Stockage chimique de l'hydrogène sous forme d'hydrures

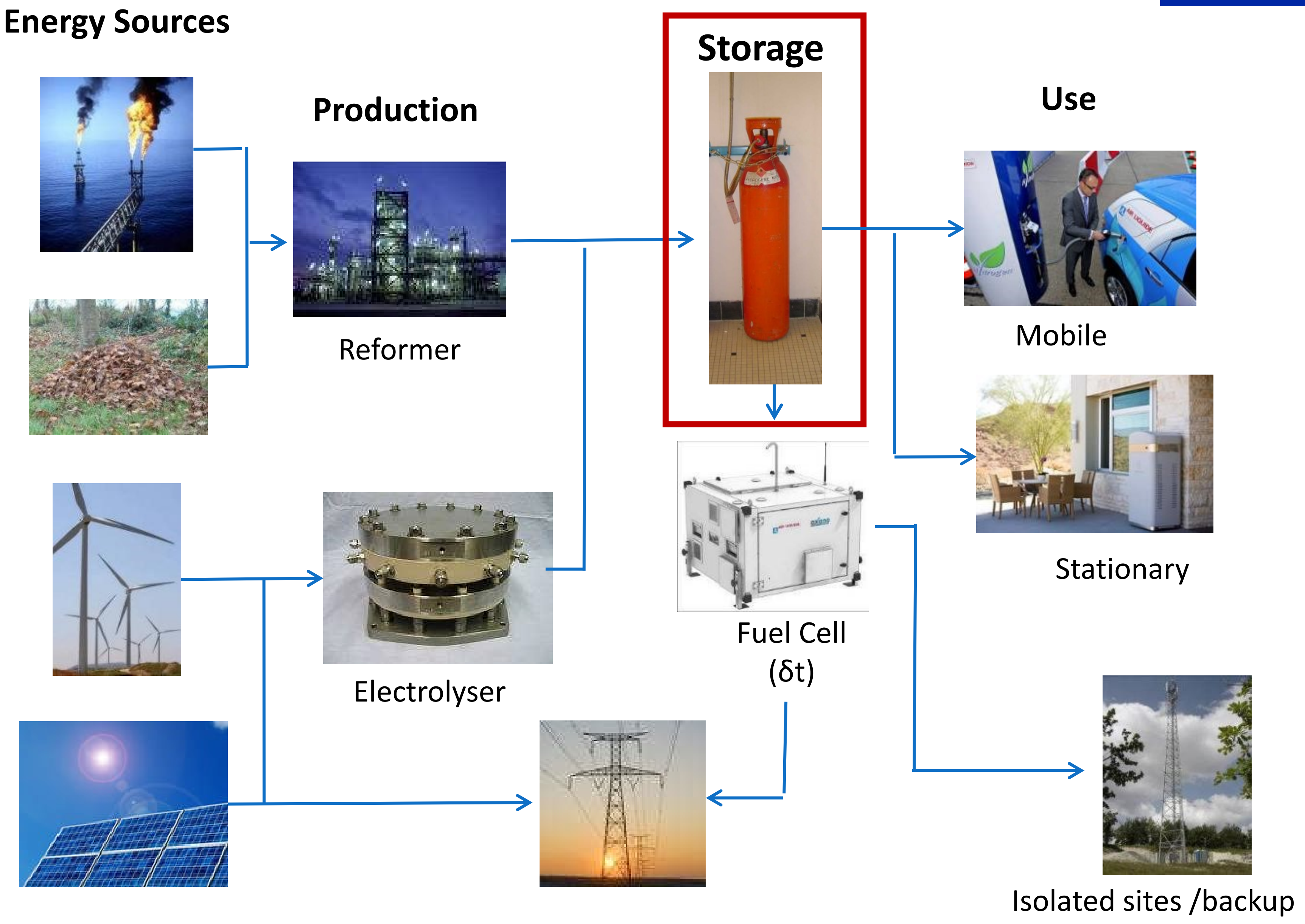
Fermin CUEVAS

Interaction of Hydrogen and Matter Research Group

East Paris Institut of Chemistry and Materials – ICMPE,

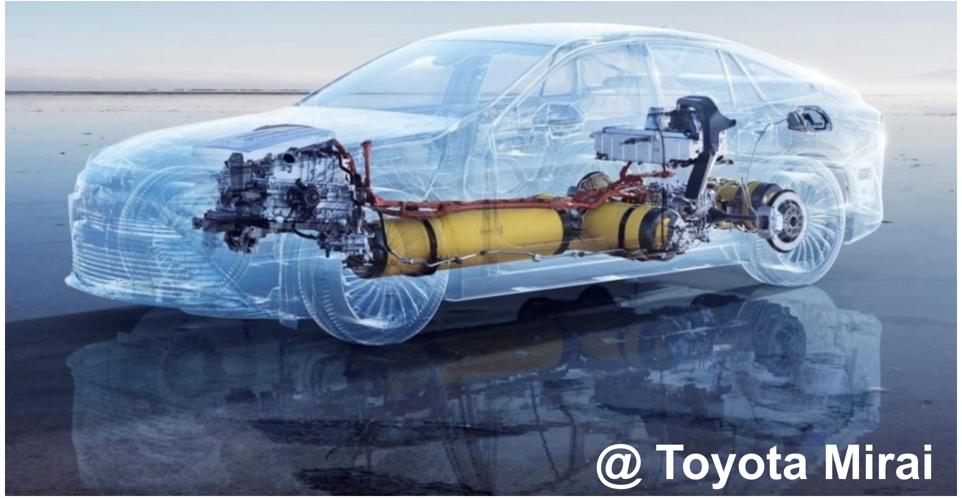
CNRS – UPEC, Thiais

The hydrogen chain



Densification: the main challenge of H_2 storage – example of light vehicles

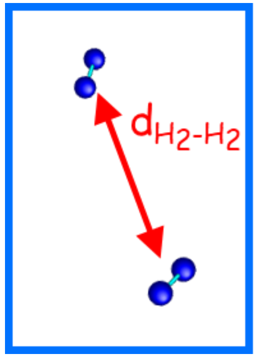
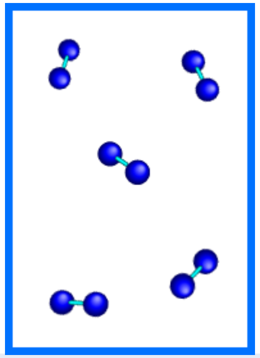
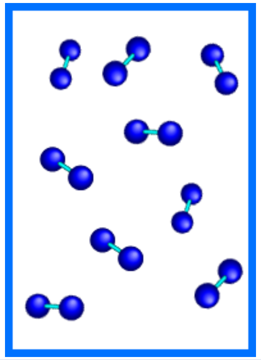
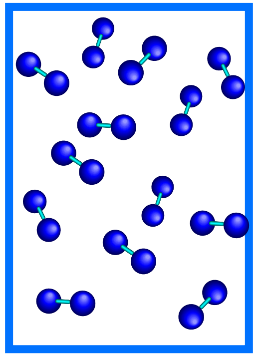
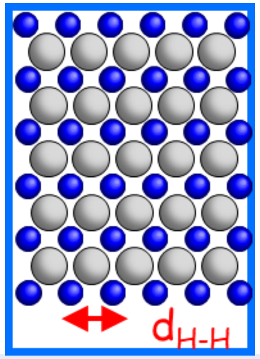
- Hydrogen density (NTP) : 0.083 g_{H2}/L
- Amount of hydrogen needed : 5.5 kgH_2 / 550 km
- Volume (5.5 kgH_2, NTP): 70 000 L (sphere, ϕ ~ 5 m)
- Volume (700 bar) : 150 L (Toyota Mirai)



Methods for hydrogen densification

Storage methods :	Compressed	Liquid	In solids
			
Pressure	**350-700 bar**	**1 bar**	**~ 1-50 bar**
Temperature	**Ambient**	**-253°C**	**~ 25 °C**

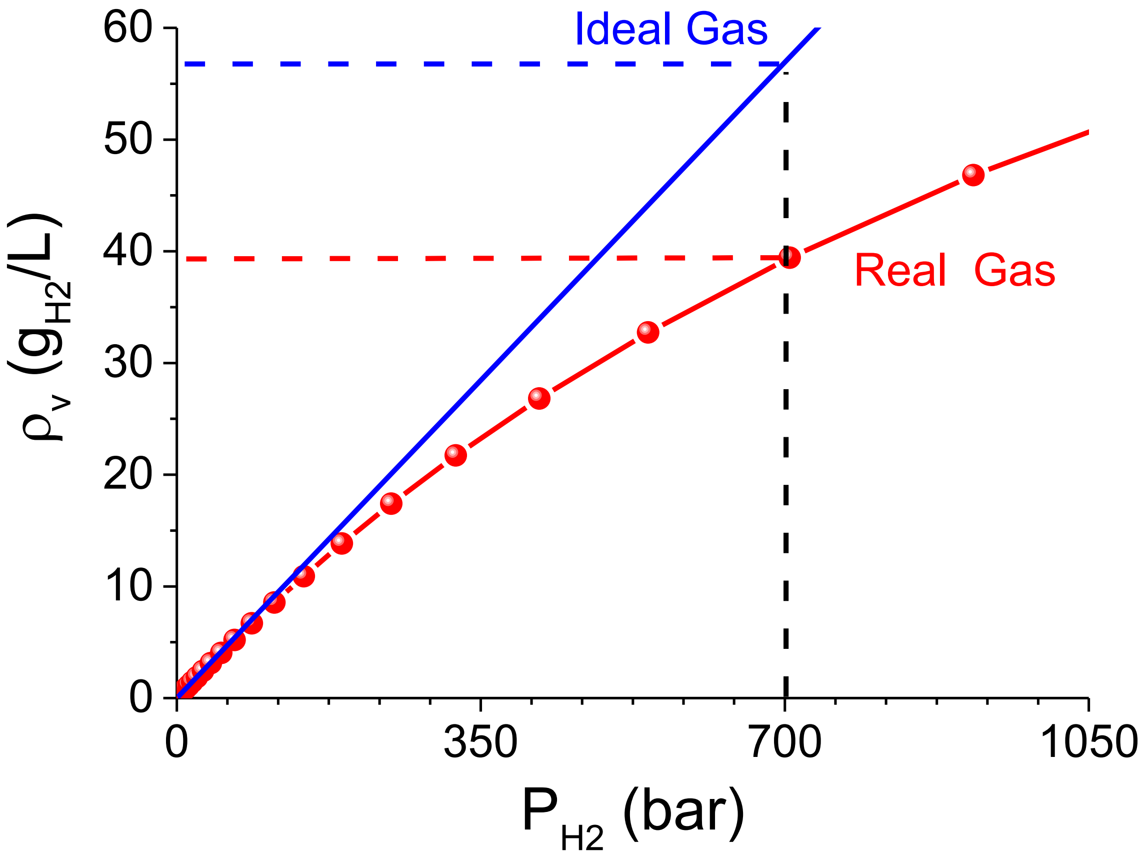
Compacity and specific capacity of hydrogen storage methods

Storage method →	**Gas**			**Liquid***	**Solid****
Pressure (bar)	1	350	700	1	10
Temperature (K)	300	300	300	20	300
					
H-distance (nm)	3.3	0.54	0.45	0.36	0.21
H-density (g_{H2}/L)	0.08	23	39	70	80-140
Specific capacity, system (wt.%)	-	4-5	5-6	6	1-2

* Alternatives to H_2-cryogenic storage: liquid organic hydrogen carriers, ammonia
** Data for metallic hydrides

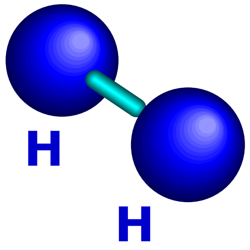
Limitations of classical compressed and liquid methods

- Non ideal behavior of hydrogen gas at high pressures
- High energy consumption for compression (15% HHV) or liquefaction (30% HHV)
- Limited conformability of tanks
- Security issues of high pressure or cryogenic temperature

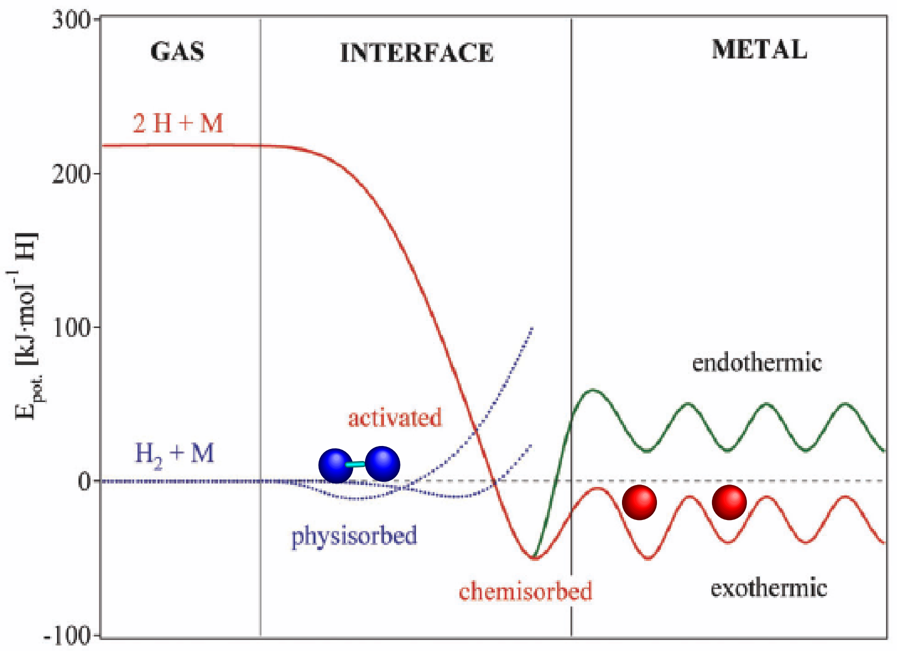


Hydrogen storage in solids

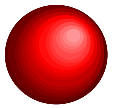
Molecular hydrogen



Adsorbed on solids



Atomic hydrogen



Absorbed in solids

Porous materials

Weak-bond energy: $\Delta H < 10$ kJ/molH_2

T ~ - 200°C

Zeolites, Carbon, MOFs

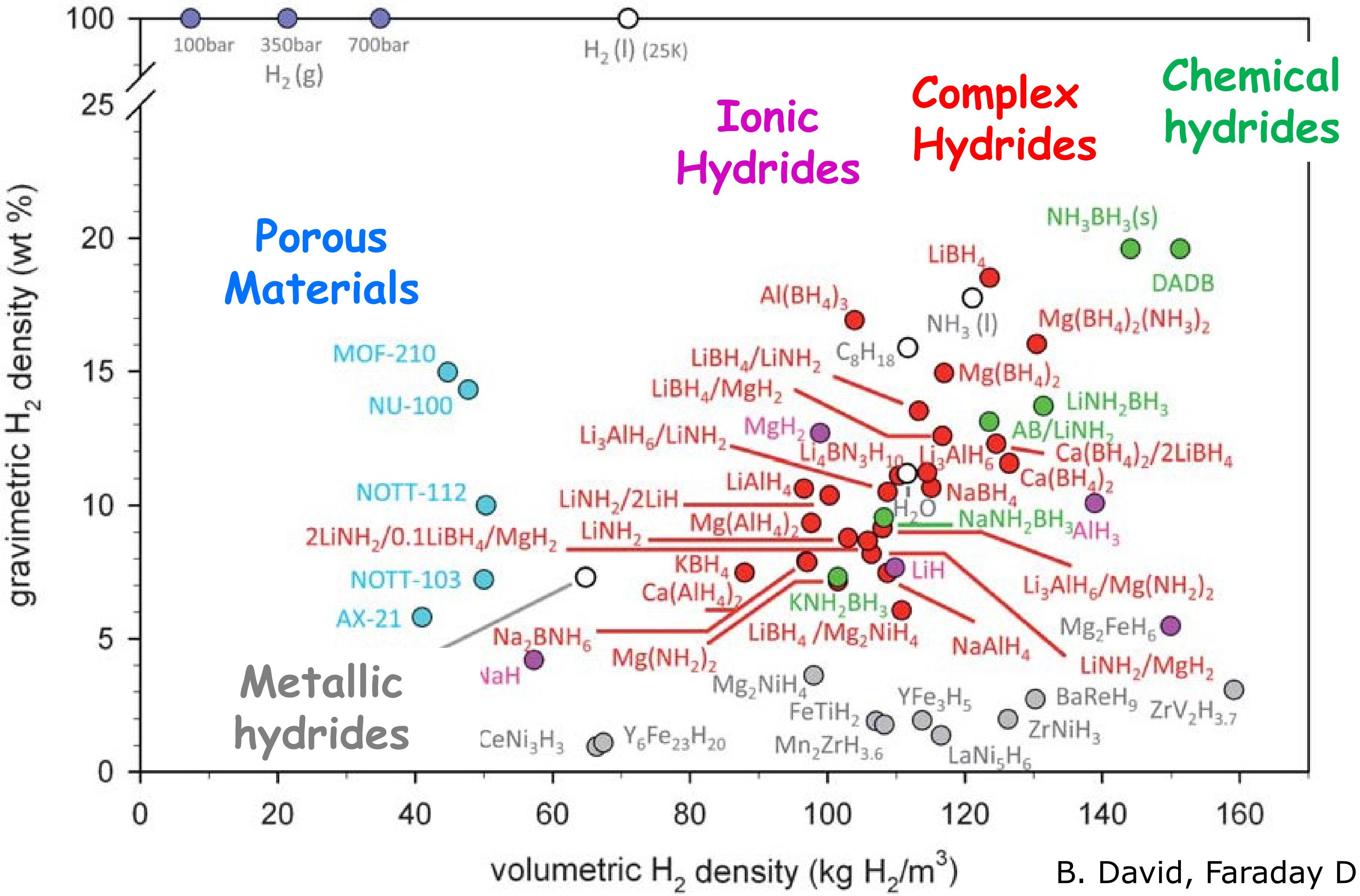
Metallic, ionic, complex, chemical hydrides

Bond energy : $20 < \Delta H < 200$ kJ/ molH_2

T ~ - 50-500°C

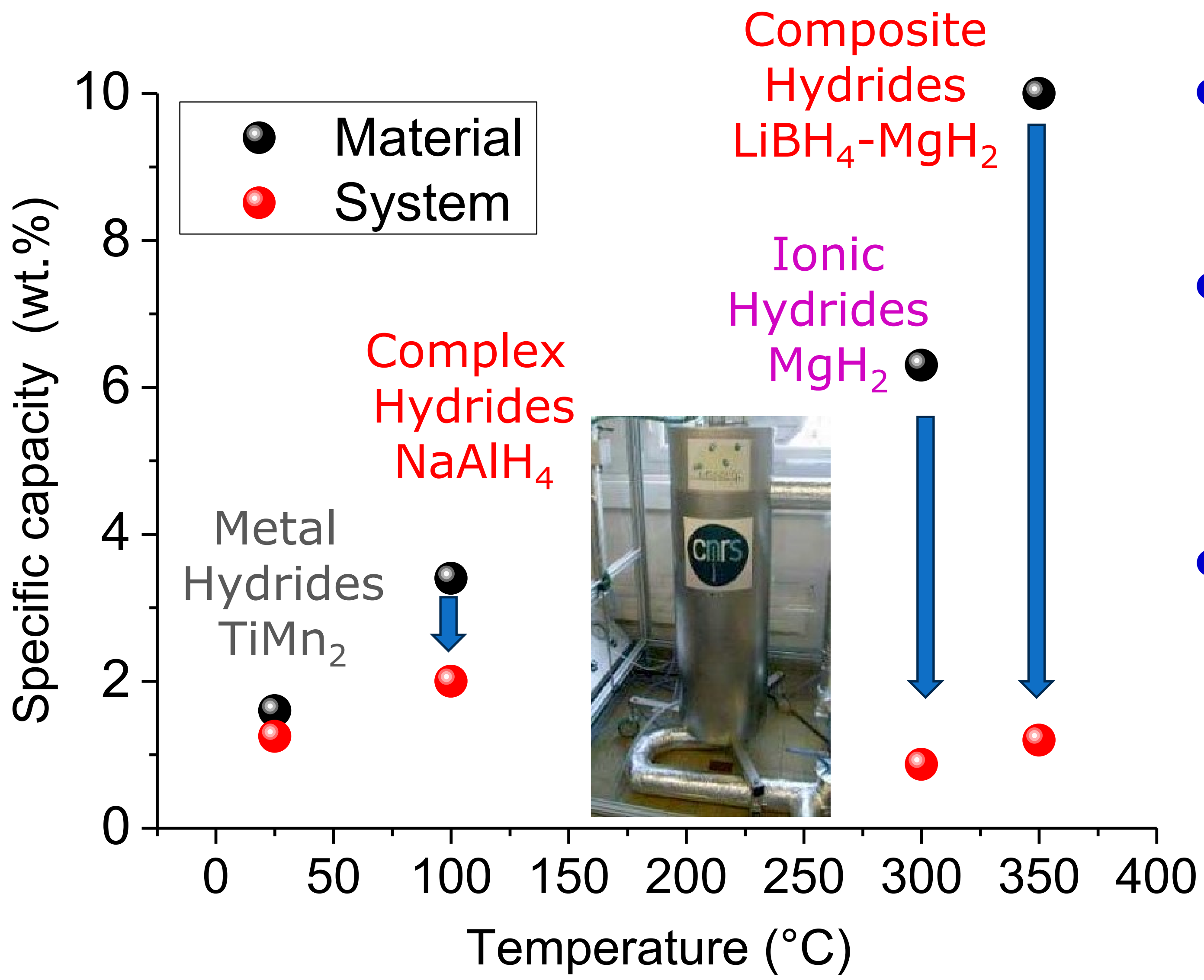
$LaNi_5H_6$, MgH_2, $LiBH_4$, NH_3BH_3

Material types and their gravimetric and volumetric capacities



B. David, Faraday Discuss., 151 (2011)151

From hydrogen storage materials to storage systems



- Materials are loaded in hydrogen tanks (system)
- The difference in specific capacity between materials and system increases with operation temperature
- Weight of hydrogen tank increases with temperature : change of composition (Al → steel) and thickness

HDW United Technologies Research Center McPhy energy BOR4STORE

PEPR-H2 : SOLHYD project

- SOLHYD aims at removing the current bottlenecks of solid-state hydrogen storage
- Target: to discover new materials C_m > 3 wt.%, C_v > 71 g_{H2} / L with good reversibility near NTP conditions.
- Partners: 6 laboratories of CNRS/University and 2 CEA Units
- People: 45 researchers & technicians, 14 Ph.D. & 7 Post-docs
- Duration: 5 years (2022-2027)

FRANCE 2030 PROGRAMME DE RECHERCHE HYDROGÈNE

Coordination

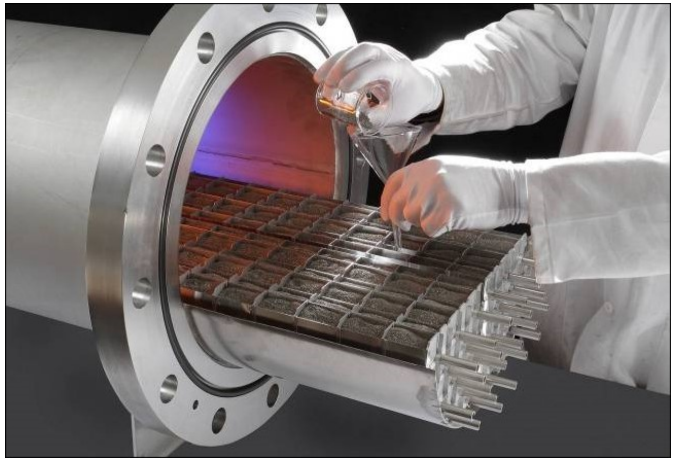
F. Cuevas
ICMPE

Animateurs /Partenaires

U.-B. Demirci	V. Faucheux	P. de Rango	C. Zlotea	J.-L. Bobet	V. Fierro	R. Janot
IEM	CEA	NEEL	ICMPE	ICMCB	IJL	LRCS

PEPR-H2 : SOLHYD project

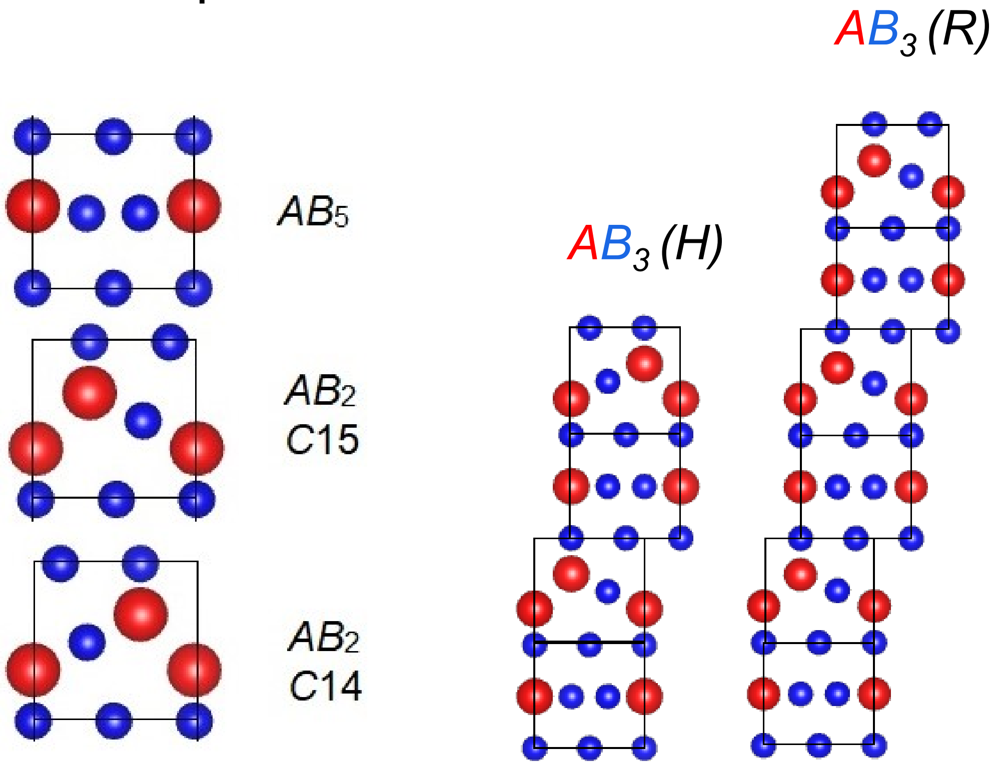
- Strategies:
  - Intensive use of modeling and computational efforts
  - Broad scope of materials:
    - Metal hydrides
    - Reversible complex hydrides & porous materials
    - Regenerable chemical hydrides
  - Use of deep characterization methods
  - Experimental validation of hydrogenation properties



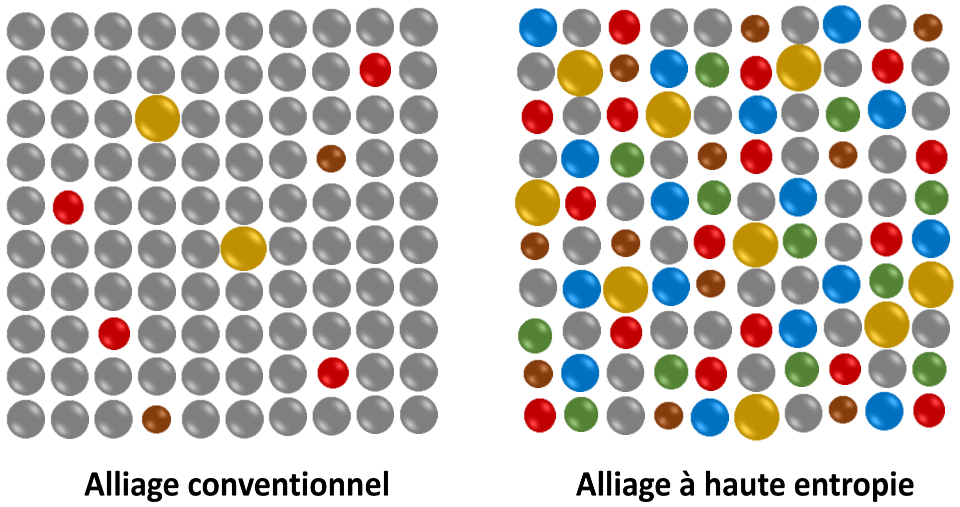
Metal hydrides

- Study of novel alloy families with highly flexible composition

➤ Stacking structures of AB_x compounds



➤ Design of High Entropy Alloys



Contact (ICMPE) : Claudia Zlotea

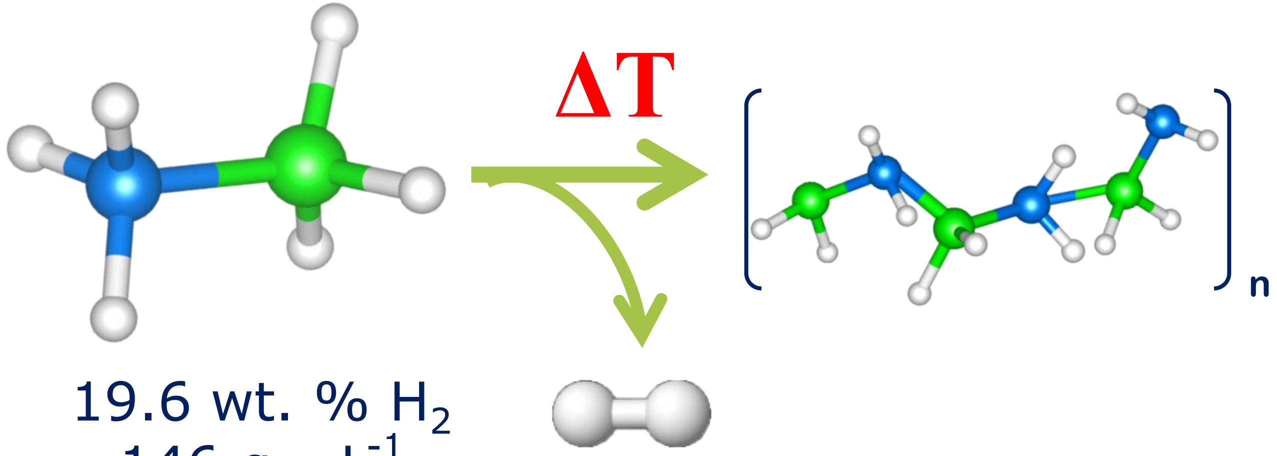
Regenerable chemical hydrides

- Study of optimized regeneration processes

➢ Regeneration of BNH polymers from ammonia borane decomposition

Ammonia borane
NH_3BH_3

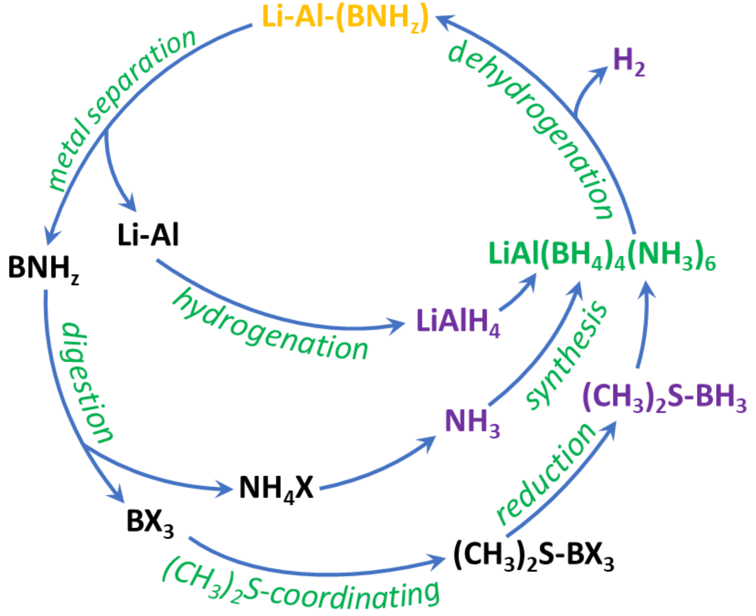
Polyaminoborane
$(–NH_2BH_2–)_n$



19.6 wt. % H_2
146 g_{H2} L^{-1}

Contact (IEM) : Umit B. Demirci

➢ Regeneration of novel Li-Al Ammine Metal-Based Borohydrides

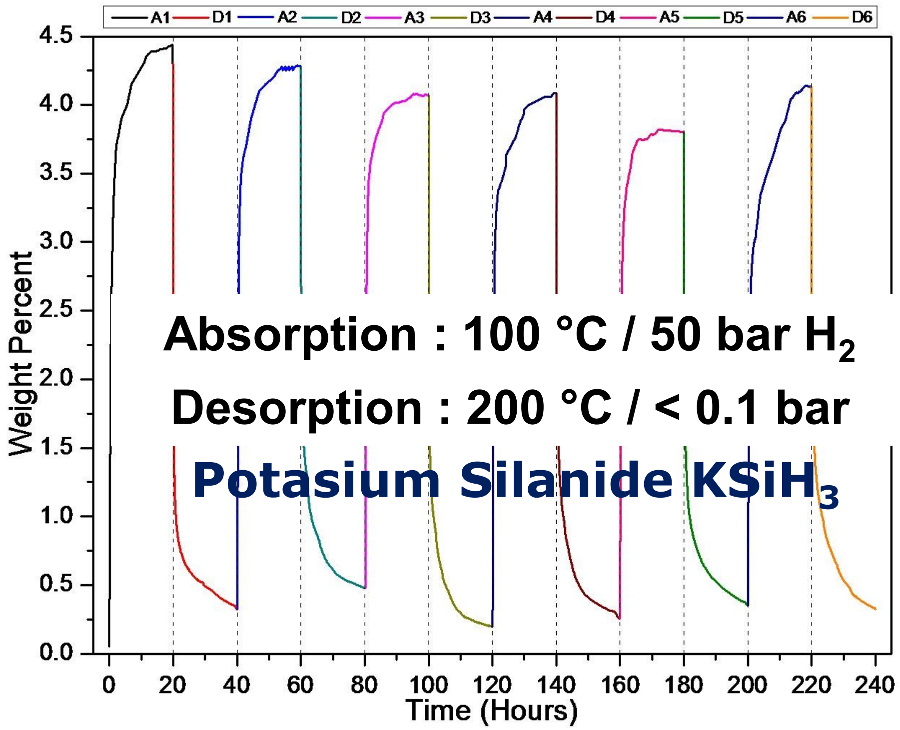


Contact (CEA/LITEN) : Vincent Faucheux

Reversible Complex Hydrides & Porous Materials

- Towards room temperature operation high-capacity reversible hydrides

➢ Novel Si-based complex hydrides K_3LiSi_4 and K_7LiSi_8



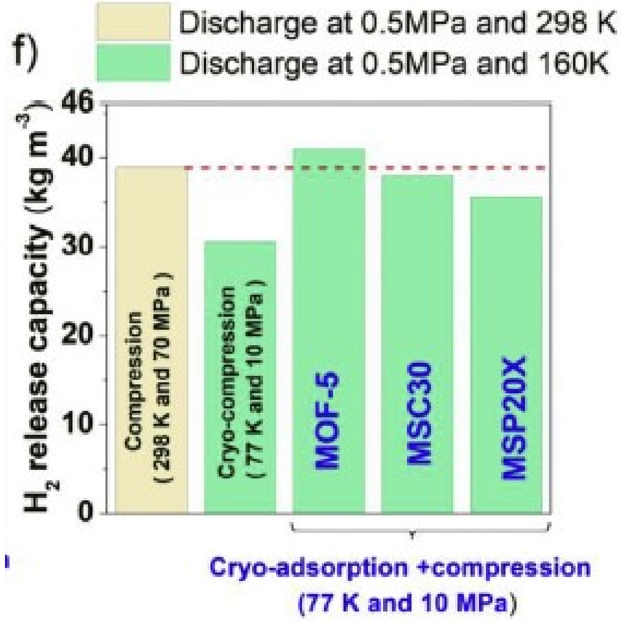
Absorption : 100 °C / 50 bar H_2

Desorption : 200 °C / < 0.1 bar

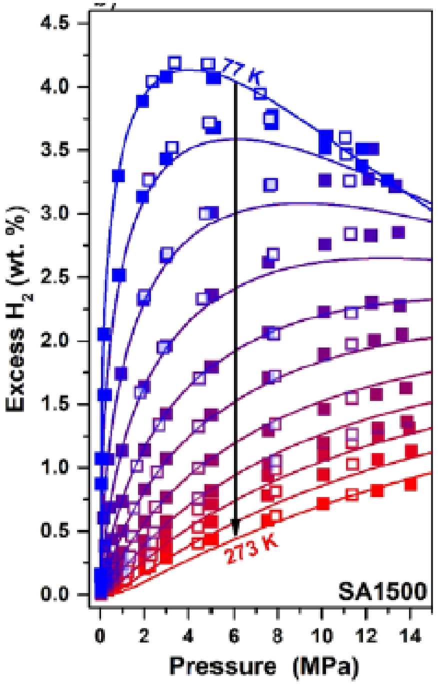
Potasium Silanide $KSiH_3$

Contact (LRCS) : Raphaêl Janot

➢ Study of H_2 adsorption and release capacities using MOFs and ACs



➢ Prediction of H_2 storage capacities based on textural characterisation



Contact (IJL) : Vanessa Fierro

Hydrides for hydrogen storage: some industrial examples

- Heavy mobility :
  AIP submarines, forklifts

HDW – Germany, Wonil - Korea
$TiMn_2$ alloys (~1 ton H_2)

HySA – South Africa
AB_2 alloys (1.7 kg H_2)

HDW WONIL WONIL T&I

HySA Systems Hydrogen South Africa

- Stationary applications:
  management of
  renewable intermittency

Toshiba H2One-Japan
$LaNi_5$ alloys (24 kg H_2)

GKN-Germany
TiFe alloys (50-500 kg H_2)

TOSHIBA

GKN HYDROGEN

Lavo -Australia

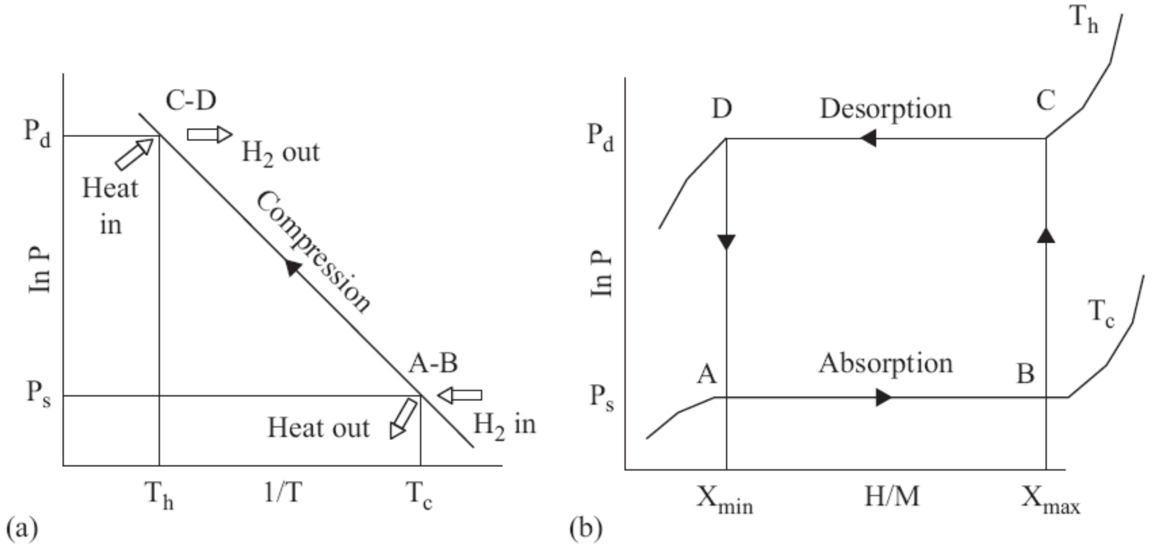
LAVO FOR LIFE

Methydor - Italy

MetHydor

Other emerging applications of hydrides

- Thermochemical hydrogen compressors

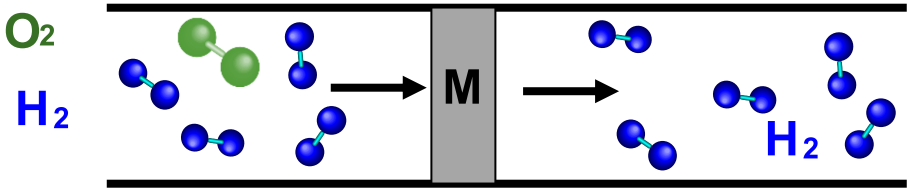


GRZ-Switzerland
P_{H2} = 8 → 150 bar

Hystorsys-Norway
P_{H2}= 50, 250 bar

MaHyTEc-France
P_{H2}= 30, 450 bar

- Hydrogen purification : Pd-membranes and hydride beds



Entegris-USA
(Pd -membranes)

Vonen-Finland
(hydride beds)

Conclusions

- Hydride compounds are attractive materials for hydrogen storage due to their high compacity, good energy efficiency and safe operation conditions
- Materials with high weight capacity while keeping reversibility at NTP conditions are under research in PEPRH2-SOLHYD project
- Increasing worldwide interest of companies on hydrides as hydrogen stores and related applications : compression and purification

MH2024 Conférence : Bienvenus à St Malo

web-site: https://mh2024.org/

➢ Topics :

- Fundamentals of M-H systems
- Surface / Interface Effects
- Catalysis
- Metallic hydrides
- Ionic and complex hydrides
- Chemical and organic hydrides
- Nanoporous materials
- Hydrogen storage systems
- Proton batteries and fuel cells
- Hydrogen production, transport and purification

Remerciements

- PEPRH2-SOLHYD partners

FRANCE 2030 PROGRAMME DE RECHERCHE HYDROGÈNE

anr agence nationale de la recherche

Ce travail a bénéficié d'une aide de l'État gérée par l'Agence Nationale de la Recherche au titre de France 2030 portant la référence « ANR-22-PEHY-0007 »