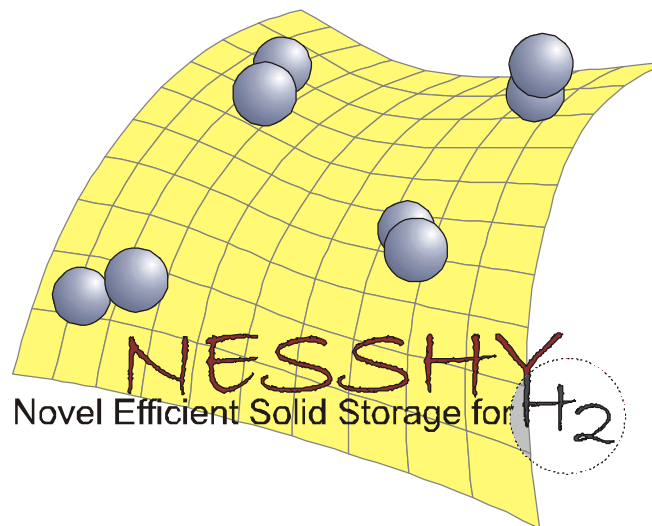


# Novel Efficient Solid Storage for Hydrogen:

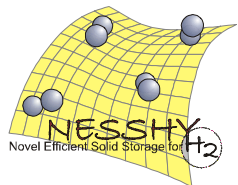
## An Overview of the NESSHY Integrated Project



**Thanos Stubos**

National Center for Scientific Research "Demokritos", Athens - Greece

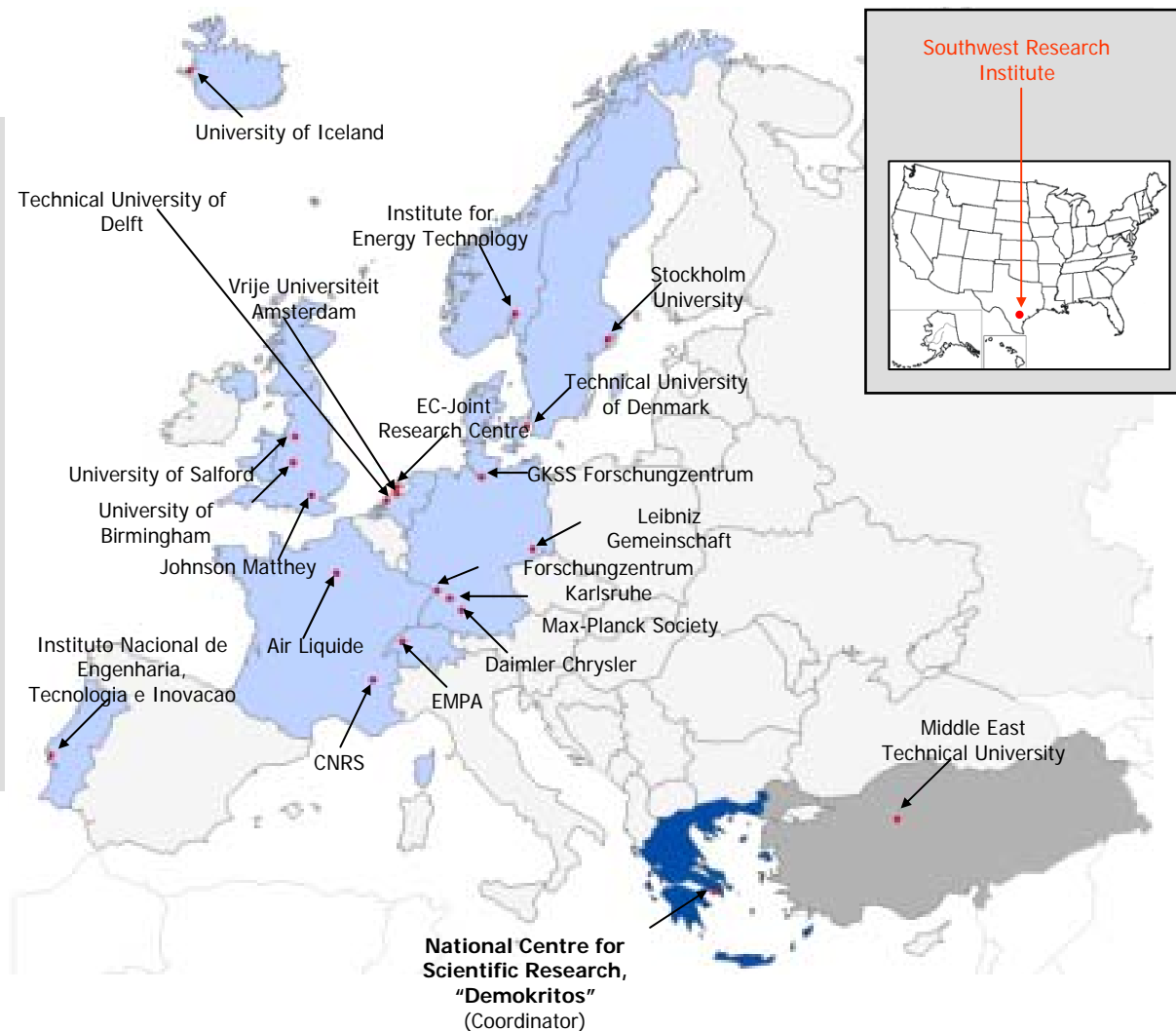
Fuel Cells & Hydrogen Joint Undertaking Stakeholders General Assembly  
9-10 November 2010  
Brussels

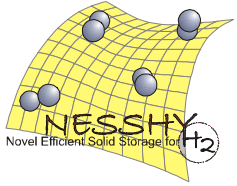


# NESSHY General facts



- 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)





## Challenges and motivation

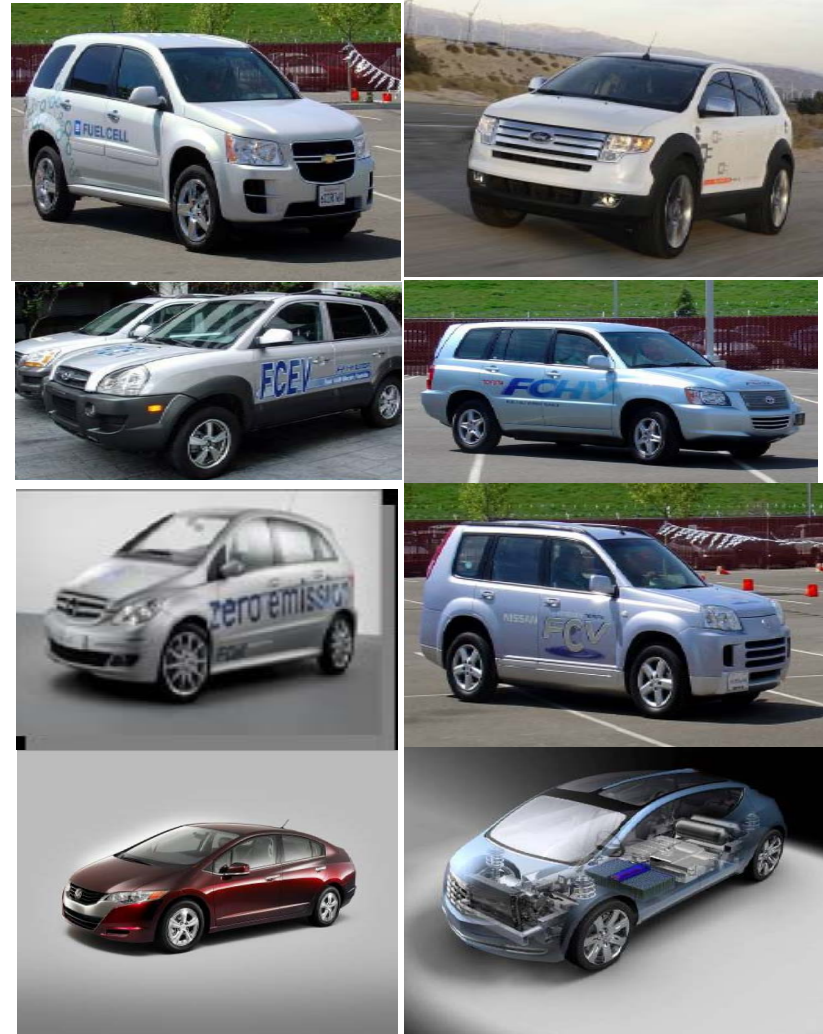


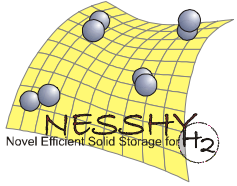
Vehicles are being designed by OEMs  
that can achieve > 300 miles

But performance, space on-board and  
cost are still challenges for mass market  
penetration...

Is there a low pressure alternative?

"Back to basics" approach



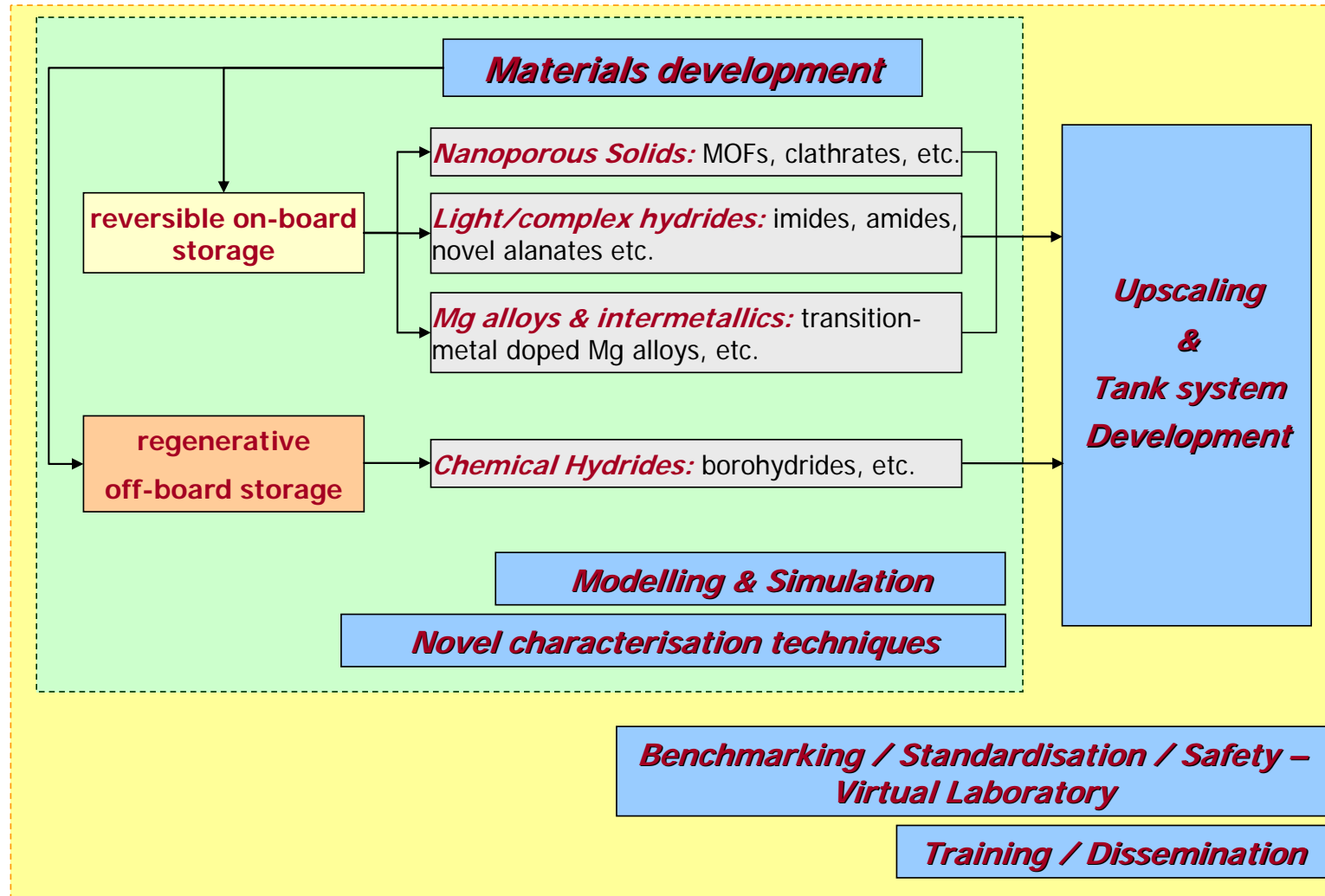


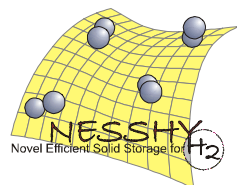
## NESSHY key objectives



Advancement of the current state of H<sub>2</sub> storage in solid materials, with respect to

- novel materials
- enhanced understanding of the physical mechanisms involved
- novel analytical and characterisation tools and measurement techniques
  - standardisation, testing protocols (virtual laboratory)
- advanced numerical methods for optimal material & storage design
  - upscaling the production processes of promising materials
  - design and testing of storage tank systems





# NESSHY targets

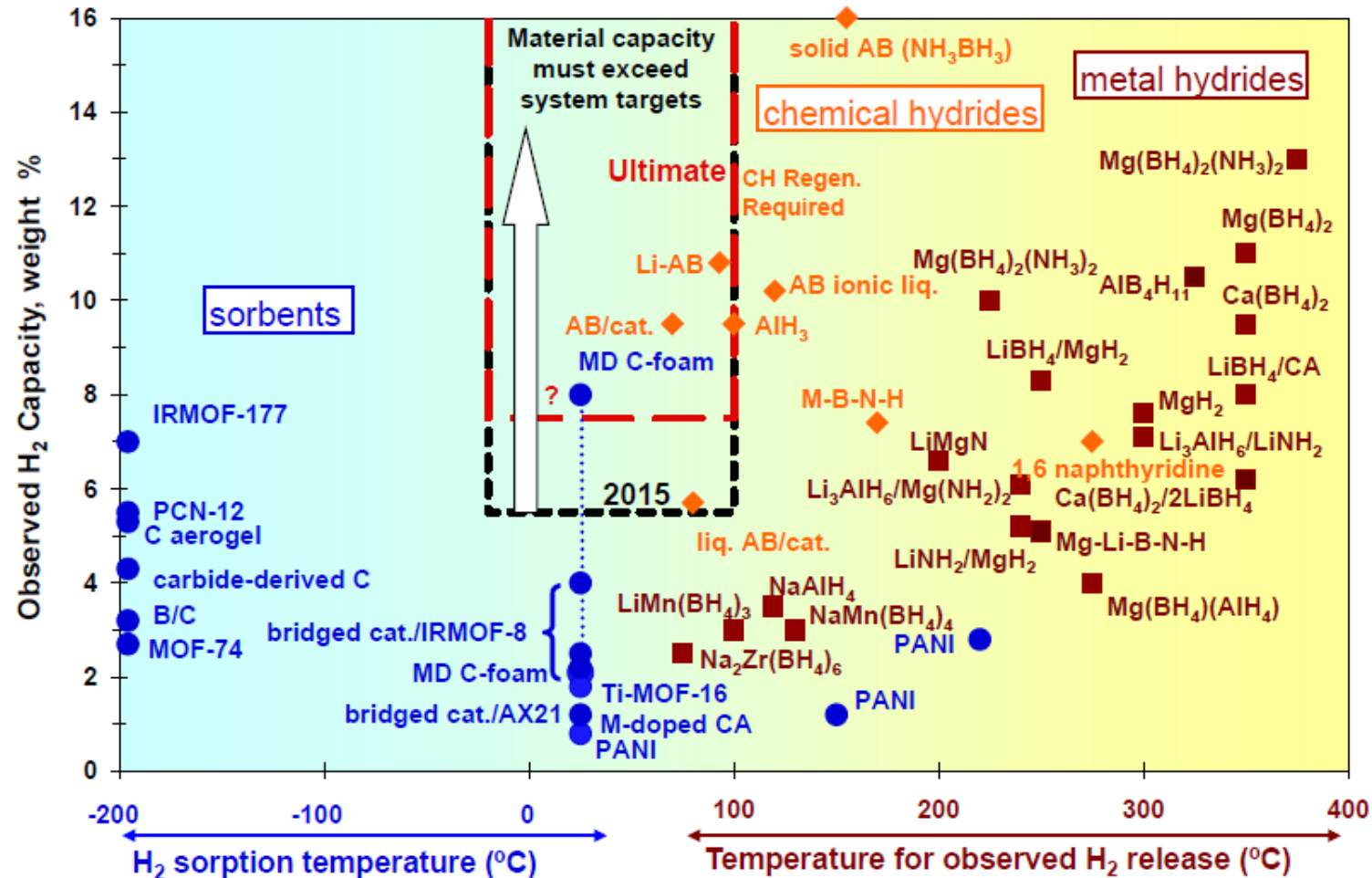
## Reversible adsorption storage



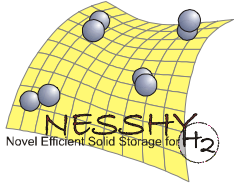
Parameter	Unit	NESSHY Reference (State of the art)		Intermediate target (mid-term)	Final target
		Automotive application	Material stand-alone		
Gravimetric Density (based on material weight)	wt%	1.8	WP1: < 4 (at 77 K) WP2-3: < 4 reversible	WP1: > 5 reversible WP2-3: 5 reversible	> 6 (WP1-3) reversible*
Volumetric density	(kg/m <sup>3</sup> )	24		50 (MgH <sub>2</sub> - WP3)	60 (MgH <sub>2</sub> - WP3)*
Refuelling rate * (for 5 kg H <sub>2</sub> tank)	kg H <sub>2</sub> / min	0.3		approx. 0.5	approx. 1 0.1 (stationary application)
Temperature of operation	°C	RT	RT – 350 depending on material type (-196 – RT for WP1)		< 90 (standard PEMFC) <180 (high temp PEMFC) <350 (ICE) <350 (stationary SOFC)
Thermal conductivity	W/mK		~0.5	> 4 for (MgH <sub>2</sub> – WP3)	> 10 (MgH <sub>2</sub> – WP3)**
H <sub>2</sub> -Pressure supplied by tank in desorption (using waste heat from FC)	bar	approx. 5		> 2 (WP1-3)	> 6 (WP1-3)
Heat management* (for 5 kg H <sub>2</sub> tank)	KW	<60 (for a 4 kg tank)		> 90 (automotive on-board)	>200 (automotive on-board) > 65 (stationary application of MgH <sub>2</sub> )
Enthalpy	kJ/mol H <sub>2</sub>	28		30-40 (for WP1: ca. 20)	30-40 (for WP1: ca. 20) 74 (MgH <sub>2</sub> – WP3)
Production costs of solid storage material (incl. catalysts)	€/kg	-	23 (for standard MHs)	< 750	< 100 << 100 (MgH <sub>2</sub> – WP3)
Amount of material produced	kg	-		Batches of 0.05-0.5 kg	Batches of 5 kg or more (or continuous production)
Tanks (lab-scale)		-	WP2: lab-scale (<1 kg) tank for Na-alanate under development (DoE project, EC-STORHY FP6) WP3: lab-scale tank for Mg alloys (EC-HYSTORY FP5 project)	Design/construction of 1-2 lab-scale tanks (approx 0.5 kg of material 2kg for MgH <sub>2</sub> )	WP8: in total 2-3 lab-scale tanks (0.5 kg of material; 2kg for MgH <sub>2</sub> )
Tanks (systems) (pilot-scale)		-		Design/study of heat manag. system for at least 1 pilot tank (approx 5 kg of material; 10kg for MgH <sub>2</sub> )	WP8: in total 1-2 pilot- tanks or systems (5 kg or more material; 10kg for MgH <sub>2</sub> )

# Materials state-of-the-art

## Status at 2009 AMR Review



N.T. Stetson, "Hydrogen Storage", 2010 DoE Annual Merit Review and Peer Evaluation Meeting, 8 June 2010, Washington - USA



## What we achieved



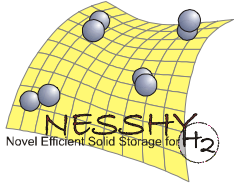
No material /system found satisfying **simultaneously** all targets



**BUT** .....







## What we achieved - **Materials**



- ✓ Developed /characterised/tested several new materials/synthesis methods and reached conclusions about their applicability as storage media
- ✓ Critical understanding on many topics that lay the foundation for developing an optimal solid-state H<sub>2</sub> storage material
  - *mechanisms*
  - *roles of additives*
  - *through advanced techniques/modelling*
- ✓ Screening - Downselection

# Nanoporous solids /Framework materials

- **Cryogenic temperatures (77 K)**

- up to 100 bar

- MOF materials

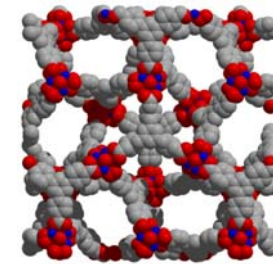
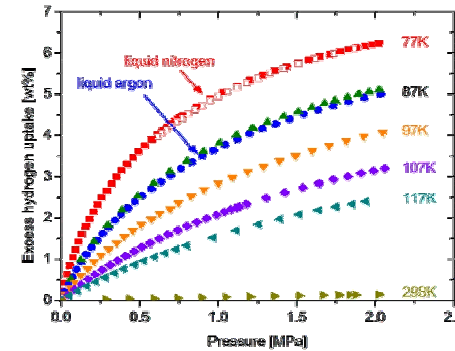
- High surface area carbons

- **Ambient temperature**

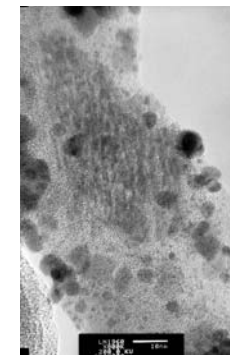
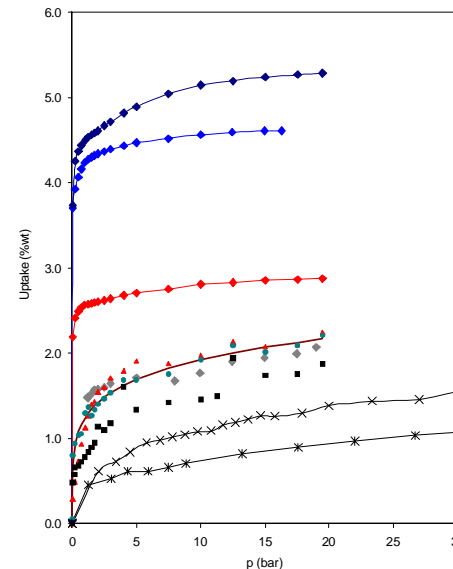
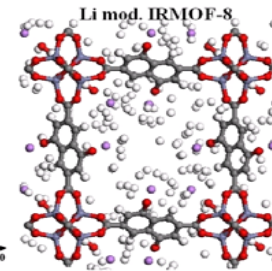
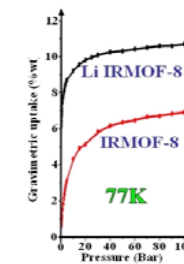
- Optimal enthalpies are required

- Increased H<sub>2</sub>/solid interactions (e.g. by metal doping)

- Weak chemisorption → H<sub>2</sub> dissociation on metal (e.g. Pd, Pt, Ni) nanocatalysts  
→ atomic H diffusion & storage



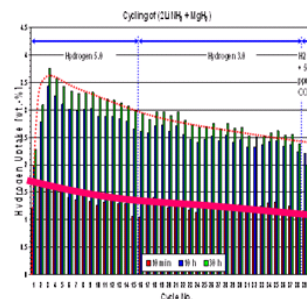
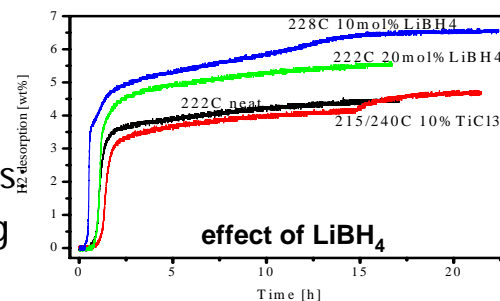
MOF-177



Pd-alloy/carbon foam nanocomposite

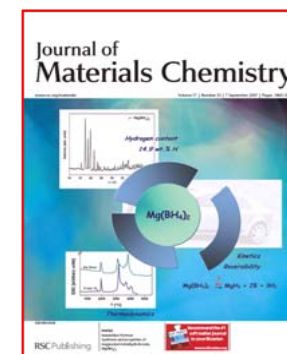
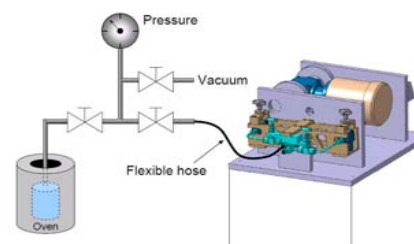
## • Composites

- Mixed alanes: Changed thermodynamics by substitution with fluorine in  $\text{NaAlH}_4$
- Imides/Amides: Li:Mg systems with  $\text{LiBH}_4/\text{KH}$  additives up to 6.5 wt%  $\text{H}_2$  at 180 °C - improved kinetics/cycling



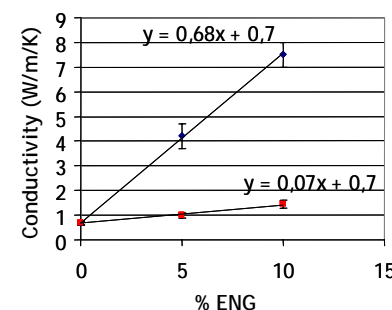
## • Borohydrides

- controlled synthesis of  $\text{LiBH}_4$ ,  $\text{Ca}(\text{BH}_4)_2$  and  $\text{Mg}(\text{BH}_4)_2$  by different methods
- characterisation (structure, decomposition routes)
  - reversibility



## • Mg based compounds

- enhanced understanding of mechanisms
- improved material (thermal conductivity, volumetric capacity)



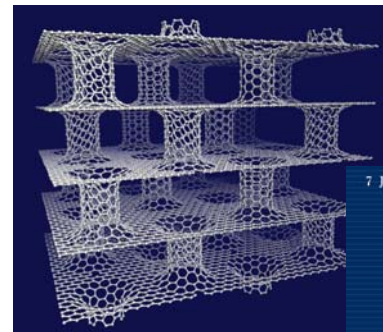
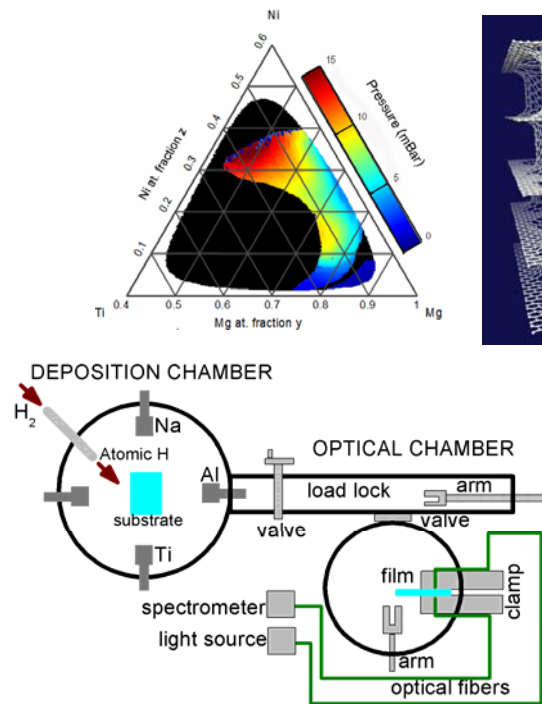
- **New FP7 projects** based on NESSHY results:  
**NANOHY, FLYHY**



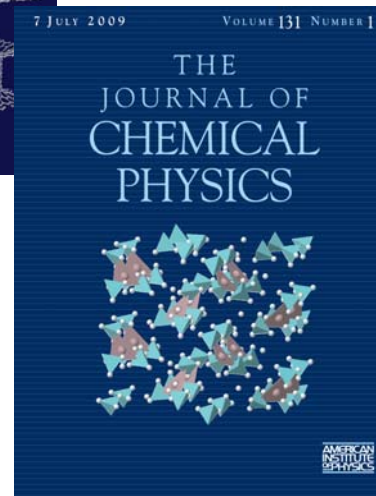
# What we achieved – Advanced methods

- ✓ Developed and exploited unique measurement capabilities and techniques to characterise storage properties (hydrogenography, neutron scattering, high pressure synthesis, TPD)
- ✓ new material design capabilities through interaction with theory / modelling
- ✓ Standardisation / best practices in measurement protocols (first European RRT's)

## Hydrogenography

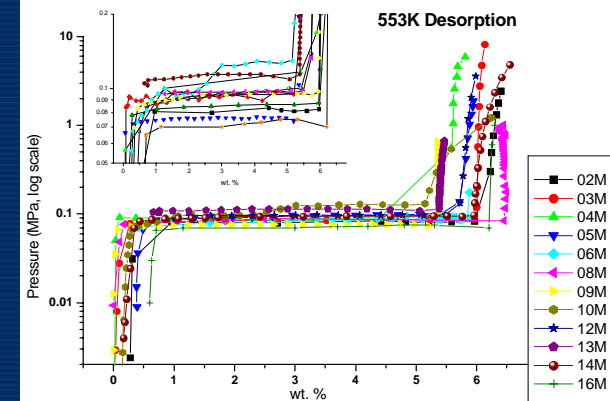


Pillared graphene



Ternary alkali-transition metal borohydrides

## MgH<sub>2</sub> RRT

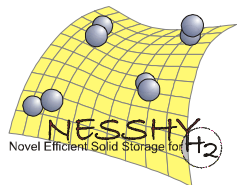


## What we achieved – Storage systems

- ✓ Tanks (lab and pilot scale) - Optimised Mg based compound / Na-alanate
  - *improved characteristics at material and system level*
  - *heat transfer / compactness / kinetics / vol. capacities*



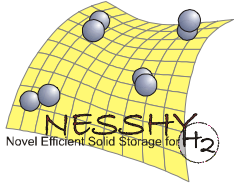




## Outcome



Material/system	Gravimetric Density (wt. %)	Volumetric Density (g/L)	Temperature range	Pressure (bar)	Kinetics	Other
MOFs/High surface area sorbents	6-7 %	25	77 K	up to 100 bar	fast	-
Doped carbons	2-5 %	-	298 K	up to 80 bar	slow	-
2Li:Mg/LiBH <sub>4</sub>	6.3 %	50 - 90	473 K	60 bar	~1 h	cycling
2Li:Mg/KH	3.5 %	50 - 90	453 K	60 bar	10 min	cycling
Mg(BH <sub>4</sub> ) <sub>2</sub>	11 % (theor.)	147	623 K	up to 20 bar	-	reversibility at high P
Pilot tank – MgH <sub>2</sub> based	2.0 % (system)	42 (system)	523-573 K	up to 50 bar	20 min	cycling
Pilot tank – NaAlH <sub>4</sub> based	2.0 % (system)	32 (system)	433 K	50 bar	10 min	cycling



## Outreach / Collaborations



- [www.nesshy.net](http://www.nesshy.net)
- Interaction with other hydrogen related projects (IP-STORHY, PICS, COSY, HYDROGEN RTNs, HYSIC, HYCONES, NANOHY, FLYHY) – **Joint workshops**
  - Joint NESSHY-HYSIC workshop, Beijing – China, 15-16 September 2008
  - SSH-IP (Solid Storage of Hydrogen – International Perspectives) workshop, co-organized by NESSHY, HYCONES and NANOHY projects, Crete - Greece, 10-11 June 2009
  - Joint European workshop on Hydrogen Storage Technologies, co-organized by NESSHY, NANOHY and FLYHY projects, Manchester – UK, 13 January 2010
  - NESSHY- COSY Joint International Workshop, Solid State Hydrogen Storage: Status, Perspectives and Industrial Application, 5 – 6 October, 2010 - Torino, Italy
- Links with- and feedback from- industry
- Continuous representation in international events, incl. all DoE Hydrogen Program Annual Review Meetings 2006-2009

INTERNATIONAL WORKSHOP

---

**Solid State Hydrogen Storage  
Status, Perspectives  
and Industrial Application**

→ October, 5.<sup>th</sup> + 6.<sup>th</sup> 2010 //  
Environment Park // Torino // Italy

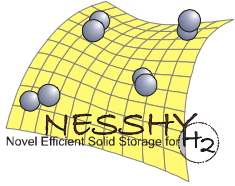
Joint Final Event of the European Integrated Project  
NESSHY - Novel Efficient Solid Storage for Hydrogen  
and the Marie Curie Research Training Network  
COSY - Complex Solid State Reactions for Energy  
Efficient Hydrogen Storage

→ No registration fee  
is required



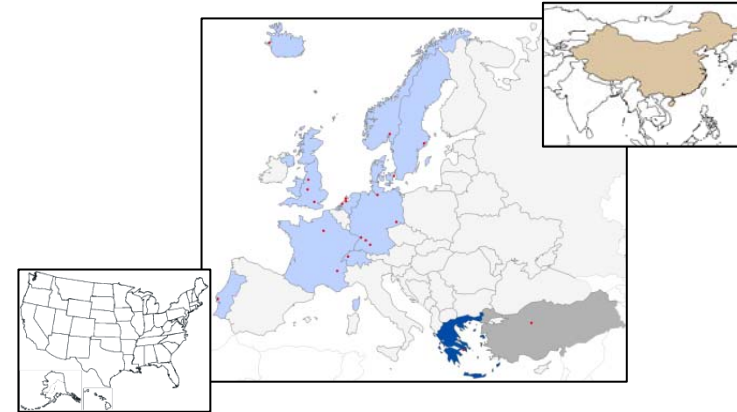
  



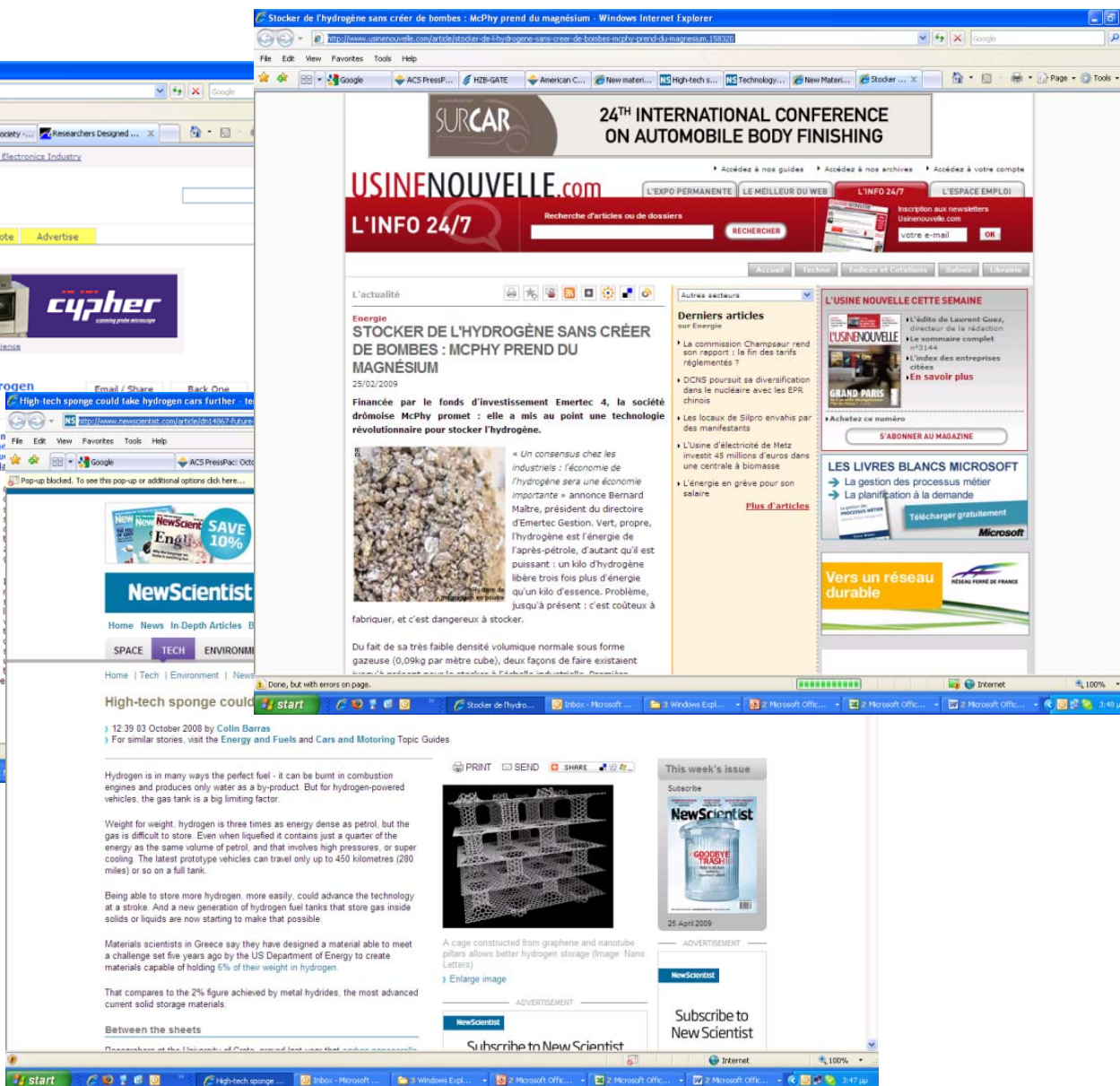
# IPHE activities / International Collaborations

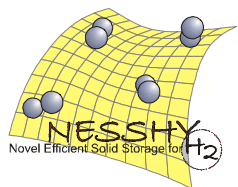


- **IPHE** label (September 2006)
- Participation of **SwRI**, the American institute officially appointed by DoE for standardisation in H<sub>2</sub> solid storage measurements
- **HySIC**: "Enhancing International Cooperation in running FP6 Hydrogen Solid Storage Activities" Specific Support Action linked to NESSHY (2007-2008)
  - 8 partners from EU, Russian Federation, P. R. China
  - Key Objectives:
    - Staff exchanges for training and R&D
    - Sample synthesis and exchanges
    - Participation to NESSHY Round Robin Tests
    - Joint dissemination campaigns









# Dissemination / Training



- Training and dissemination events (Summer Schools) with wide multi-national participation have been supported up to now by NESSHY
  - Hydrogen Summer School, University of Iceland - Reykjavik (2006, 2008)
  - One day Magnesium Titanium Hydride workshop, Vrije Universiteit - Amsterdam (August 2006)

- NESSHY Newsletters
- More than 470 publications/presentations
- 9 patent applications

**Journal of Materials Chemistry**

**NEWSLETTER**

**HYNOR - THE HYDROGEN ROAD OF NORWAY**

A new hydrogen filling station on the Norwegian hydrogen road will open at Ørland near Porsgrunn in the spring of 2007, representing another milestone in the national hydrogen strategy. The goal of the project is to establish a hydrogen road between Stavanger and Oslo so that, in 2008, it will be possible to drive hydrogen-powered vehicles along the entire length of this route. Further hydrogen filling stations will therefore be built. There are now 40 partners involved in the project, a partnership connecting major industrial and energy companies, transport companies, regional and national public authorities as well as R&D institutes.

The "Scandinavian Hydrogen Highway" project, of which Hynor is part, together with H2Linc of Denmark and H2Future of Sweden, will create a hydrogen infrastructure within 2012. Scandinavia will then be connected to the European hydrogen highway and it will be possible to drive a passenger car, hydrogen-powered car from Stavanger to Utsjok. Hynor is a unique Norwegian joint industry with the initiative to demonstrate real implementation of hydrogen energy infrastructure along a route of 500 kilometers from Oslo to Stavanger. The project comprises all steps required to develop a hydrogen infrastructure and includes various hydrogen production technologies and uses of hydrogen, in all cases with an adaptation to local conditions.

**AN ITALIAN HYDROGEN VEHICLE FOR THE OLYMPIC GAMES OF BEIJING 2008**

Presented during Hynor 19-21 April 2007, the International Exhibition of Water Technologies, held in Palermo (Sicily), the hydrogen vehicle built by the Italian Group of Motorcycles (IGM), will run inside the 21 Olympic arena during the games of Beijing 2008. This four wheels vehicle has a charge capacity of 300 kg, with a reservoir containing up to 30 bars of hydrogen and a maximum speed of 40 km/h for a total autonomy of 300 km.

**CONTENTS**

**IMPORTANT DATES**

CONFERENCES: SUMMER SCHOOLS, EVENTS, EXHIBITIONS

CONFERENCE REPORTS

SCIENCE NEWS (PUBLICATIONS FROM THIRD PARTIES)

PUBLICATIONS

NESSHY NEWS MEETINGS

NESSHY MAIN ACHIEVEMENTS

EU NEWS

PARTNERS (PRESENTATION OF ONE PARTNER)

NESSHY PAST MEETING INFORMATION

EDITORIAL

MESSAGE FROM THE COORDINATOR

INDUSTRY

**IMPORTANT NESSHY DATES**

12 - 14, Dec 2007, NESSHY 2<sup>nd</sup> annual meeting in Istanbul (METI), Turkey.

**CONFERENCES**

MI 2008 Symposium on Hydrogen-metal systems, June 24 - 28, 2008, University of Iceland, Reykjavik, Iceland. <http://www.mi2008.is>

Scandinavian Hydrogen Highway symposium, June 19 - 23, 2008, University of Iceland, Reykjavik, Iceland

WHC 2008 17th World Hydrogen Energy Conference, 15-19 June 2008, Brisbane Convention and Exhibition Centre, Queensland, Australia. <http://www.whc2008.com/>

IC Expo 2008, 27 - 29, 2, 2008, Tokyo, Japan. <http://www.icexpo.jp/>

**Journal of Chemistry**

**Communications**

**Hydrogen Storage**

B. Panella,\* K. Höres, U. Müller, N. Trühan, M. Schubert, H. Pütter, M. Hirscher

Desorption Studies of Hydrogen in Metal-Organic Frameworks

The diameter is decisive: Adsorption sites for hydrogen in the metal-organic frameworks Cu-BTC, MIL-53, MOF-5, and IRMOF-8 could be identified by using thermal desorption spectroscopy at very low temperatures (see graph). The correlation between the desorption spectra and the pore structure of these MOFs shows that at high hydrogen concentrations the diameter of the cavity determines the heat of adsorption.

**ELSEVIER**

**A Round Robin characterisation of the hydrogen sorption properties of a carbon based material**

Claudia Zlotica\*, Pietro Moretto\*, Theodore Steriotis\*

\*Institute for Energy Joint Research Centre, European Commission, P.O. Box 2, ND-1755 Petten, The Netherlands

\*National Centre for Scientific Research "Demokritos", Institute of Physical Chemistry, 15310 Agia Paraskevi Attika, Athens, Greece

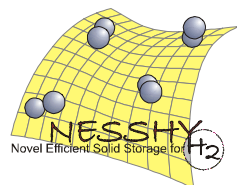
**Solid-state synthesis of LiBD<sub>4</sub> observed by *in situ* neutron diffraction**

A. Remhof,<sup>a,d</sup> O. Friedrichs,<sup>a</sup> F. Buchter,<sup>a</sup> Ph. Maun,<sup>a</sup> A. Züttel<sup>a</sup> and D. Wallacher<sup>b</sup>

Received 20th May 2008, Accepted 25th June 2008

First published as an Advance Article on the web 11th August 2008

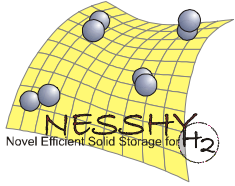
DOI: 10.1039/b808549h



## Exploitable results



WP	Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Time table for commercial use	Patents or other IPR protection	Owner & Other Partner(s) involved
1	Carbon material for hydrogen storage	Carbonaceous material with remarkable H <sub>2</sub> storage capacity	Chemical Industry	Premature to define	US Application No. 12/272,488 (filed on November 17, 2008)	NCSR, SwRI
2	Adjusting the stability of complex metal hydrides	Alanes with changed stability	Research Institute	Premature to define	Norwegian patent application NO2006 0430, international patent application PCT/NO07/00025	IFE
2	Wasserstoff speichernde Kompositmaterialien	Composite hydrogen storage materials	Research Institute	Premature to define	German patent DE 10 2007 054 843.7	GKSS
3	Activated nanocrystalline Mg-hydride with very fast kinetics	Composite Nanocrystallin pour le stockage de l'Hydrogène	Chemical industry	2011	WO2007125253 "Nanocrystalline composite for storage of hydrogen"	CNRS Licensed McPhy Energy
3	Mg-based composite materials	Mg-based composite materials	Chemical industry	2011	WO2009080986 "Matériau de stockage d'hydrogène à base d'hydru de magnesium"	CNRS Licensed McPhy Energy
3	Hydrogen storage tank for MgH <sub>2</sub> based composites	Hydrogen storage tank	Energy production & storage industry	2011	WO2009080975 "Hydrogen Storage Tank"	CNRS Licensed McPhy Energy
4	New scheme for NaBH <sub>4</sub> synthesis	No exploitation foreseen because of the failure in cost reduction	Chemical industry	N/A	Invention disclosures	Air Liquide, Aviator
4	New catalyst chamber	High yield hydrogen production	Chemical industry	2009	A materials patent is planned	INETI
7	Repository, archive and comparison tools for experimental and literature data on performance of materials for hydrogen solid-state storage	NESSHY_DB, a database for experimental and literature data on performance of materials for hydrogen solid-state storage	Research Institute	No commercial use, open for consultation and use end 2009	The database structure, relationship and source code belongs to JRC, the data contained to the individual user	JRC & all potential customers

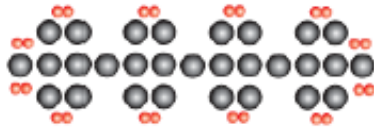


## Closure / Recommendations

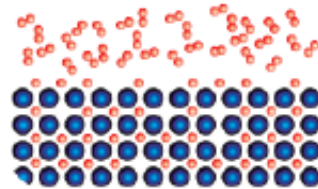


**Advanced materials development is still needed for long-term solutions**

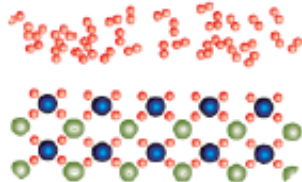
A) Surface Adsorption



B) Intermetallic Hydride



C) Complex Hydride

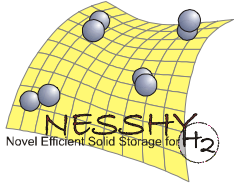


D) Chemical Hydride



**Materials discovery research is still needed for long-term, advanced materials with full set of properties for materials-based hydrogen storage options!**

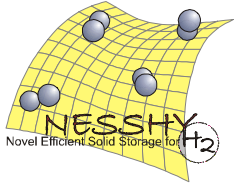




## Closure / Recommendations



- **Continue R&D efforts** where viable routes exist for developing materials & systems that can meet specific targets, e.g.
  - nanoporous / framework materials: increase  $H_2$ /solid interaction to achieve high temperature operation (weak chemisorption)
  - hydrides: composite materials, new additives to improve kinetics and lower temperature of operation
  
- Promote further **interaction between theory / computations and experimental activities**
  
- **Hybrid concepts**: high pressure (350 bar) – solid storage → required material capacity to satisfy targets can be reduced to 4 %wt (Toyota)



## Closure / Recommendations



- Sustain **H<sub>2</sub> Storage Working Group** – JU
- Promote **cooperation** at international level
- Importance – Need of **breakthroughs**
- Secure the necessary **R&D funding**



Thank you!