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Hydrogen storage materials and their development

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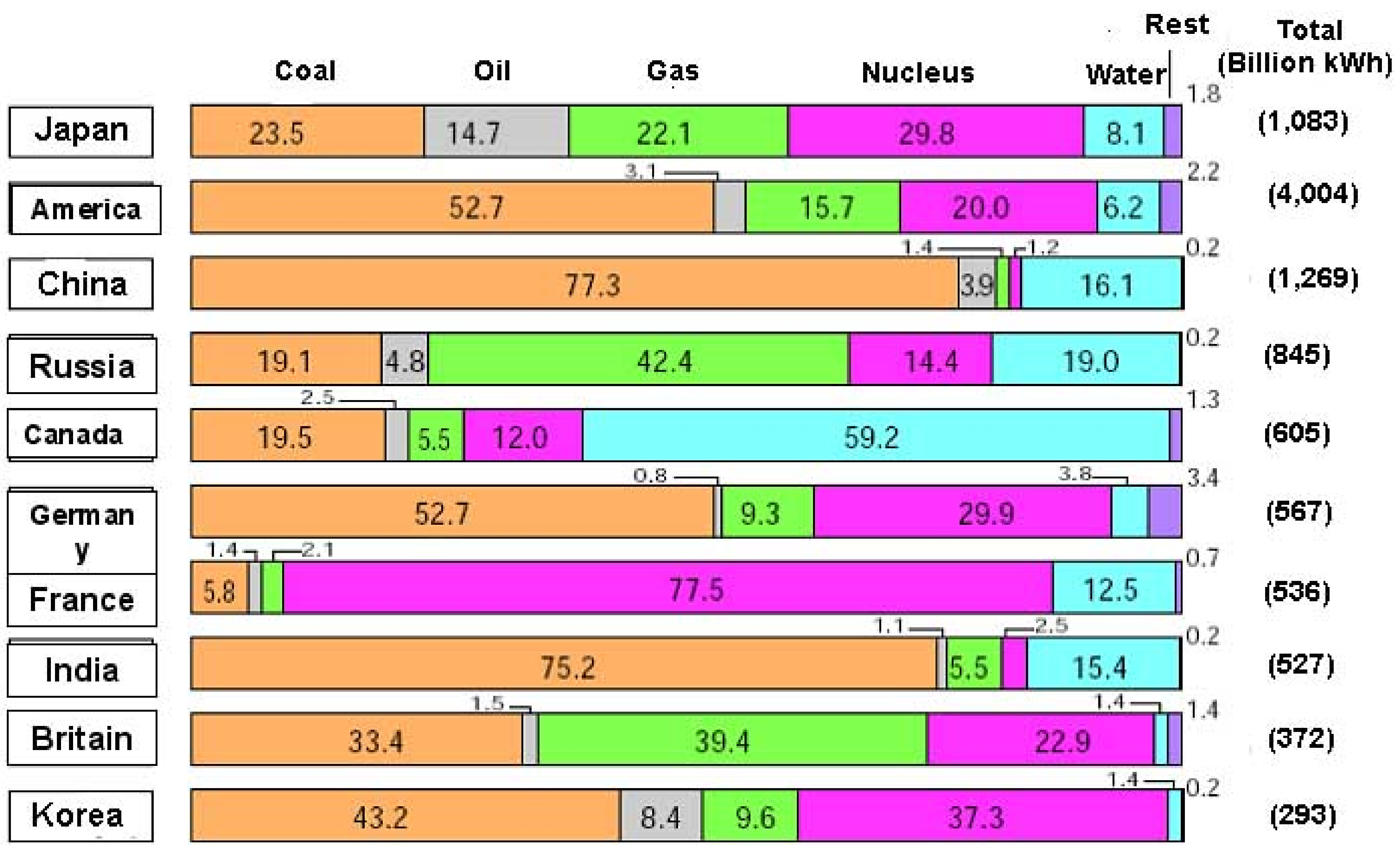
Power generation percent of different energy

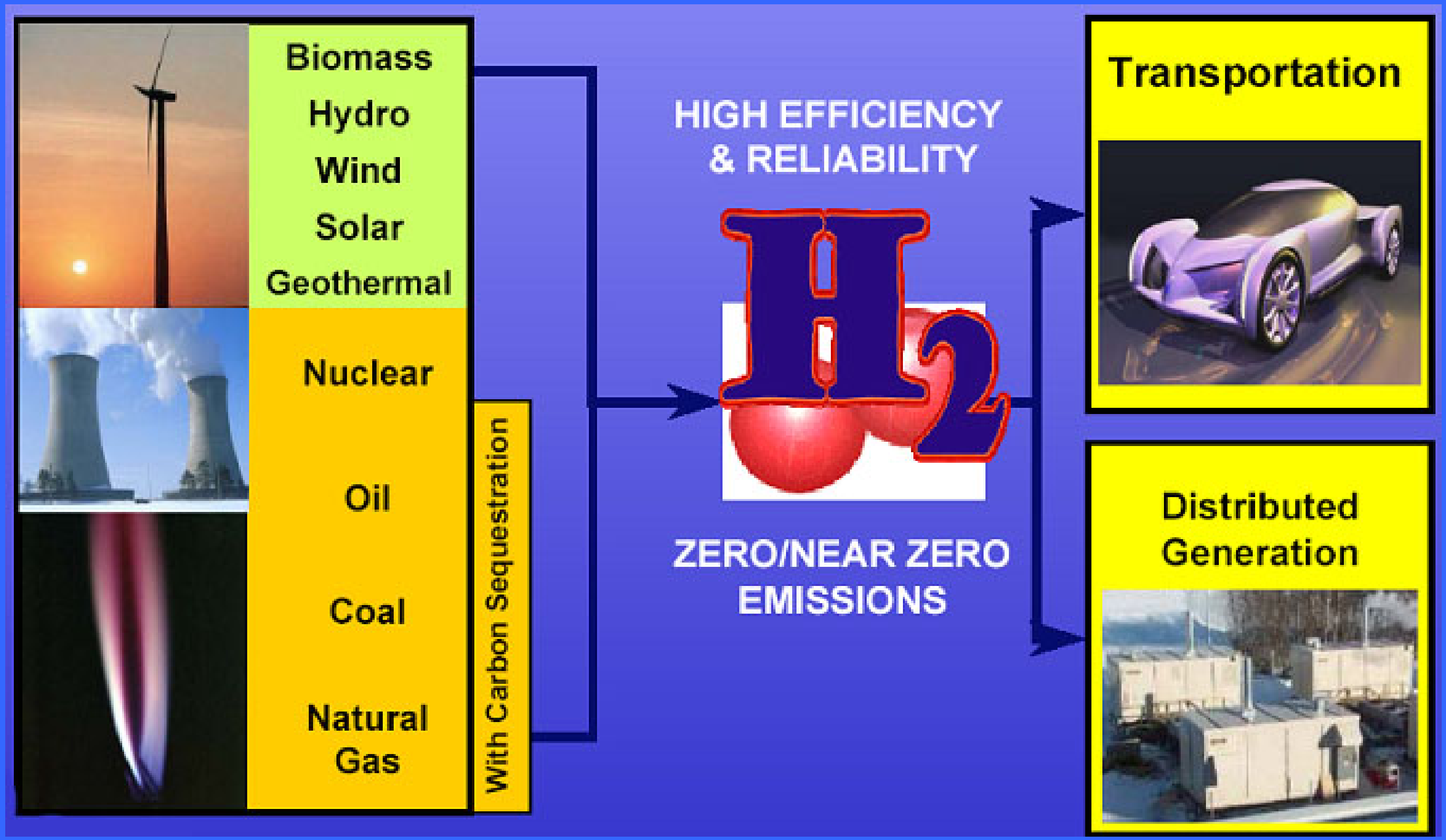


Global carbon dioxide generation by mineral fuel (from Scientific American 2002)

	Exhaust percent(wt%)	Exhaust amount of per person (ton)
America	24	5．4
China	14	0．7
Russia	6	2．7
Japan	5	2．5
India	5	0．3
Germany	4	2．8
Canada	2	4．2
Britain	2	2．5
Korea	2	2．2
Italy	2	2．0
France	2	1．7
Mexico	2	1．1

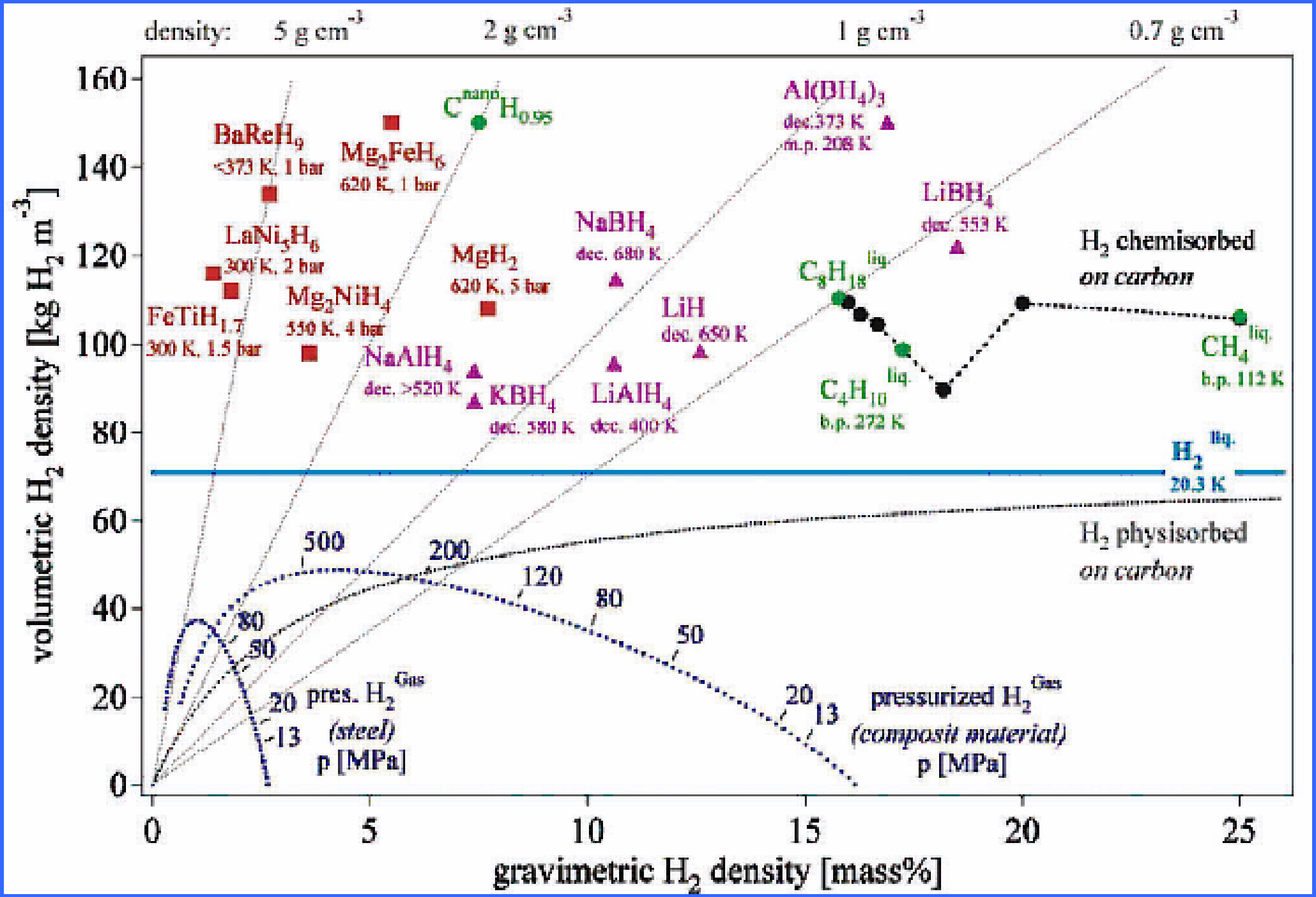
It has become increasingly clear that hydrogen as an energy carrier is ‘in’ and carbonaceous fuels are ‘out’. Hydrogen energy is high efficiency and near zero emissions. The hydrogen economy is coming.

James A. Ritter, *Materials today, September 2003*



Hydrogen energy is widely used in transportation

Volumetric and gravimetric hydrogen density of some selected hydrides.



Three options exist for storing hydrogen: as a highly compressed gas, a cryogenic liquid, or in a solid matrix.

James A. Ritter *Materials today, September 2003, 24*

15 MPa compressed hydrogen gas cylinder

The hydrogen storage capacity is only 1.2 mass%.

35 and 70MPa compressed hydrogen gas cylinders

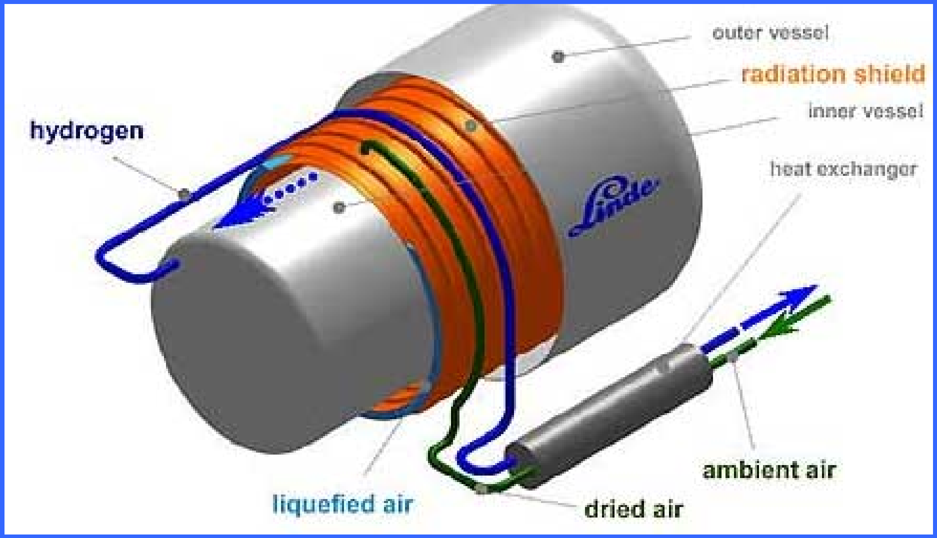
100 MPa compressed H_2 cylinder is also being developed.

Dangerous!

The hydrogen storage is about 2.7% at 35 MPa and 5.5 mass% at 70 MPa.

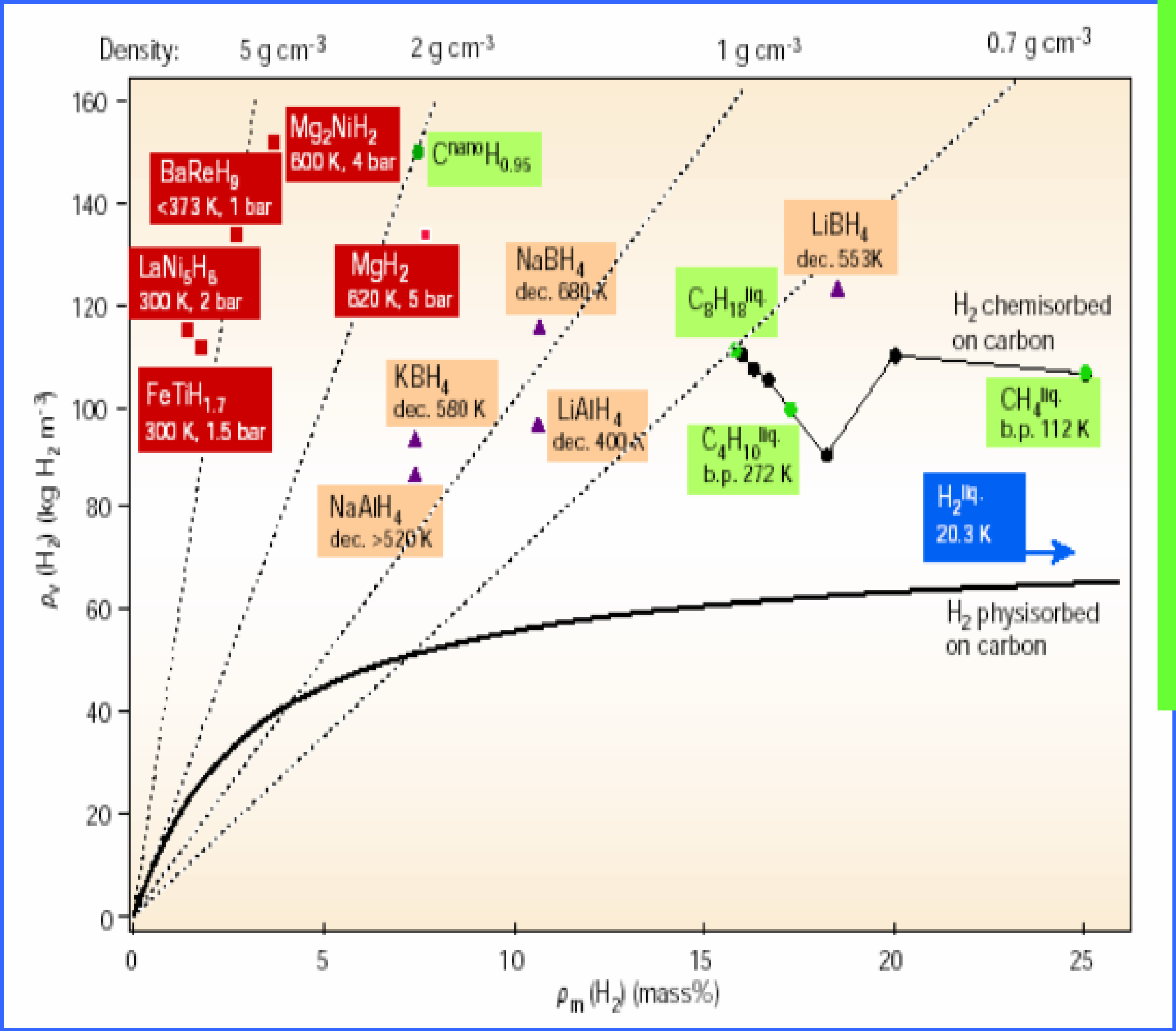
Hydrogen storage in liquid state

Hydrogen storage in liquid state has high storage capacity, but it resumes a lot of energy in liquation and low temperature keeping, therefore, the energy utilization efficiency is low.



Requirements for hydrogen storage materials

Hydrogen storage properties	Requirement
Capacity (mass%)	>6 %
Capacity (g/l)	>60
Hydrogen absorption rate	<5min
Hydrogen desorption rate	<3h
plateaus pressure	Near several Bar at room temp.
Security	No ignition, explosion, poison
Cyclic life	>500
Working temperature	25-100^{o}C



1.Chemical absorption

a. Metallic compounds

b. complex hydrides

c. other compounds

2.Physical adsorption

a. Carbon materials

b. **Metal-organic frameworks**

c. Molecular sieve

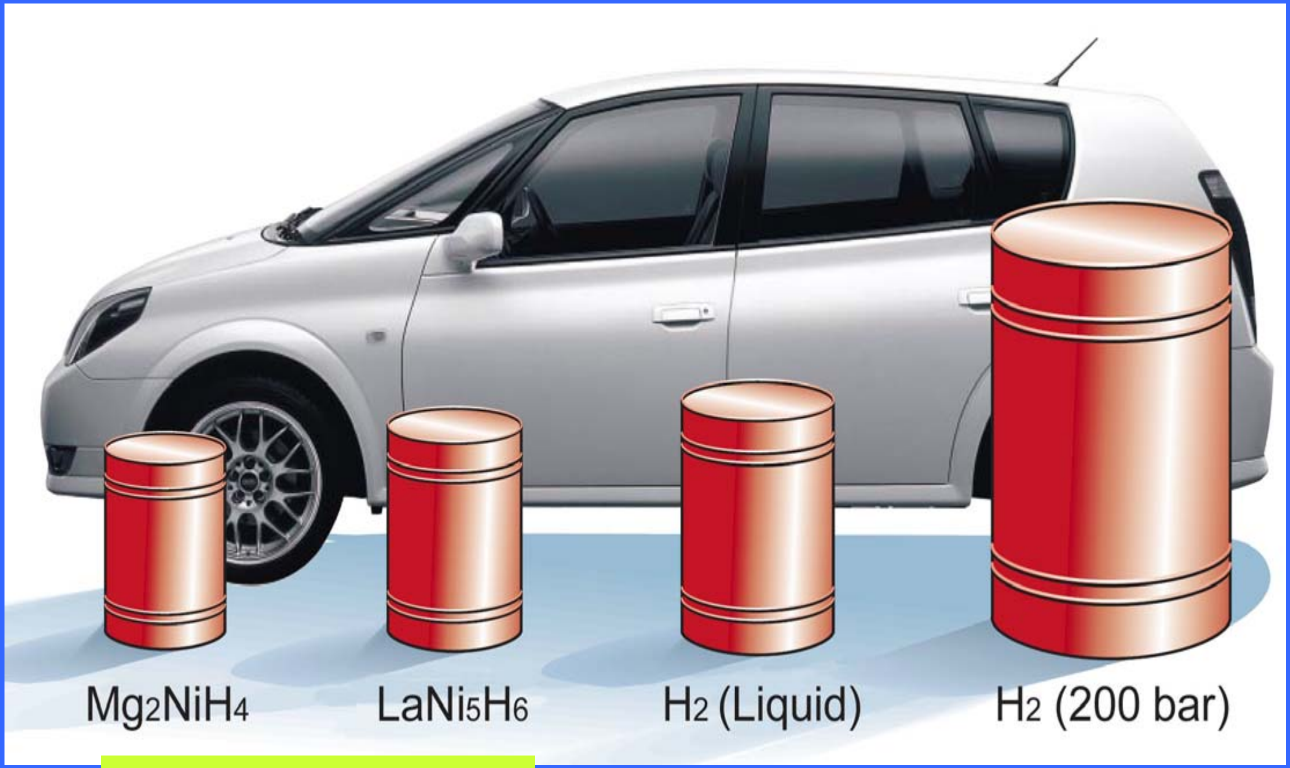
d. clathrate hydrates

Schlapbach & Züttel, NATURE , 414 (2001) 353

Intermetallic compounds and their hydrogen-storage properties

Types/Properties	AB_5	AB_2	AB	A_2B
	$LaNi_5$ (Mm, ML)	ZrM_2 , TiM_2 (M: Mn,Ni,V)	TiFe	Mg_2Ni
Storage capacity (mass %)	1.4% Low	1.8~2.4%	1.86%	3.6% High
Activation	Easy	Difficult in first process	Difficult	Difficult
Storage rate	Fast at room Temp.	Absorption and desorption at room temp.	Absorption and desorption at room temp.	low rates Working temp. > 300 C.
Cyclic life	Excellent	Poor	Poor	Fine
Stability	Excellent	Fine	Weak	Fine
Cost	High	Cheap	Cheap	Quite cheap

Volume for storage of 4 kg H2 in different states



3.6 wt%   1.4 wt%

Mg-based compounds

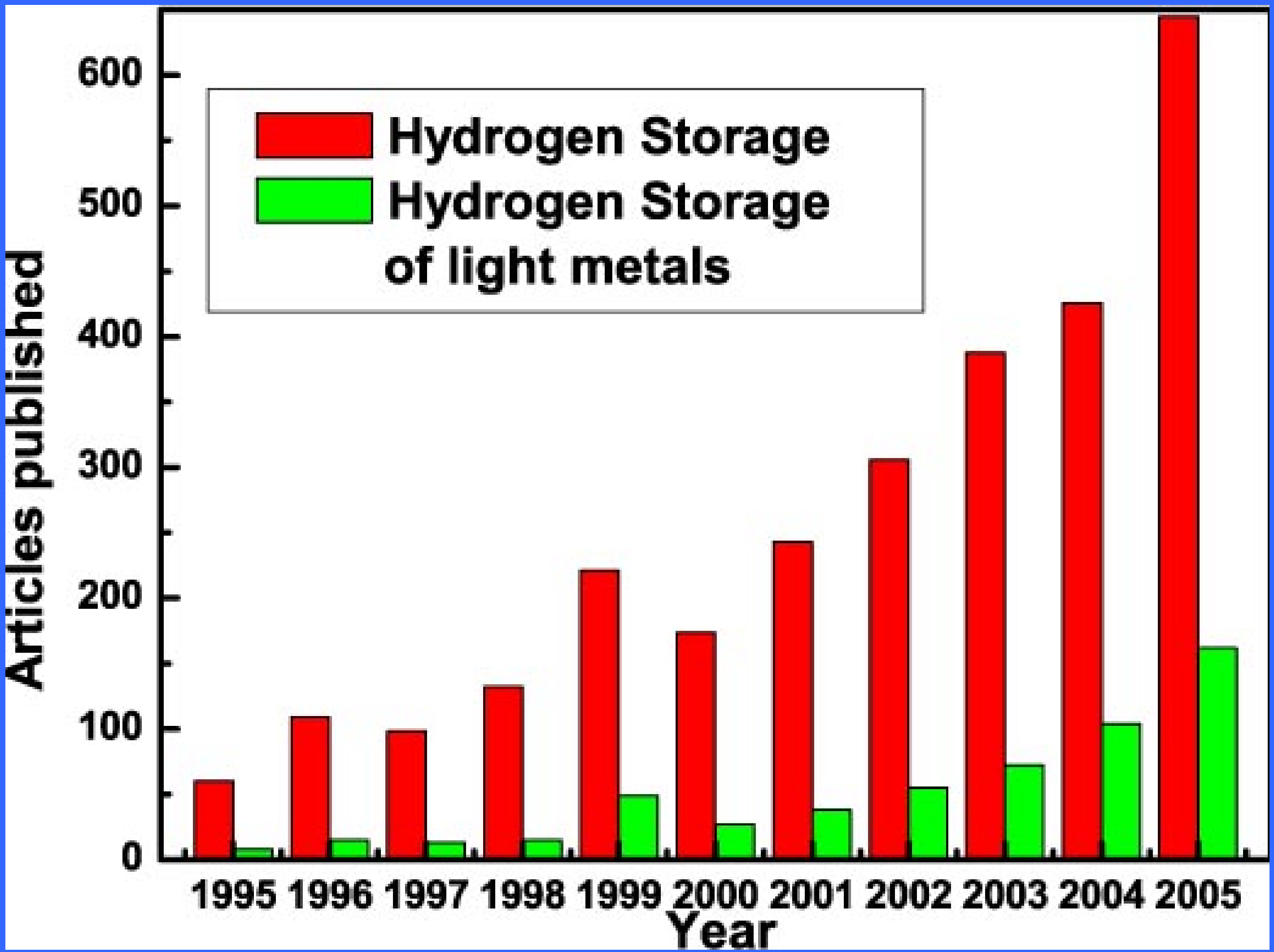
Compounds	Hydrogen storage capacity (wt%)
Mg_2NiH_4	3.6
Mg_2CoH_5	4.3
Mg_2Cu	2.4
Mg_2FeH_6	5.5
MgH_2	7.7

For improving Mg2Ni's properties, many researches are carried out and many kinds of Mg-based compounds are studied. As Mg-based compounds have high storage capacity and low cost, it will receive more and more attention in future.

Complex hydrides for hydrogen storage applications

Hydride	Mass% hydrogen	Availability
$KAlH_4$	5.8	*J. Alloy. Compd*(2003) 353,310
$LiAlH_4$	10.6	Commercially available
LiBH4	18.5	Commercially available
$Al(BH_4)_3$	16.9	*J.Am.Chem.Soc.*(1953) 75,209
$LiAlH_2(BH_4)_2$	15.3	British patents 840 572,863 491
$Mg(AlH_4)_2$	9.3	*Inorg. Chem.*(1970) 9,235
$Mg(BH_4)_2$	14.9	*Inorg. Chem.*(1972) 11,929
$Ca(AlH_4)_2$	7.9	*J.Inorg.Nucl.Chem.*(1955) 1,377
$NaAlH_4$	7.5	Commercially available
$NaBH_4$	10.6	Commercially available
$Ti(BH_4)_3$	13.1	*J.Am.Chem.Soc.*(1949),71,2488
$Zr(BH_4)_3$	8.9	*J.Am.Chem.Soc.*(1949),71,2488
Mass% of hydrogen in each molecule is based on theoretical maximum		

James A. Ritter*, Armin D. Ebner, Jun Wang, and Ragaiy Zidan, *Mater, Today* 2003, 9, 18



Paper number increase in recent ten years, red: the total paper number of all hydrogen storage materials, Green: the paper number of complex hydrides.

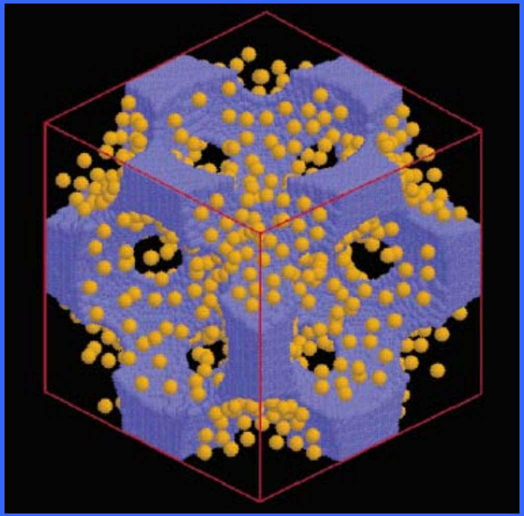
For physical adsorption group, most widely studied materials are porous materials, such as carbon materials and metal organic frameworks.

Carbon materials

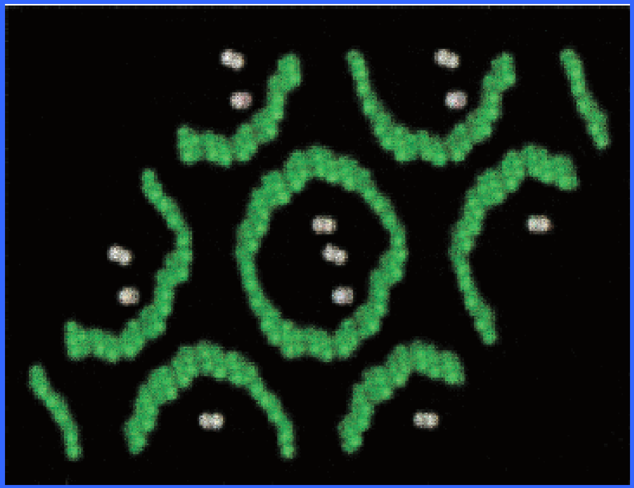
Mesoporous carbon

Carbon NTs

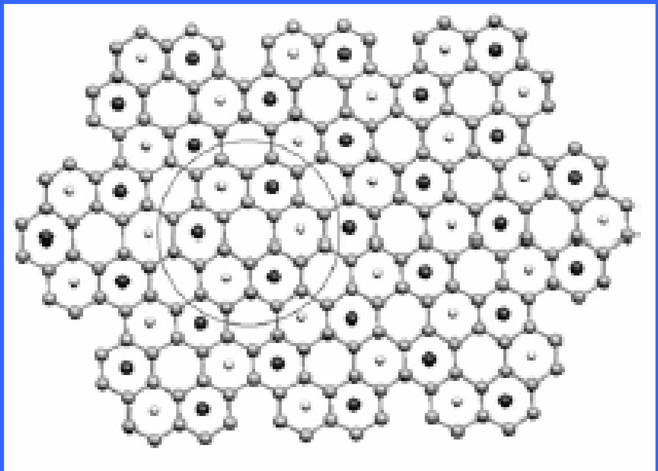
Active carbon



Nano. Lett. Vol. 4 No. 8, 2004 1489-1492



J. Am. Chem. Soc. 2001, 123, 5845



Phys. Chem. Chem. Phys., 2004, 6, 980-984

Maximum storage capacity : 1.2 mass% at room temperature 10 bar
4.5 mass% at 77 K at 10 bar

Hydrogen storage in metal-organic frameworks

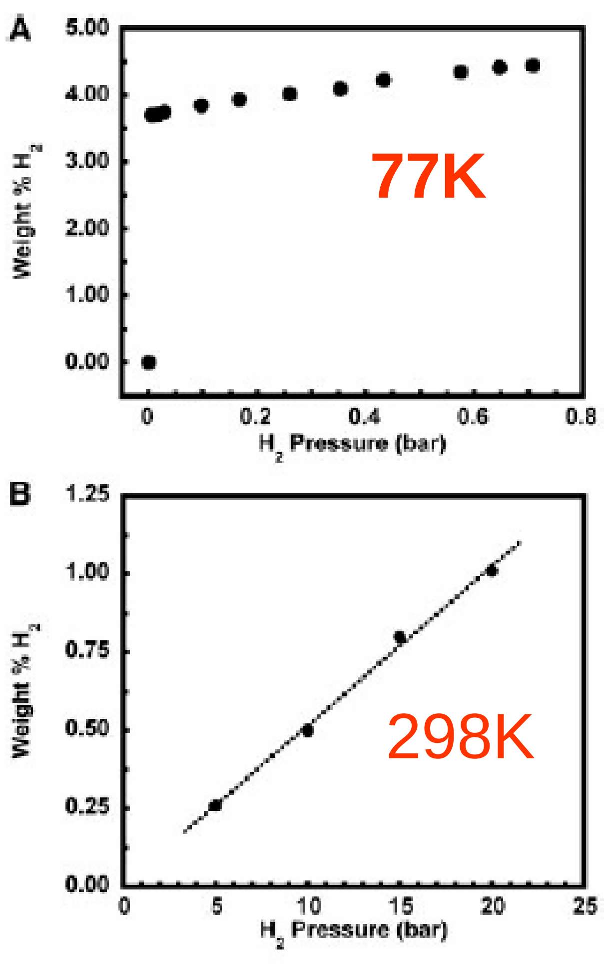


Fig. 2. Hydrogen gas sorption isotherm for MOF-5 at (A) 78 K and (B) 298 K.

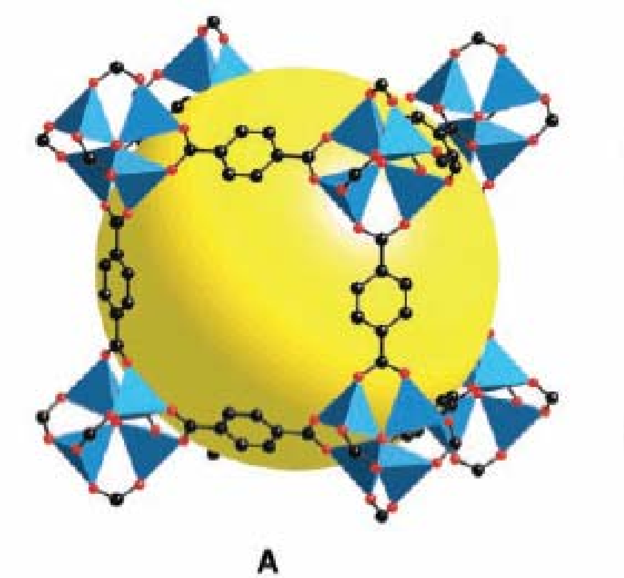


Fig. 1. Single-crystal x-ray structures of MOF-5

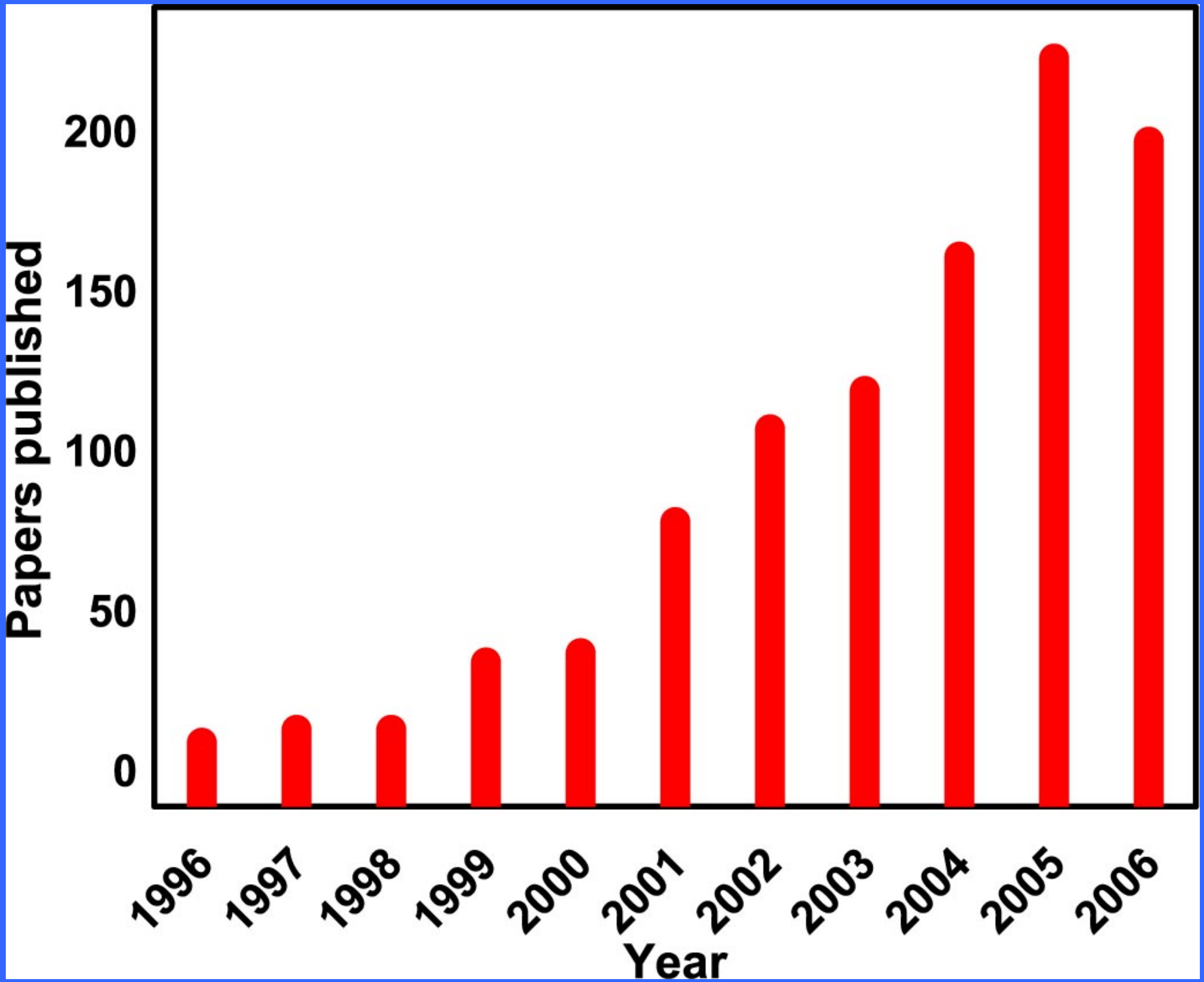
Huge specific surface area: 3000 m^2/g

Pore diameter : 1.3 nm

Max storage at 77K : 4.5% at 1 bar

at room temp.: 1.0 at 20 bar

Yaghi O.M. etc. al. Science Vol 300 2003 1127-1129



Published paper numbers of hydrogen storage in porous materials

Summary

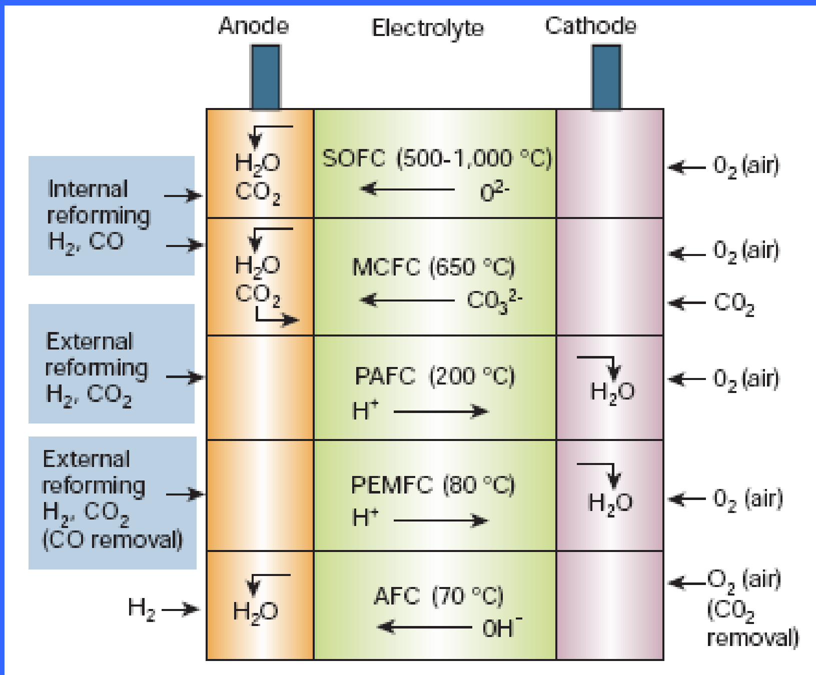
1) Hydrogen storage materials have chemical storage and physical storage types. Actually applied ones are in chemical storage.

2) Hydrogen storage capacity of conventional metallic compounds is lower than 2 mass%, and materials with capacity larger than 5% are explored. Mg-based alloys and complex hydrides are most expected to get high storage capacity.

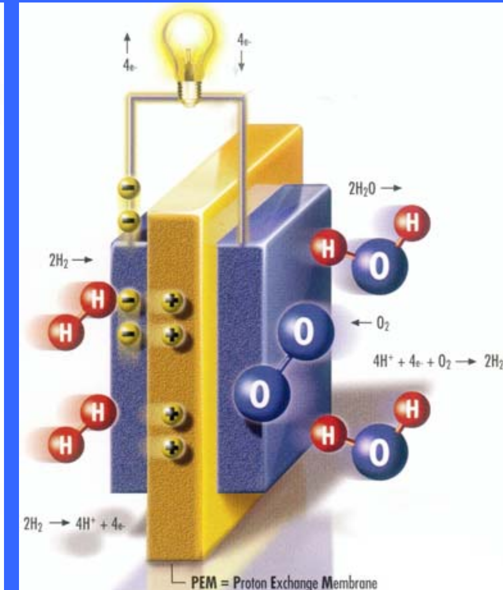
3) Porous materials such as carbon materials and metal-organic frameworks are studied with special interest in their different storage mechanism. For these materials, hydrogen storage usually needs high pressure and low temperature.

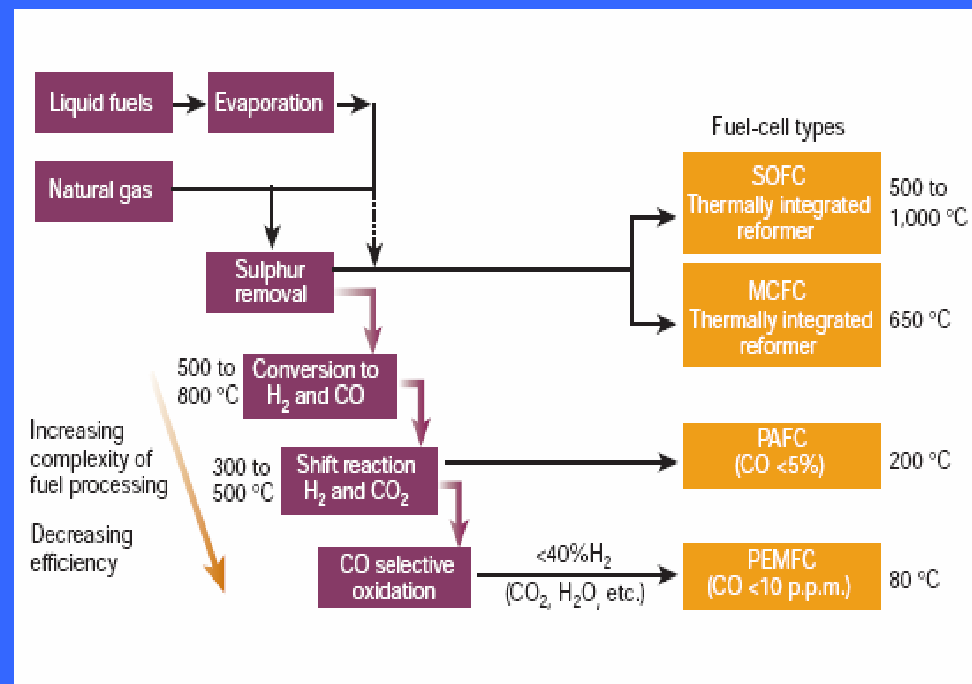

Thank you very much
for your kind
attention !

Fuel cell battery



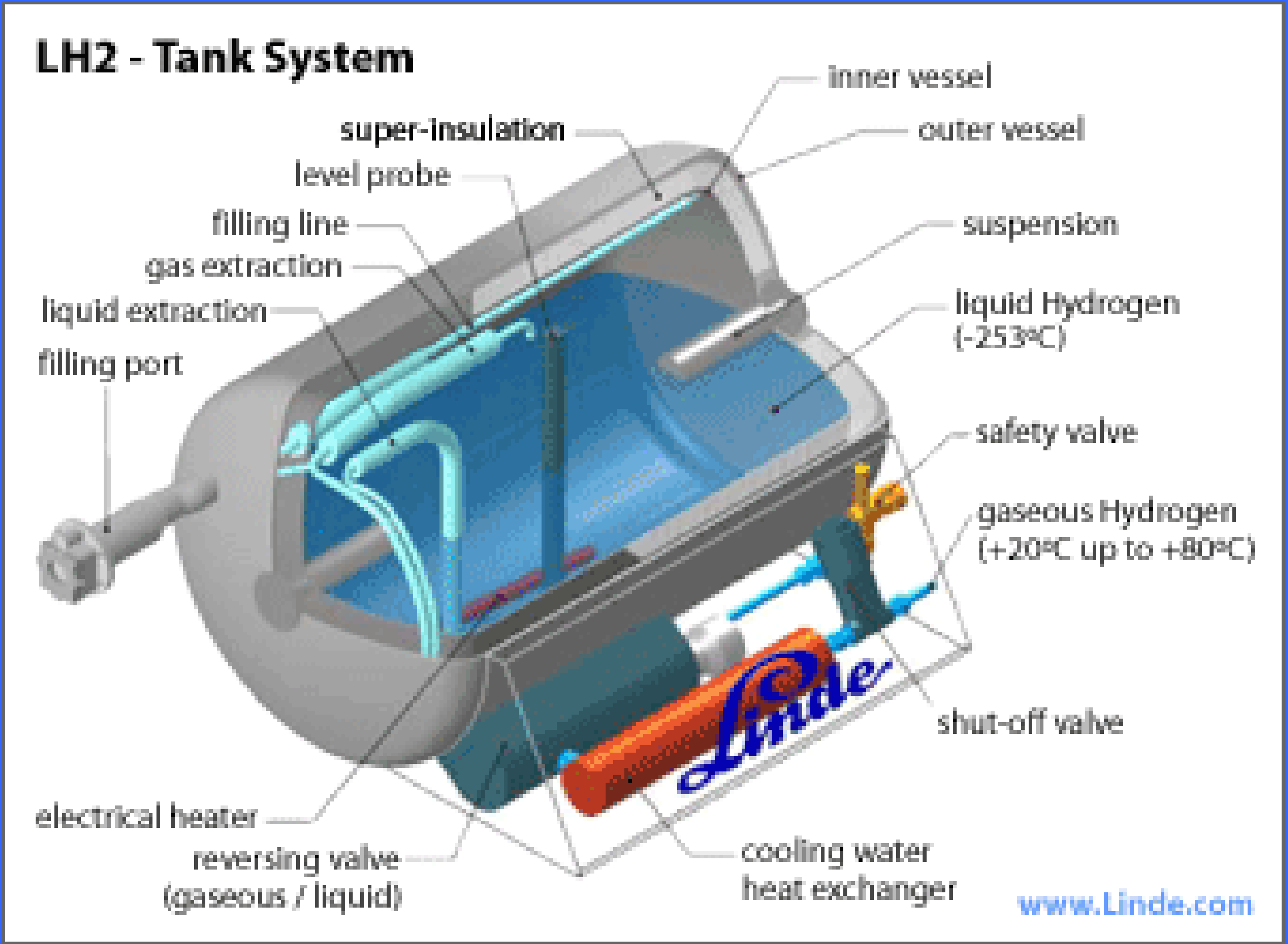
Summary of fuel-cell types.

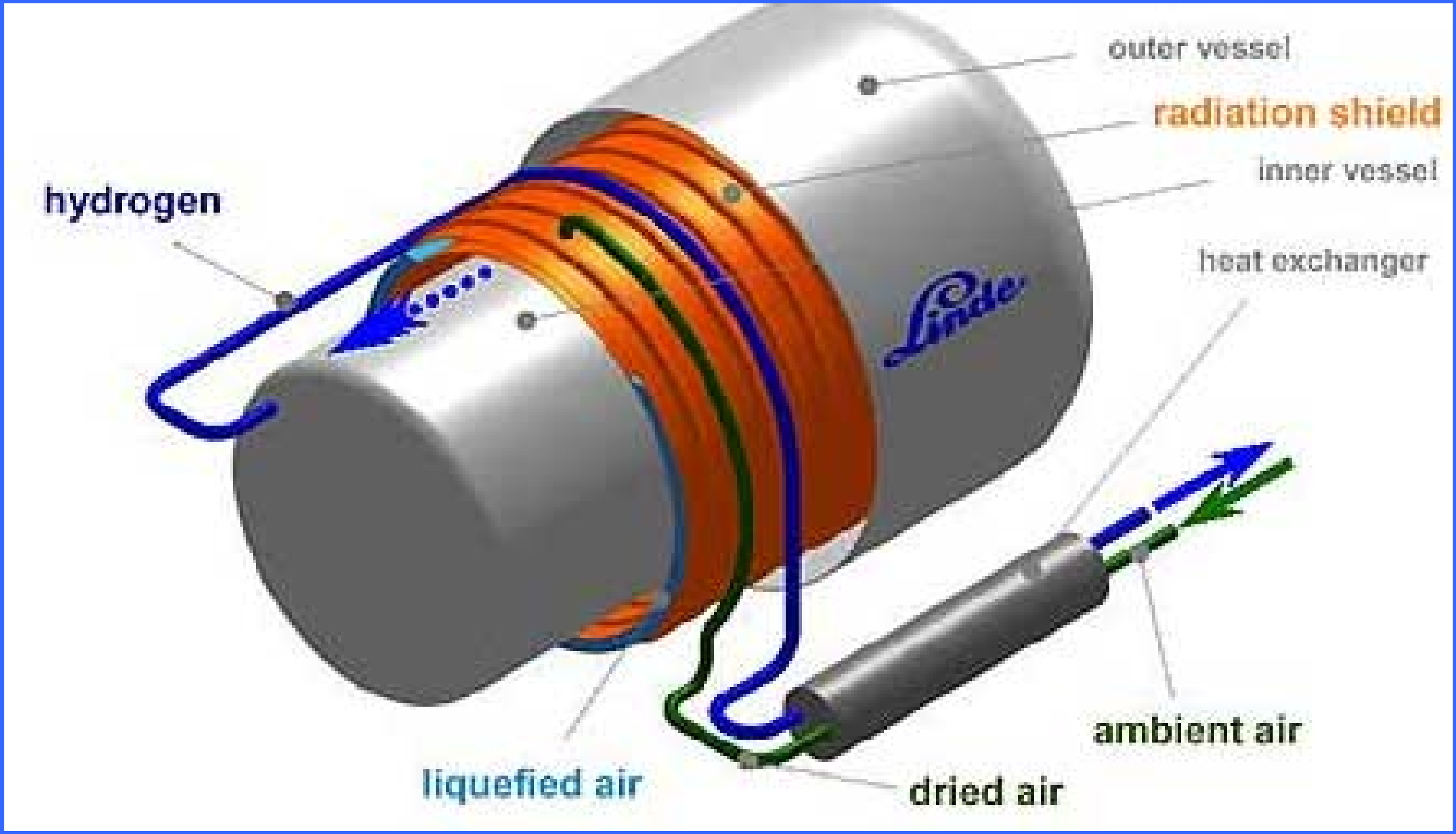




Fuel-cell types and fuel processing.

Brian C. H. Steele et.al, ***Nature.,*** 2001,414, 345-352


LH2 - Tank System
inner vessel
super-insulation
outer vessel
level probe
filling line
suspension
gas extraction
liquid extraction
liquid Hydrogen
(-253°C)
filling port
safety valve
gaseous Hydrogen
(+20°C up to +80°C)
Linde
shut-off valve
electrical heater
reversing valve
(gaseous / liquid)
cooling water
heat exchanger
www.Linde.com


outer vessel
radiation shield
inner vessel
hydrogen
heat exchanger
ambient air
dried air
liquefied air


LIQUIFIED HYDROGEN
FLAMMABLE GAS
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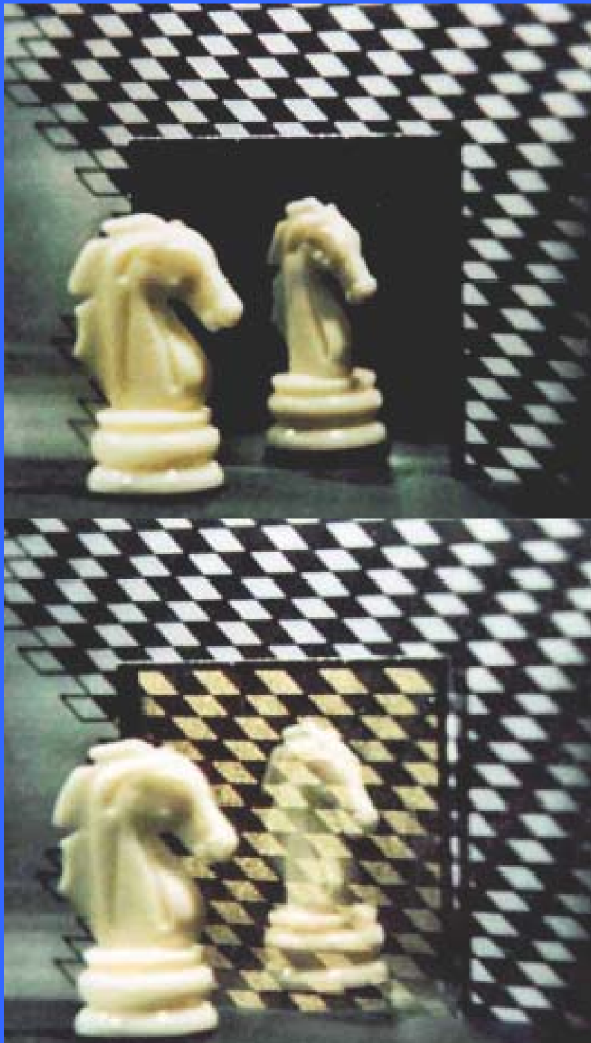
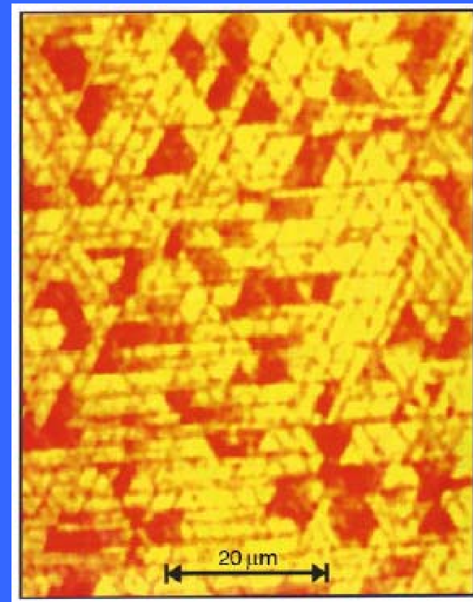
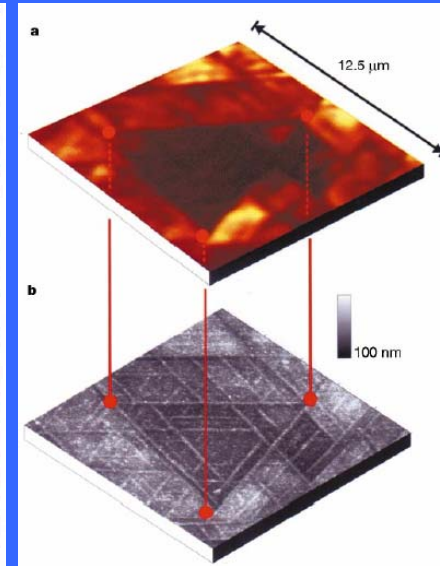
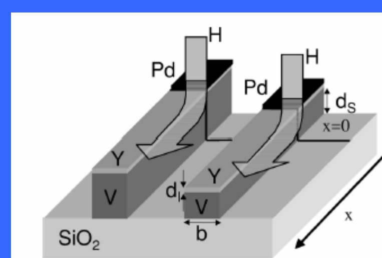


Switchable Mirrors

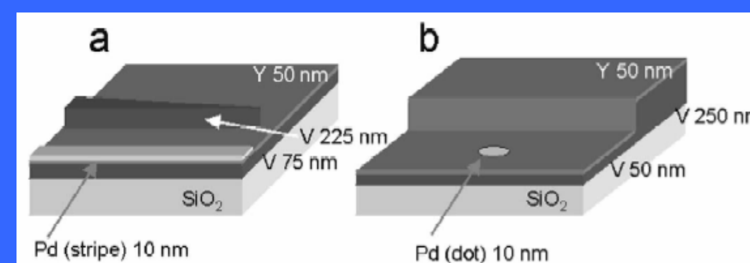


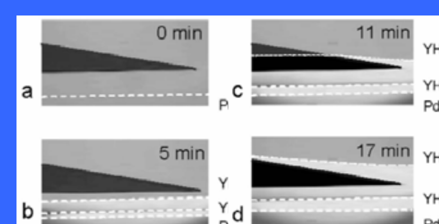


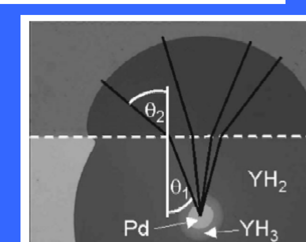
Optical domain switching. 400-nm-thick Y film capped with 7 nm of Pd

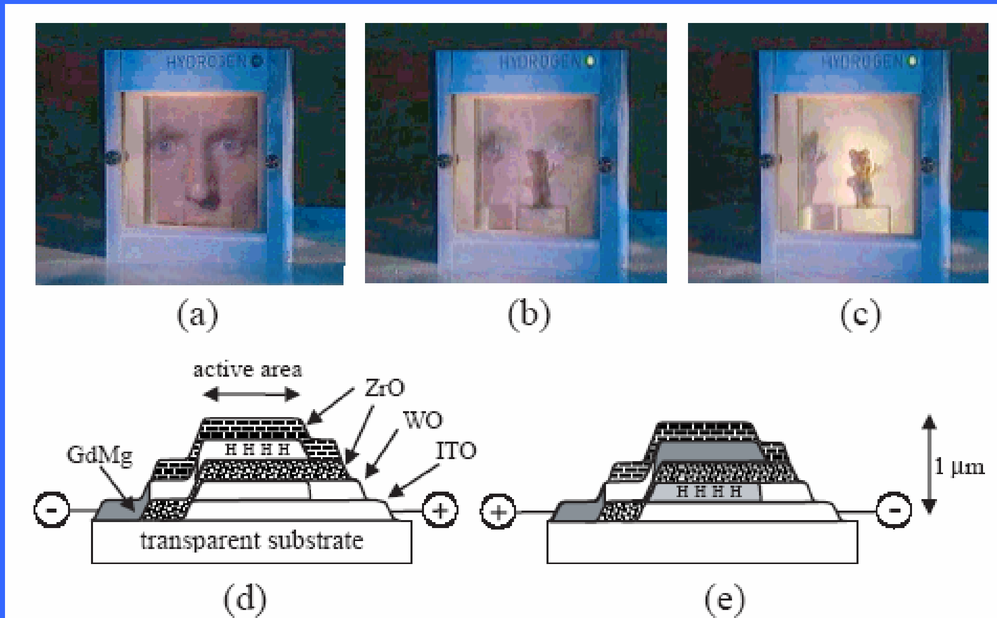


Visualization and control of hydrogen diffusion in transition metals

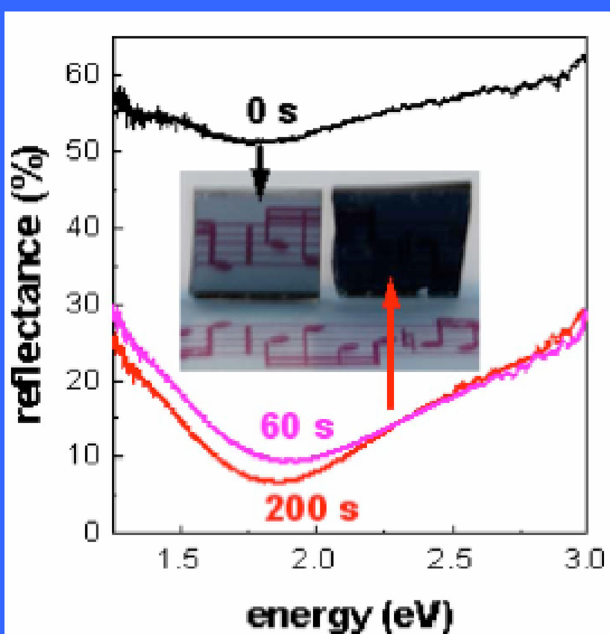




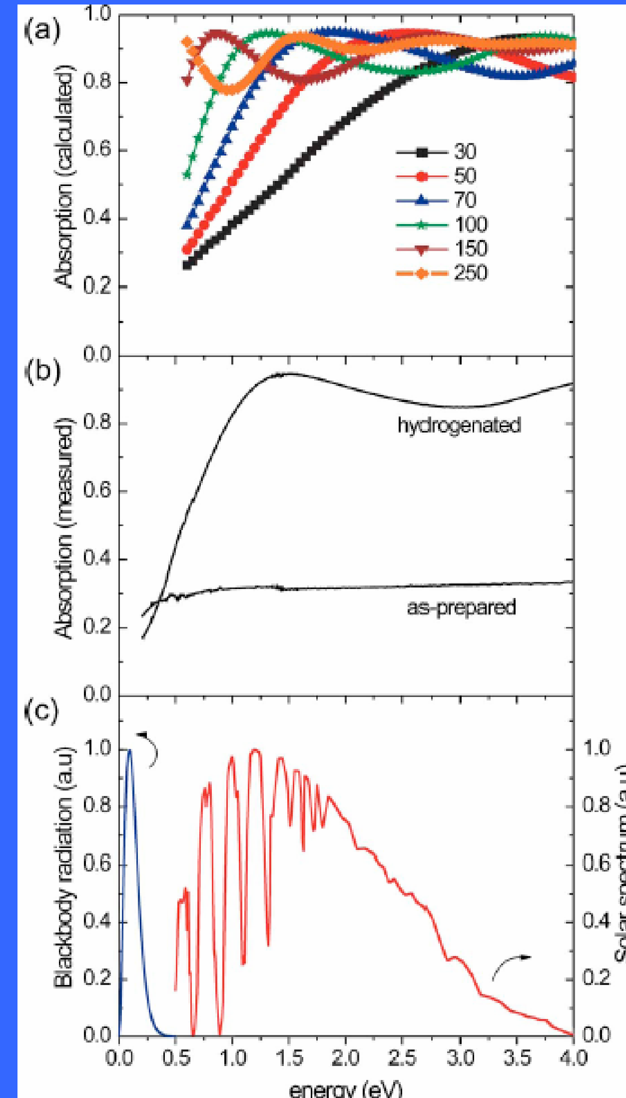




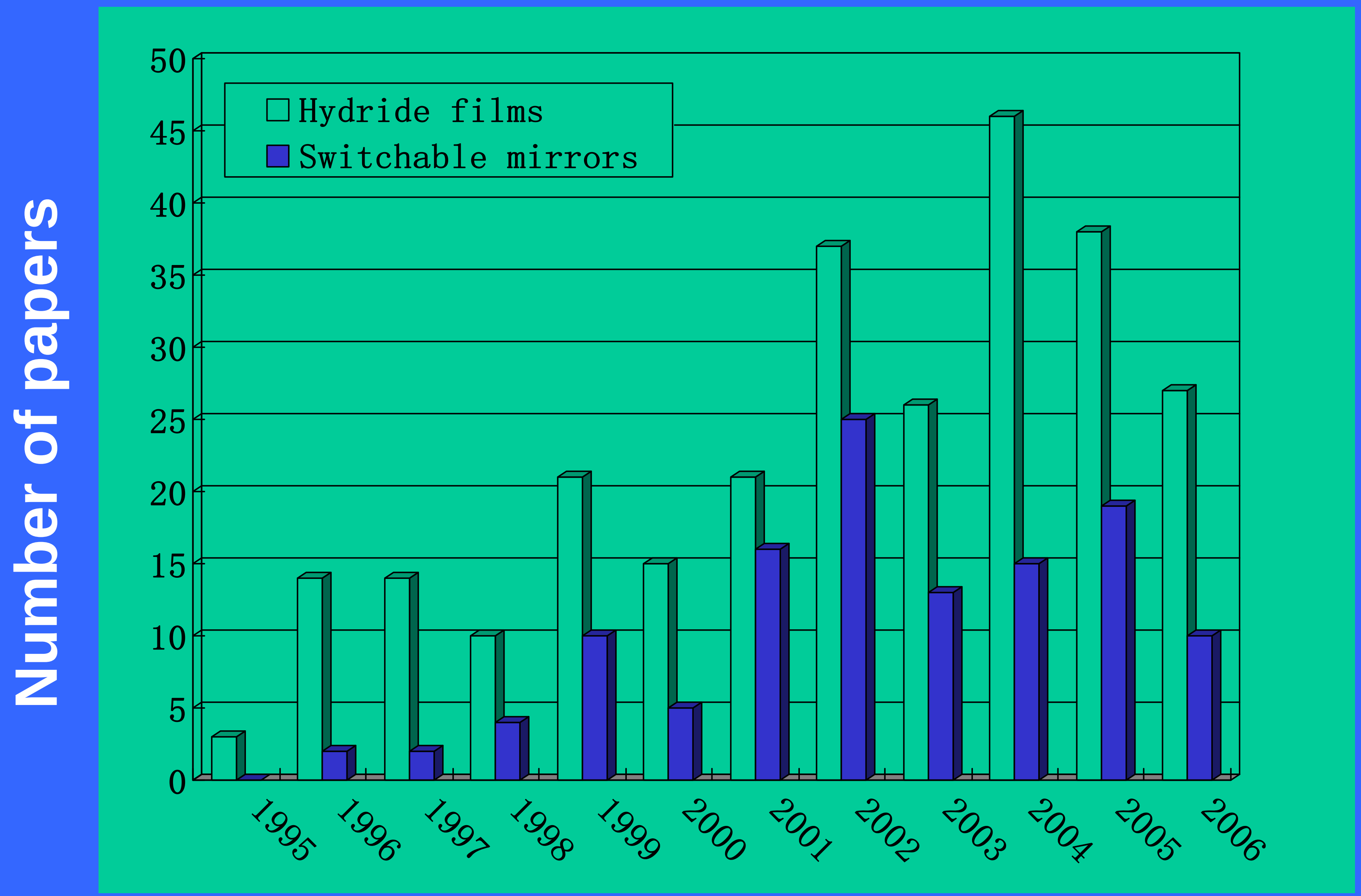
Reversible optical switching device



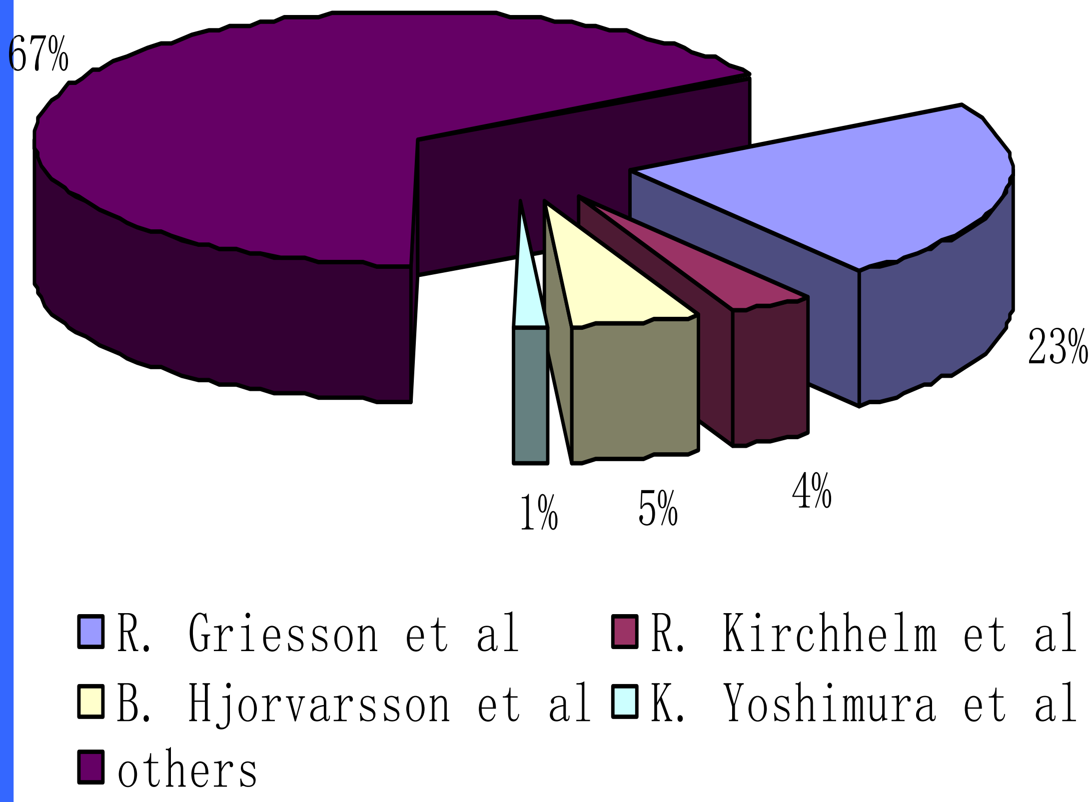
Mg_2NiH_4 / Ti / Pd thin films for optical hydrogen sensing



Mg–Ti–H thin films for smart solar collectors



Statistic of published papers on hydride films and switchable mirrors



Main research groups in the world on hydride films

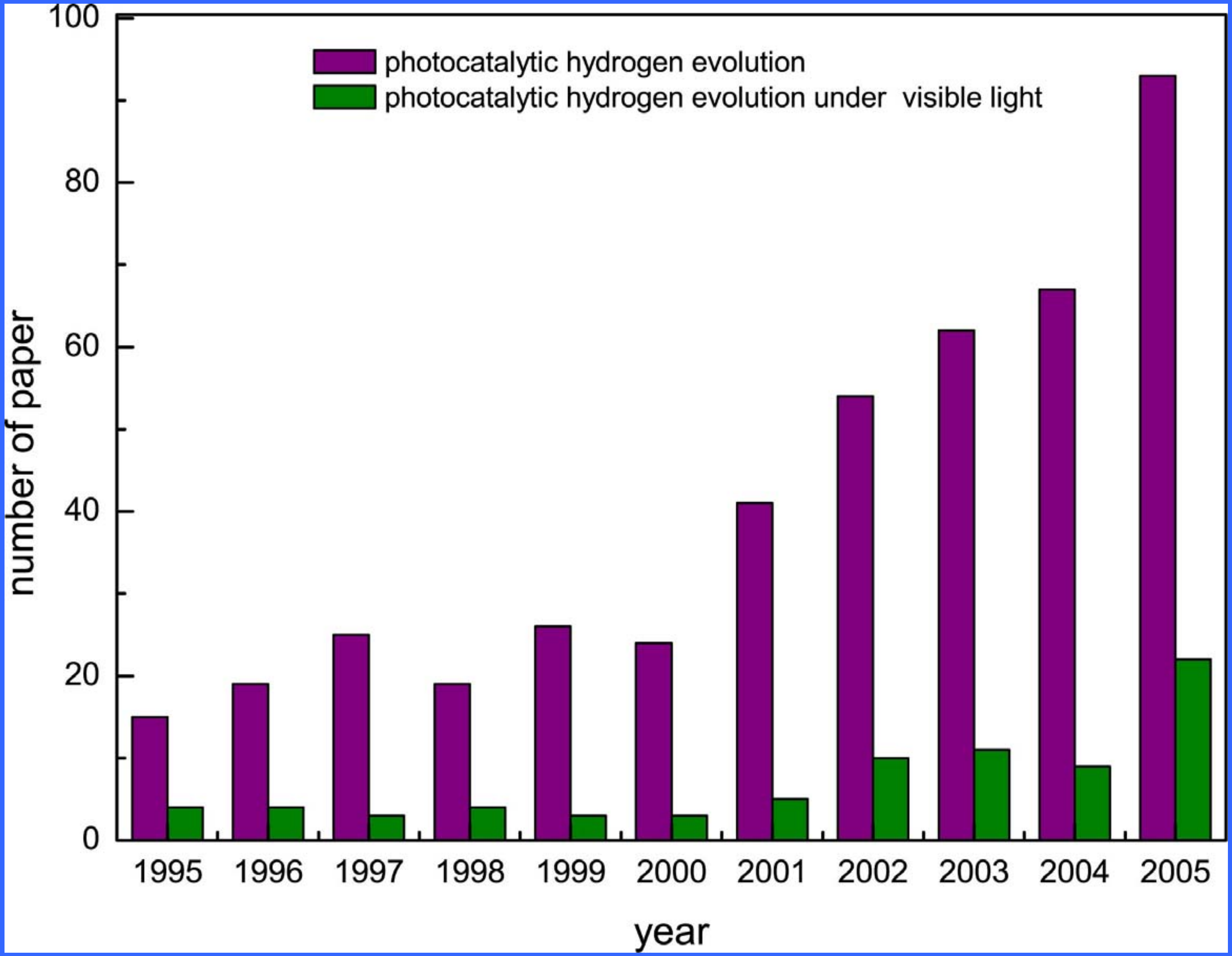
Photocatalytic hydrogen evolution under UV light

Species	photocatalyst	Band gap (eV)	Quantum efficiency （%）	Rate of hydrogen evolution （mmol/h)
Oxide and Nitride	NiO/TiO_2	3.2	-	0.16
	RuO_2-$ZnGa_2O_4$	2.8	-	1
	$CdS/K_2Ti_{3.9}Nb_{0.1}O_9$	3.0	-	4.7
	RuO_2/Ge_3N_4	3.8-3.9	9	0.47
Titanate	$La_4CaTi_5O_{17}$	3.8	20	0.5
	Ni(4%)-$Rb_2La_2Ti_3O_{10}$	3.4-3.5	30	0.3
	$RuO_2/Ba_2Ti_4O_9$	3.5	-	1.4
Tantalate	NiO(0.2%)-La(2%)-$NaTaO_3$	4.1	-	2.2
	$NiO/Sr_2Ta_2O_7$	4.6	-	1.0
Niobate	Ni(0.1%)-$K_4Nb_6O_{17}$	3.3	5	0.073
	Pt/(Ca,Sr)2Nb2O7	4.1-4.3	-	0.42

Photocatalytica hydrogen evolution under visible light

species	photocatalyst	Band gap (eV)	Quantum efficiency （%）	Rate of hydrogen evolution （umol/h)
Oxide	NiO-$In_{0.9}Ni_{0.1}TaO_4$	2.3	0.66	16.6
	$PbBi_2Nb_2O_9$	2.9	0.95	7.6
	Cr-$Ba_2In_2O_5/In_2O_3$	2.9-3.0	0.3	0.03
Nitride	Rh2-yCryO3-(Ga1-xZnx)($N_{1-x}O_x$)	2.68	-	358
	$LaTiO_2N$	2.1	1.5	8
	Pt(0.15%)-$Y_2Ta_2O_5N_2$	2.2	-	10
	Ru(0.25%)-$Y_2Ta_2O_5N_2$	2.2	-	50
	Pt(0.15%)- Ru(0.25%)-$Y_2Ta_2O_5N_2$	2.2	-	250
	GaN:ZnO	2.6	0.14	0.06
Sulfide	$Zn_{0.999}Ni_{0.001}S$	2.3	-	380
	ZnS-$CuInS_2$-$AgInS_2$	2.3	7.4	2300

The number of papers on photocatalytic hydrogen evolution

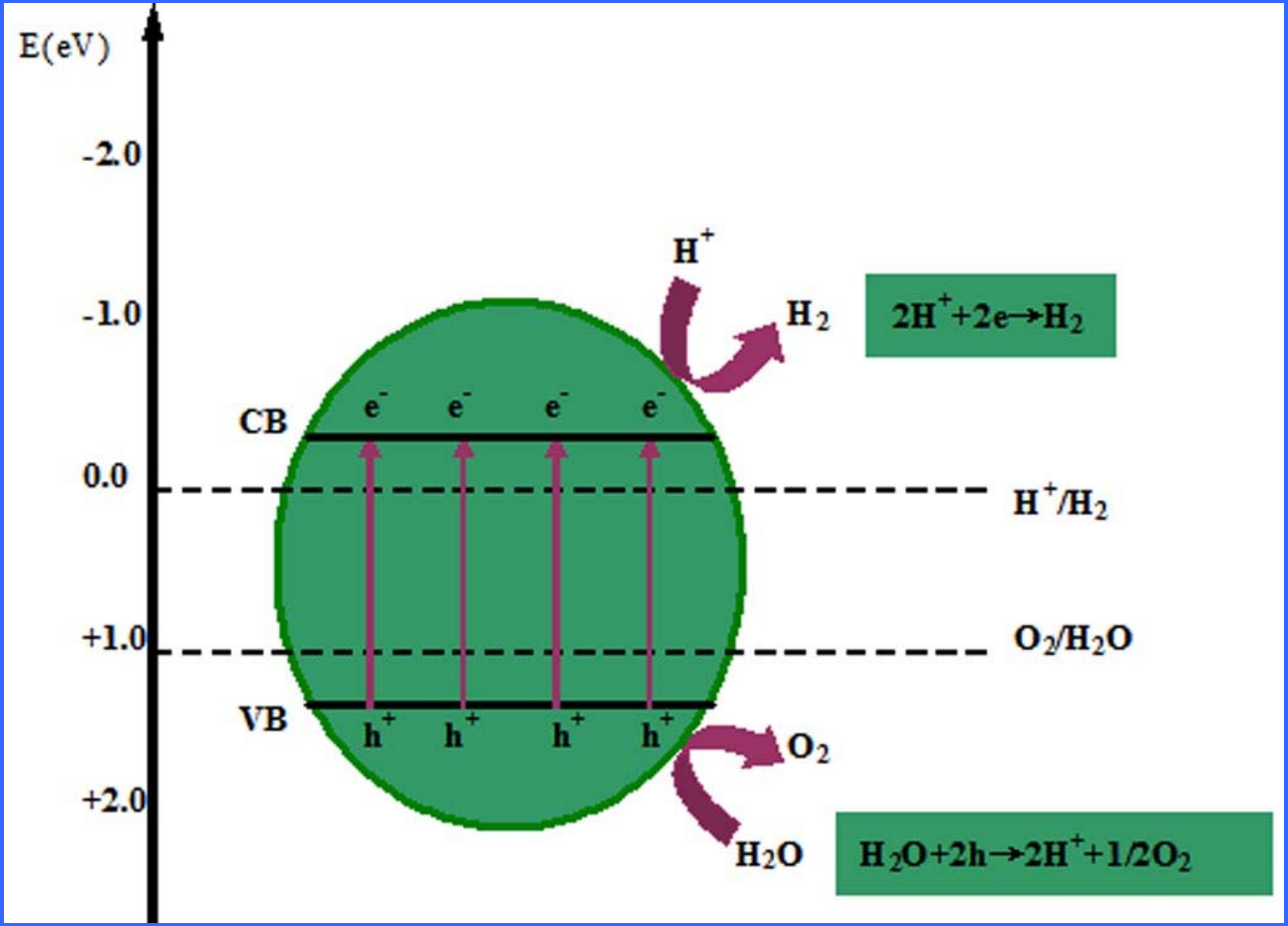


Intermetallic compounds and their hydrogen-storage properties

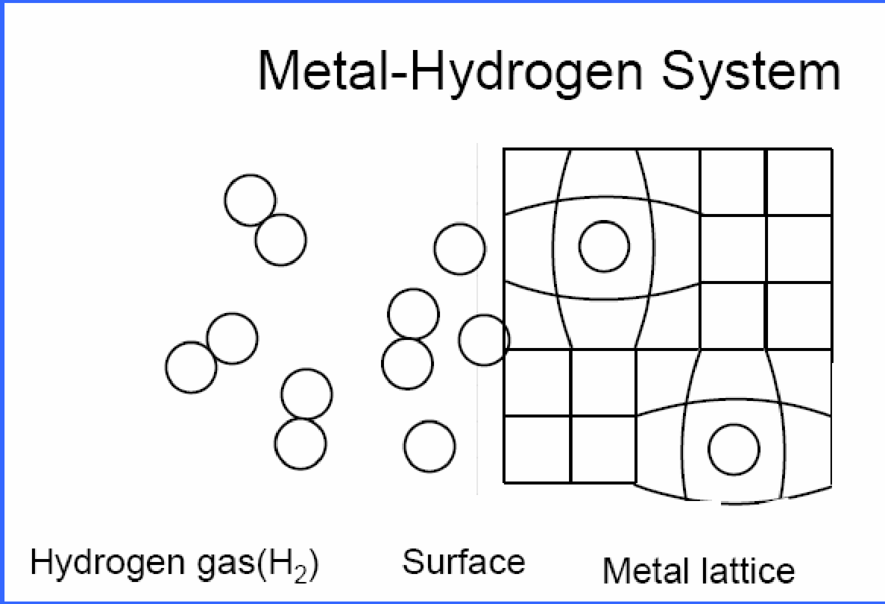
Type	Metal	Hydride	Structure	mass%	p_{eq}, T
Elemental	Pd	$PdH_{0.6}$	*Fm3m*	0.56	0.020 bar, 298 K
AB_5	$LaNi_5$	$LaNi_5H_6$	*P6/mmm*	1.37	2 bar, 298 K
AB_2	ZrV_2	$ZrV_2H_{5.5}$	*Fd3m*	3.01	10^{-8} bar, 323 K
AB	FeTi	$FeTiH_2$	*Pm3m*	1.89	5 bar, 303 K
A_2B	Mg_2Ni	Mg_2NiH_4	*P6222*	3.59	1 bar, 555 K
Body-centred cubic	TiV_2	TiV_2H_4	b.c.c.	2.6	10 bar, 313 K

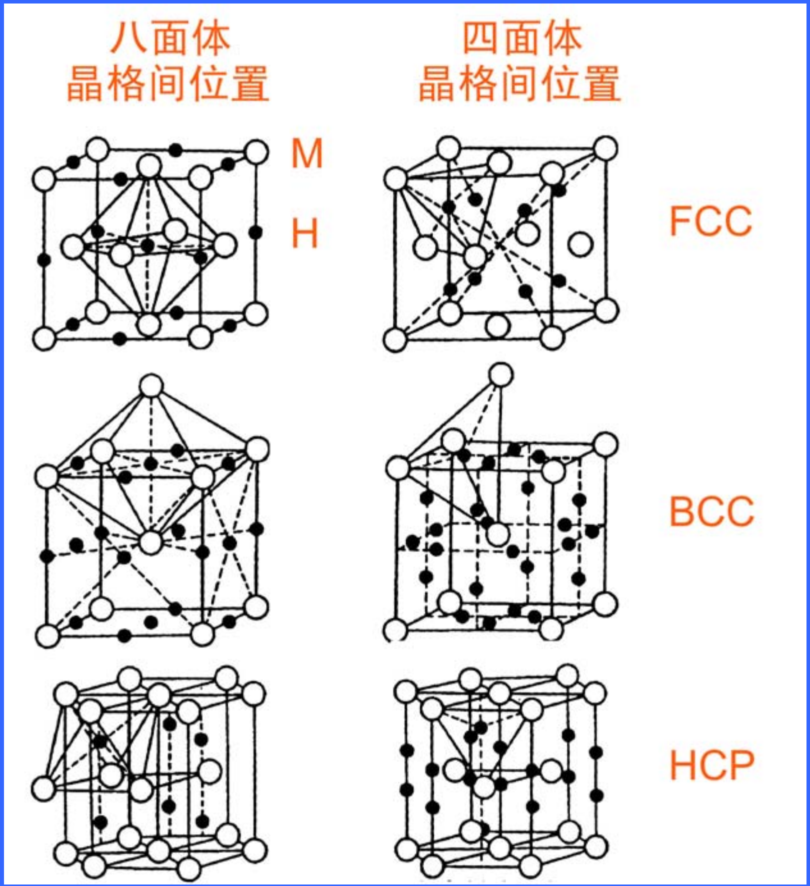
Louis Schlapbach* & Andreas Züttel, *Nature* 2001, 414, 353.

mechanism of photocatalytic hydrogen evolution



氢气在晶体中的位置





大角泰章 水素吸藏合金の基礎

1997.1 大阪

Some results in this area

- Yaghi O.M. ect. al.
  - Many MOFs based on the $[Zn_4O]^{6+}$ units
  - Large specific surface area. Max storage 4.5
- Long J. R. ect. al.
  - Prussian blue analogues
  - Strong interaction. 6.9-7.4 kJ/mol about 50% higher than MOF-5
- Kubota Y. ect. al.
  - [Cu2(pzdc)2(pyz)]n (pzdc=pyrazine-2,3- icarboxylate, pyz=pyrazine),
  - Direct Observation of Hydrogen Molecules Adsorbed
- And so on.