Novel Efficient Solid Storage for Hydrogen:

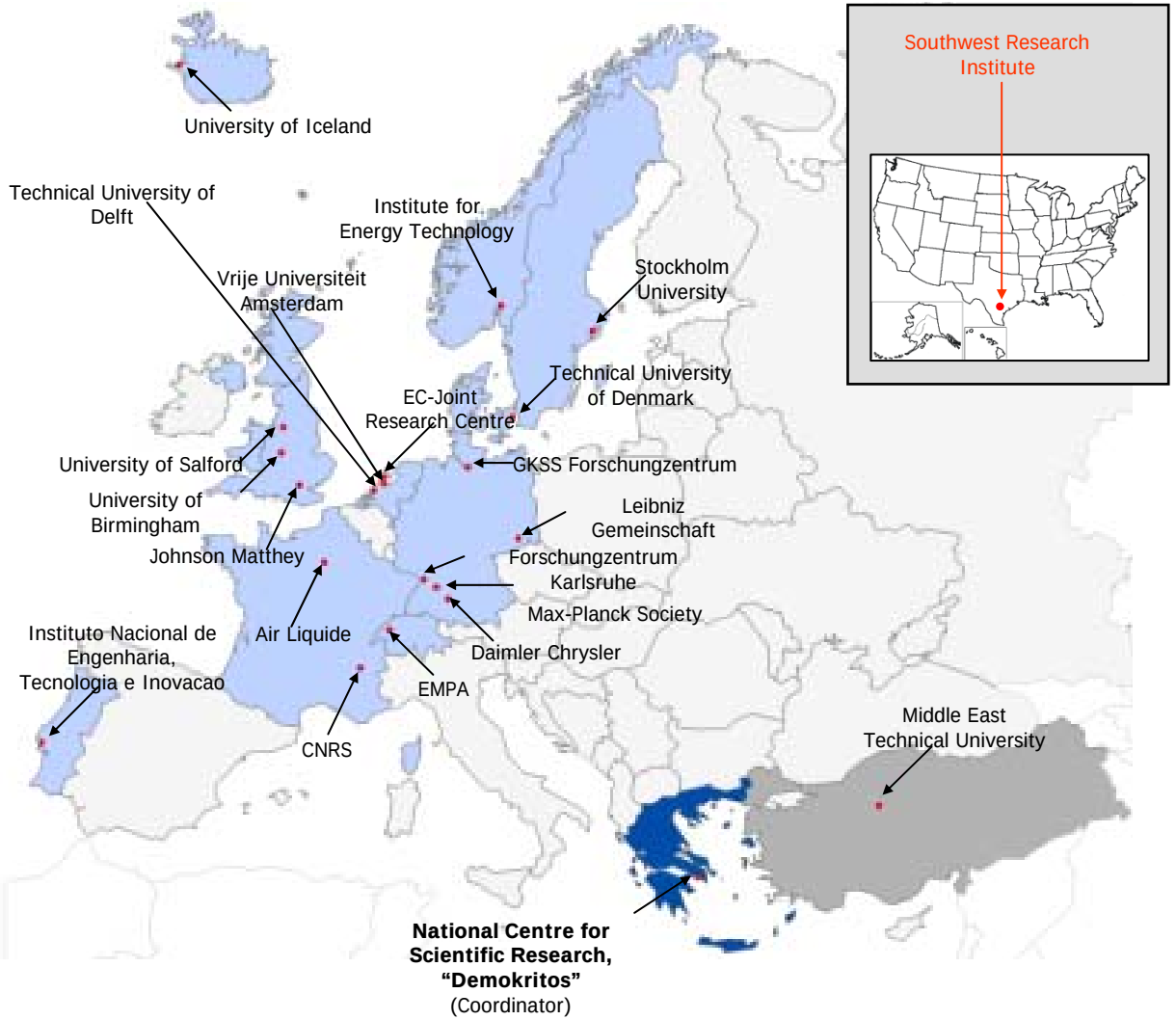
An Overview of the NESSHY Integrated Project

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?

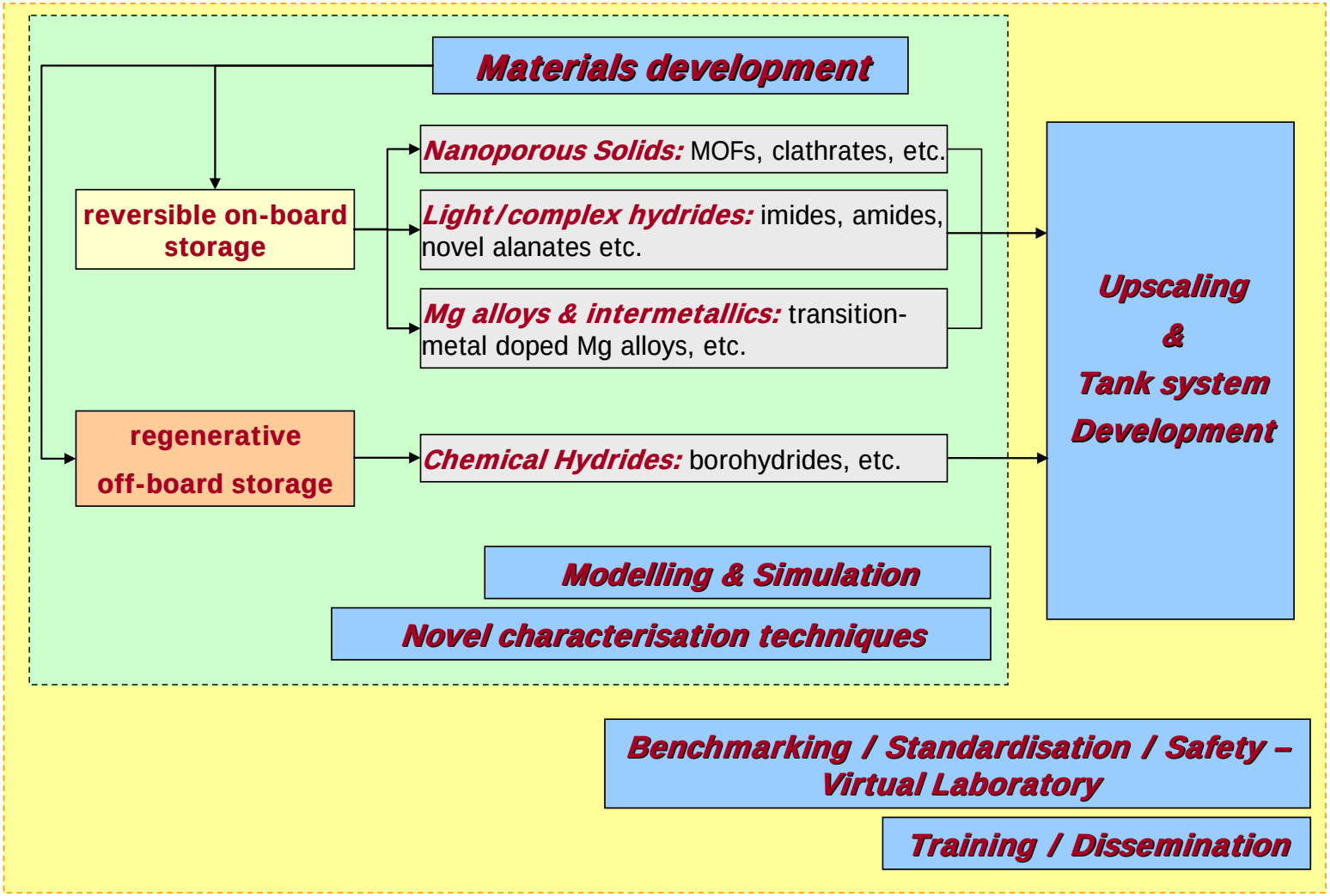
“Back to basics” approach

NESSHY key objectives

Advancement of the current state of H_2 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

Overall approach

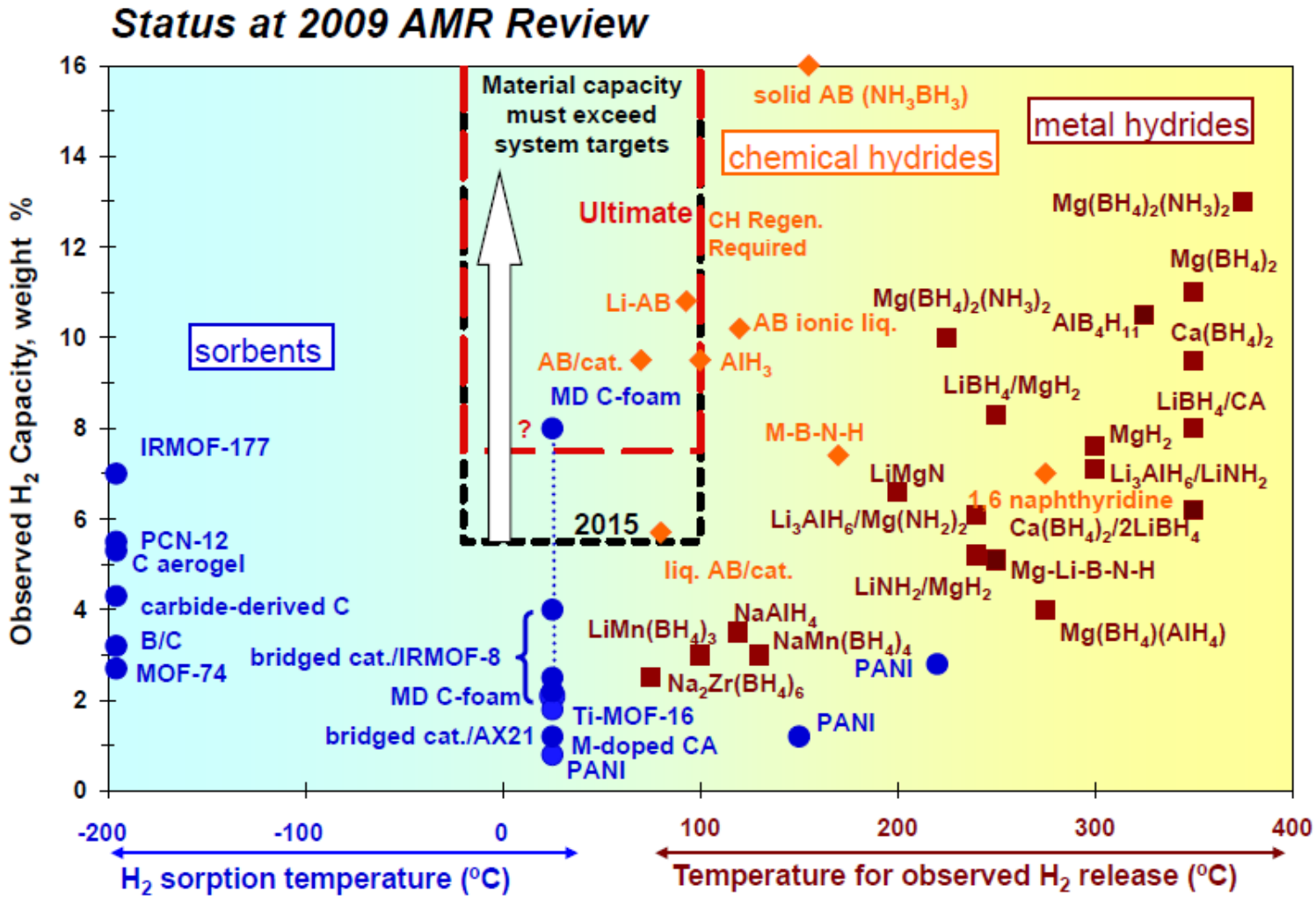


NESSHY targets

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^3)	24		50 (MgH_2 - WP3)	60 (MgH_2 - WP3)*
Refuelling rate * (for 5 kg H_2 tank)	kg H_2 / 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_2 – WP3)	> 10 (MgH_2 – WP3)**
H_2-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_2 tank)	KW	<60 (for a 4 kg tank)		> 90 (automotive on-board)	>200 (automotive on-board) > 65 (stationary application of MgH_2)
Enthalpy	kJ/mol H_2	28		30-40 (for WP1: ca. 20)	30-40 (for WP1: ca. 20) 74 (MgH_2 – WP3)
Production costs of solid storage material (incl. catalysts)	€/kg	-	23 (for standard MHs)	< 750	< 100 << 100 (MgH_2 – 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_2)	WP8: in total 2-3 lab-scale tanks (0.5 kg of material; 2kg for MgH_2)
Tanks (systems) (pilot-scale)		-		Design/study of heat manag. system for at least 1 pilot tank (approx 5 kg of material; 10kg for MgH_2)	WP8: in total 1-2 pilot- tanks or systems (5 kg or more material; 10kg for MgH_2)

Materials state-of-the-art



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_2 storage material

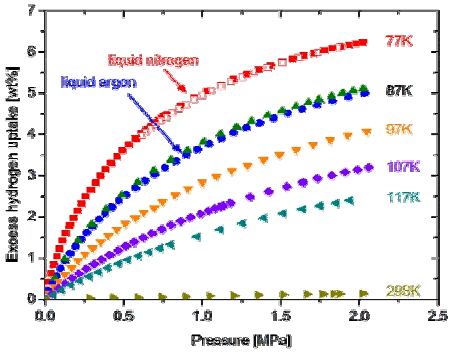
- *mechanisms*
- *roles of additives*
- *through advanced techniques/modelling*

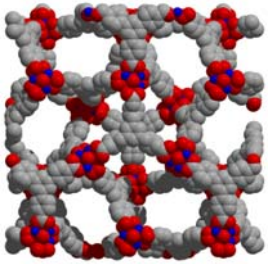
✓ Screening - Downselection

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_2/solid interactions (e.g. by metal doping)
  - Weak chemisorption → H_2 dissociation on metal (e.g. Pd, Pt, Ni) nanocatalysts → atomic H diffusion & storage





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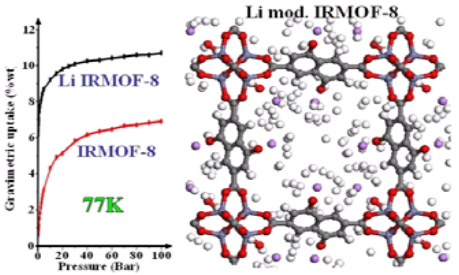
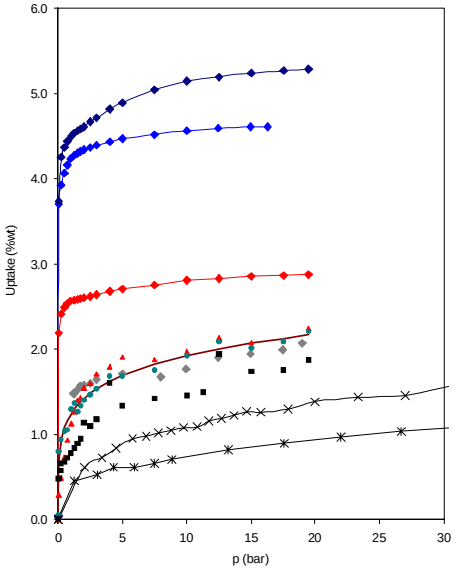
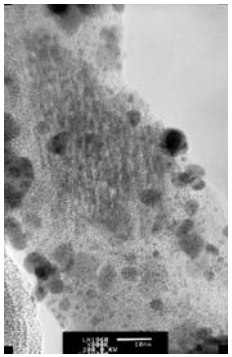






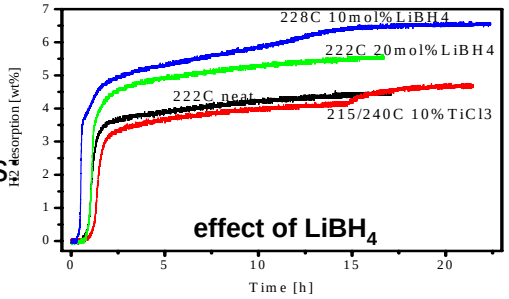
Pd-alloy/carbon foam nanocomposite

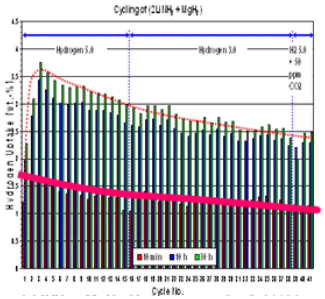
Light / Complex hydrides

• Composites

- Mixed alanates: Changed thermodynamics by substitution with fluorine in $NaAlH_4$

- Imides/Amides: Li:Mg systems with $LiBH_4$/KH additives up to 6.5 wt% H_2 at 180 °C - improved kinetics/cycling



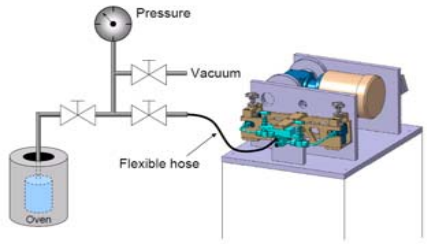


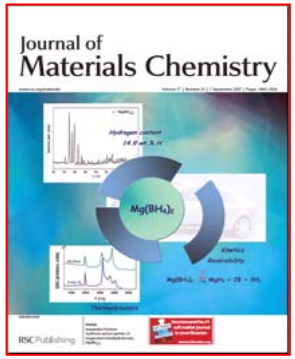
• Borohydrides

– controlled synthesis of $LiBH_4$, $Ca(BH_4)_2$ and $Mg(BH_4)_2$ by different methods

– characterisation (structure, decomposition routes)

– reversibility

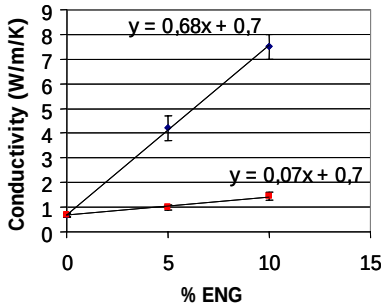


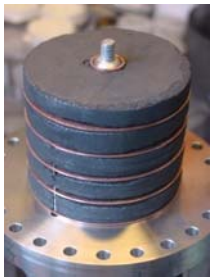


• Mg based compounds

- enhanced understanding of mechanisms

- improved material (thermal conductivity, volumetric capacity)



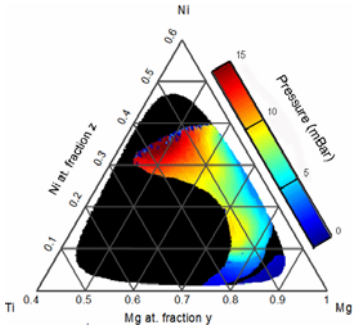


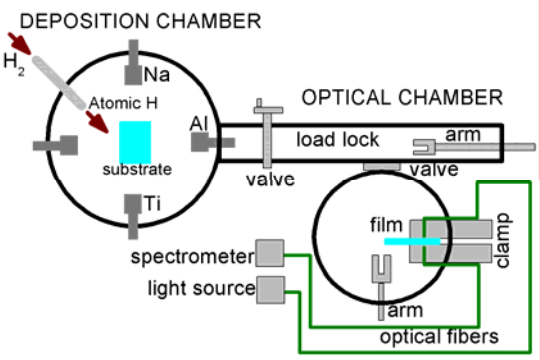
• **New FP7 projects** based on NESSHY results: **NANOHY, FLYHY**

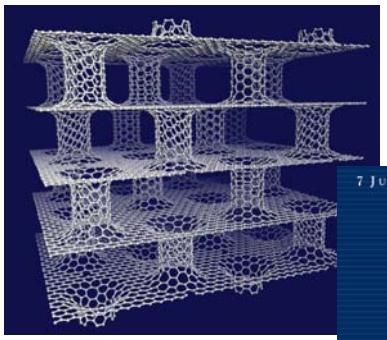
What we achieved – Advanced methods

- ✓ 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)

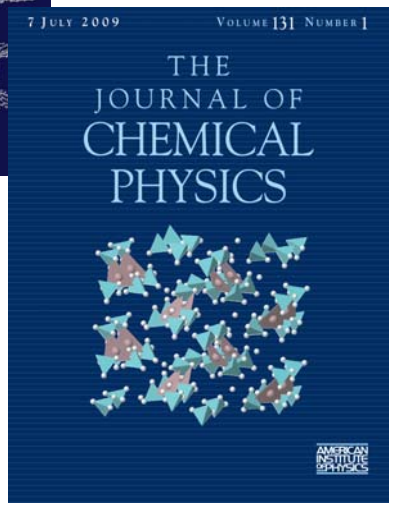
Hydrogenography





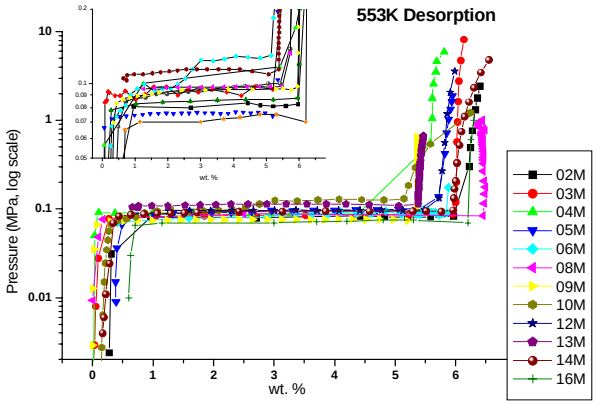


Pillared graphene



Ternary alkali-transition metal borohydrides

MgH_2 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

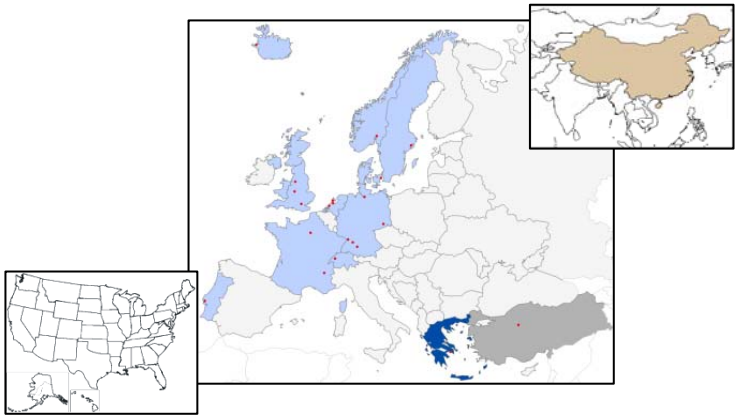
Material/system	Gravimetric Density (wt. %)	Volumetric Density (g/L)	Temperature range	Pressure (bar)	Kinetics	Other
MOFs/High surface area sorbents	6-7 %	25	77 K	up to 100 bar	fast	-
Doped carbons	2-5 %	-	298 K	up to 80 bar	slow	-
2Li:Mg/$LiBH_4$	6.3 %	50 - 90	473 K	60 bar	~1 h	cycling
2Li:Mg/KH	3.5 %	50 - 90	453 K	60 bar	10 min	cycling
$Mg(BH_4)_2$	11 % (theor.)	147	623 K	up to 20 bar	-	reversibility at high P
Pilot tank – MgH_2 based	2.0 % (system)	42 (system)	523-573 K	up to 50 bar	20 min	cycling
Pilot tank – $NaAlH_4$ based	2.0 % (system)	32 (system)	433 K	50 bar	10 min	cycling

Outreach / Collaborations

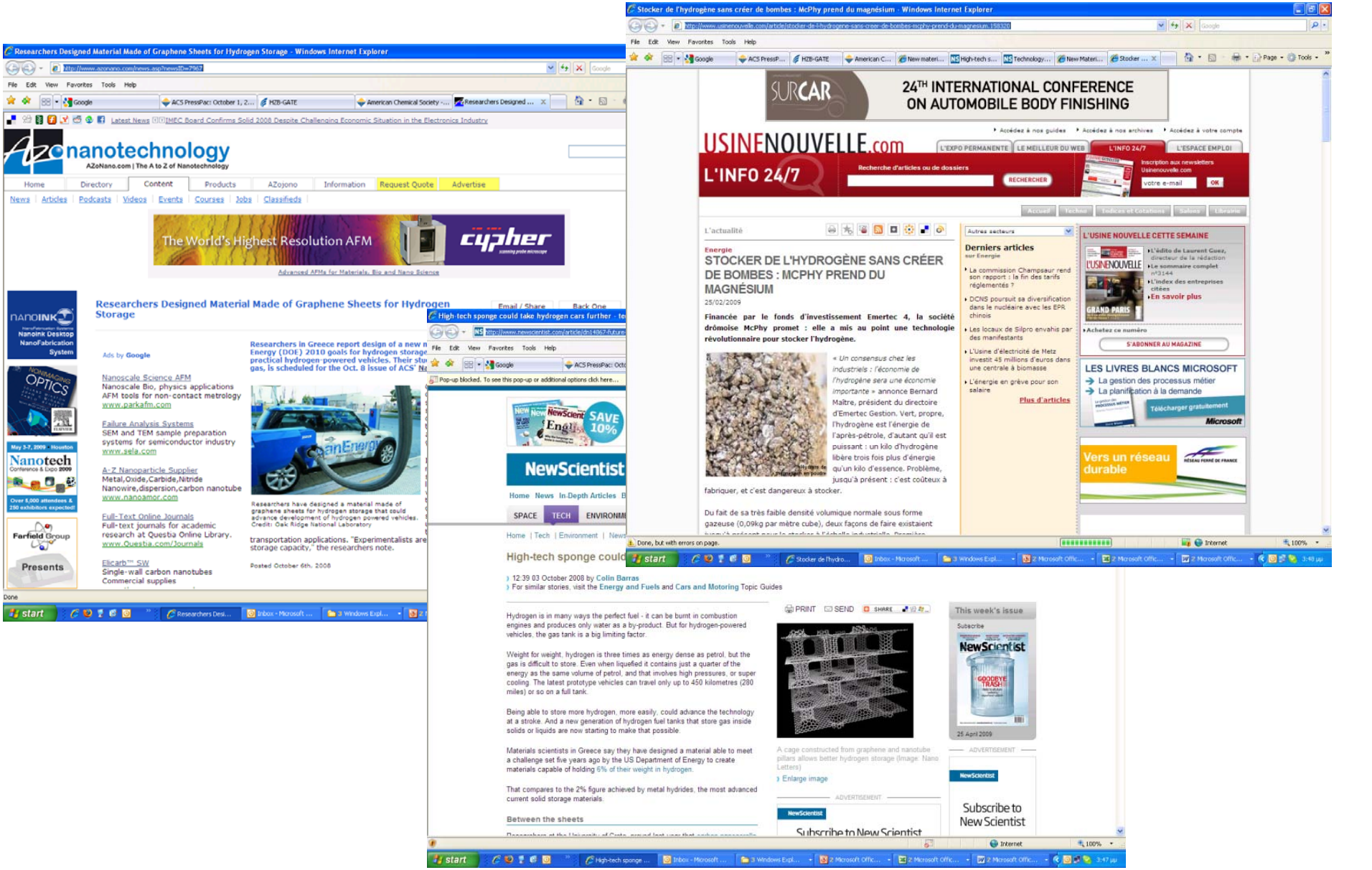
- www.nesshy.net
- Interaction with other hydrogen related projects (IP-STORHY, PICS, COSY, HYDROGEN RTNs, HYSIC, HYCONES, NANOHY, FLYHY) – Joint workshops
  - Joint NESSHY-HYSIC workshop, Beijing – China, 15-16 September 2008
  - SSH-IP (Solid Storage of Hydrogen – International Perspectives) workshop, 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

IPHE activities / 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**: "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

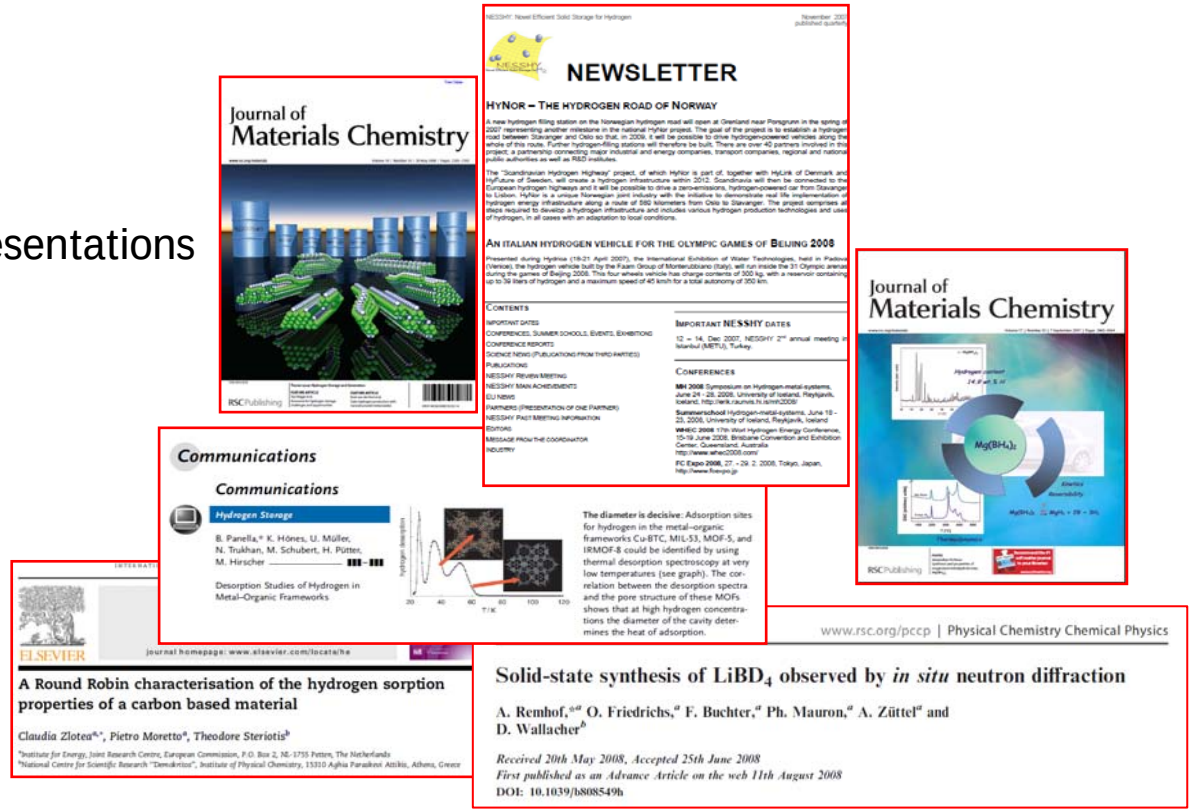


Dissemination of NESSHY scientific results through widely circulating magazines / journals and visited websites



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



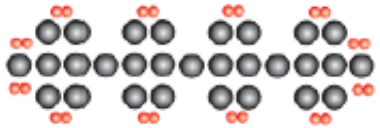
Exploitable results

WP	Exploitable Knowledge (description)	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable for commercial use	Patents or other IPR protection	Owner & Other Partner(s) involved
1	Carbon material for hydrogen storage	Carbonaceous material with remarkable H_2 storage capacity	Chemical Industry	Premature to define	US Application No. 12/272,488 (flied on Noember 17, 2008)	NCSRD, SwRI
2	Adjusting the stability of complex metal hydrides	Alanates 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 Nanocristallin 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'hydrure de magnesium"	CNRS Licensed McPHy Energy
3	Hydrogen storage tank for MgH_2 based composites	Hydrogen storage tank	Energy production & storage industry	2011	WO2009080975 "Hydrogen Storage Tank"	CNRS Licensed McPHy Energy
4	New scheme for $NaBH_4$ synthesis	No exploitation foreseen because of the failure in cost reduction	Chemical industry	N/A	Invention disclosures	Air Liquide, Aviabor
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 coude belongs to JRC, the data contained to the individual user	JRC & all potential customers

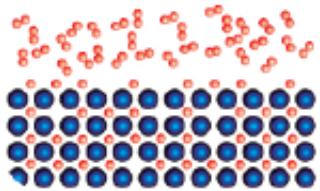
Closure / Recommendations

Advanced materials development is still needed for long-term solutions

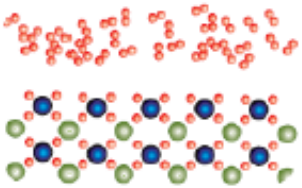
A) Surface Adsorption



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!

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

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_2 Storage Working Group** – JU
- Promote **cooperation at international level**
- Importance – Need of **breakthroughs**
- Secure the necessary **R&D funding**


Thank you!