Institute of Problems of Chemical Physics of RAS
Laboratory of Hydrogen Storage Materials

MATERIALS FOR HYDROGEN STORAGE IN BOUNDED STATE

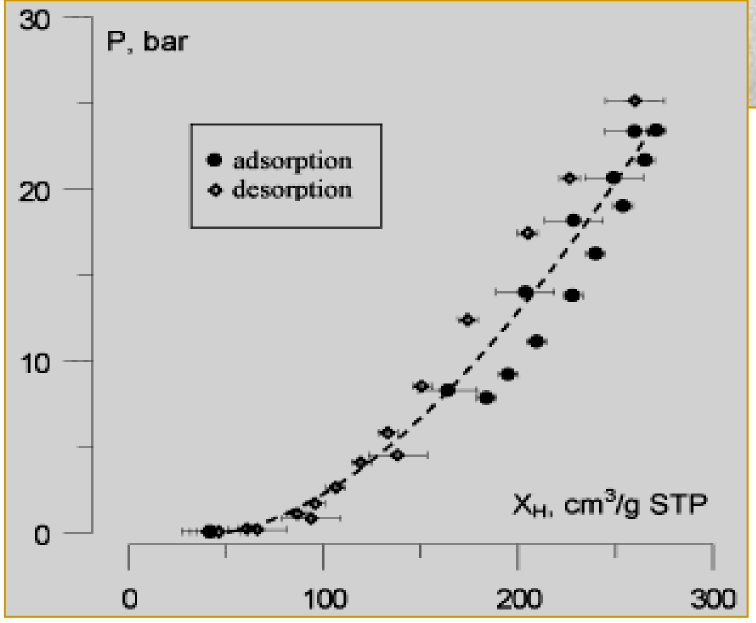
Boris P. Tarasov
Tel./Fax: +7 496 522 1743
E-mail: tarasov@icp.ac.ru

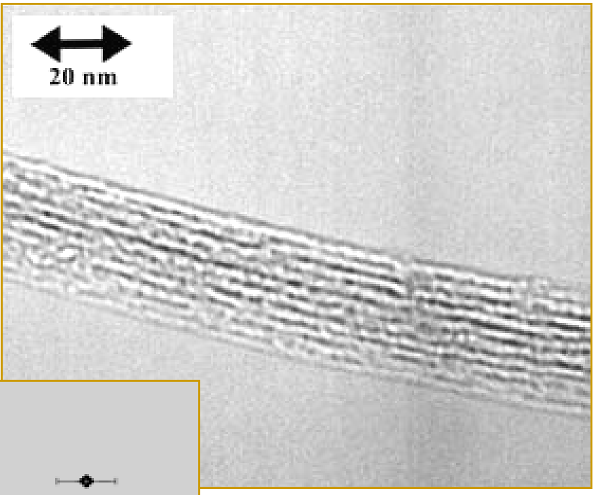
Methods for hydrogen storage in bounded state

Hydrogen sorbents	Reversible hydrides and organic compounds	Irreversible hydrides and compounds	Water reacting metals and hydrides
Activated carbon, Carbon nanotubes and nanofibers, Metal-organic frameworks, Ceolites, Clatrates, ...	Metals, Intermetallides, Alloys, Organic compounds, Nanocomposites: metal hydrides, MH–MNH_2, MH–carbon, MH–organic comp., …	AlH_3, NH_3BH_3, $LiAlH_4$, $LiBH_4$, $LiNH_2$, H_2O, CH_3OH, CH_3OCH_3, CH_4, C_2H_4, …	Al, AlH_3, Mg, MgH_2, Ca, CaH_2, $LiAlH_4$, $NaBH_4$, NaH, LiH, Al + LiH, Si + LiH, …

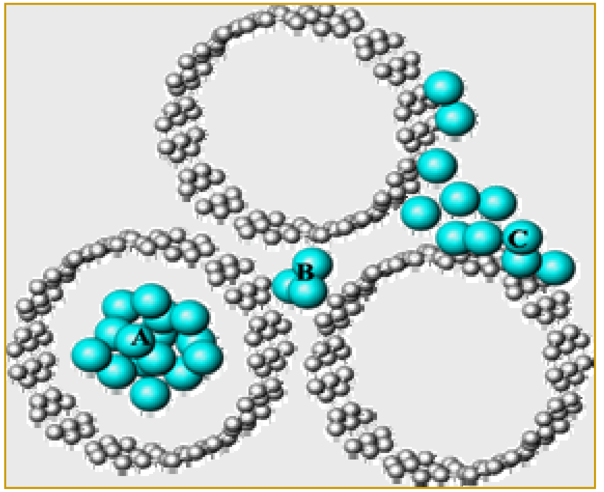
Hydrogen sorption by carbon nanotubes and nanofiberes

H_2 sorption-desorption isotherms at 77 K





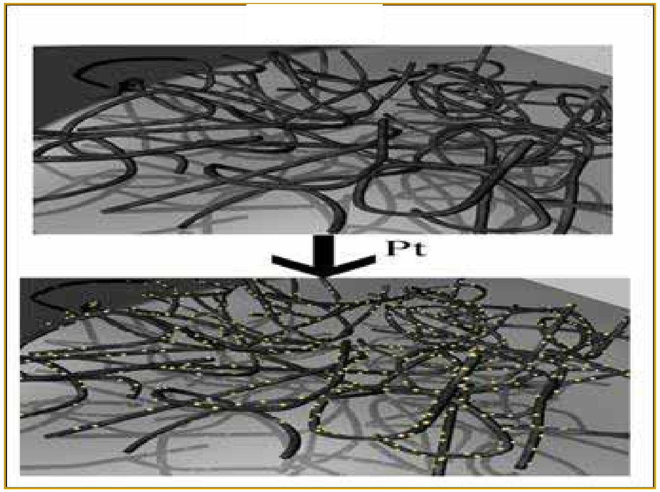
SWNT bundle

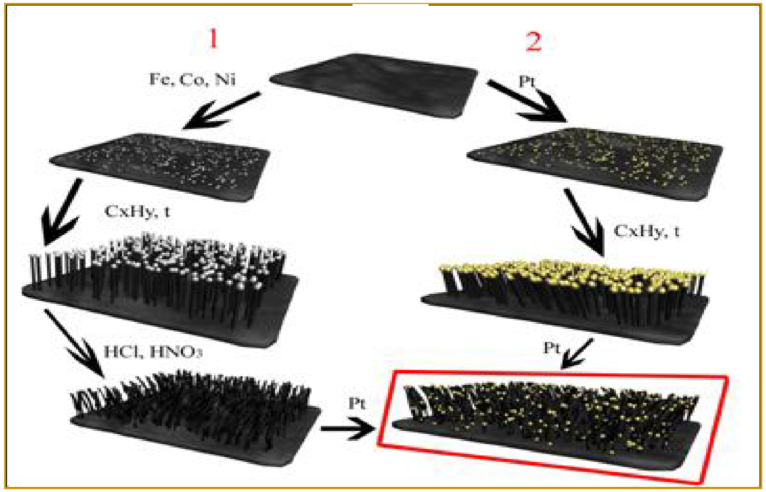


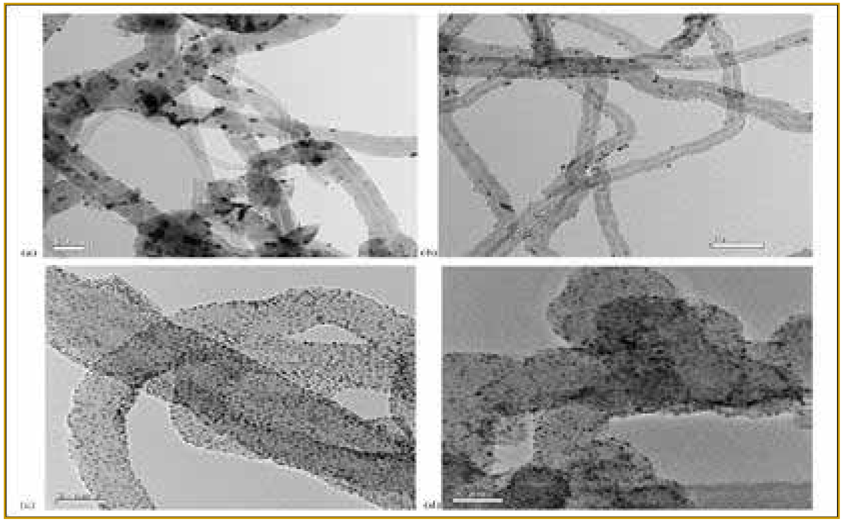
Available places of hydrogen location

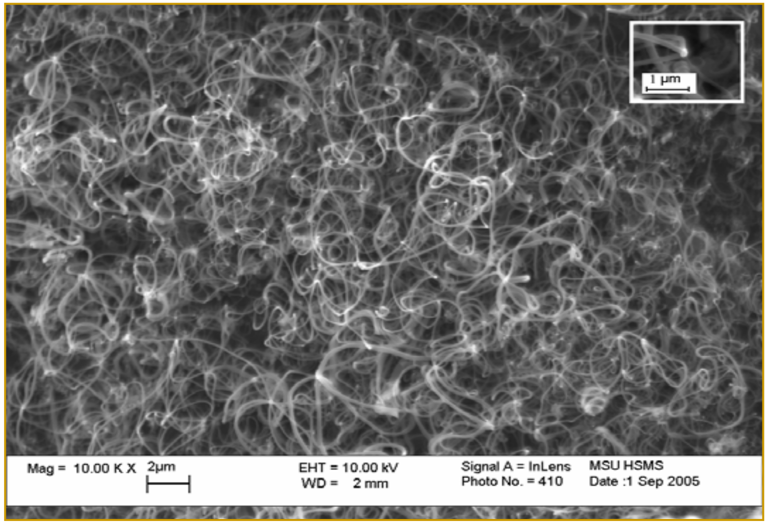
Tarasov B.P., Maehlen J.P., Lototsky M.V., Muradyan V.E., Yartys V.A. Hydrogen sorption properties of arc generated single-wall carbon nanotubes. *J. Alloys Comp.* 2003. V. 356–357. P. 510–514.

Platinum-coated CNM as hydrogen sorbents and electrocatalysts for PEMFC

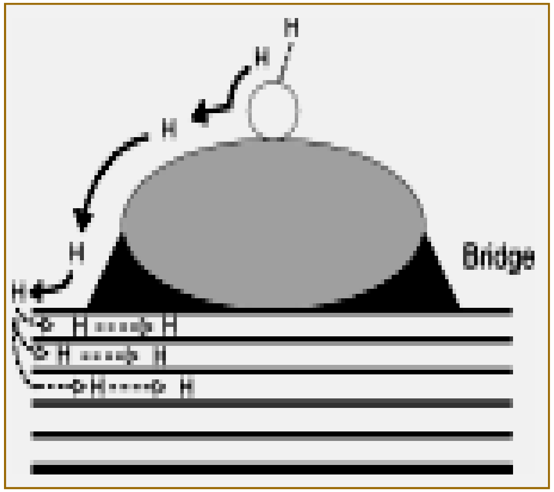


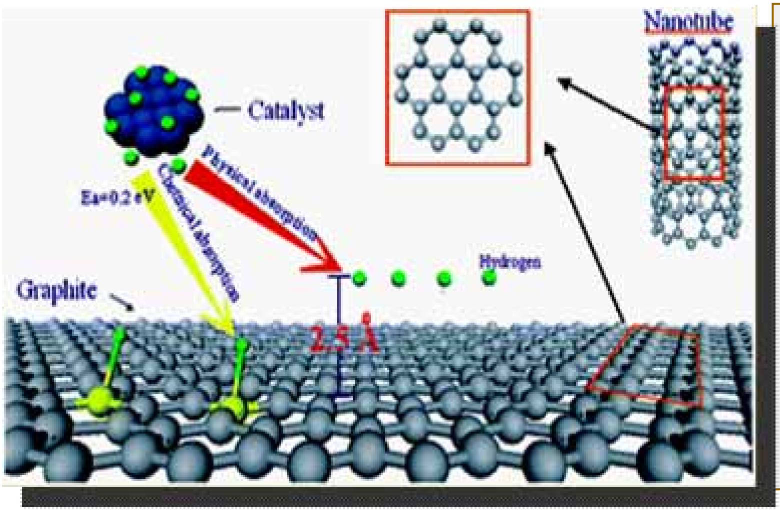


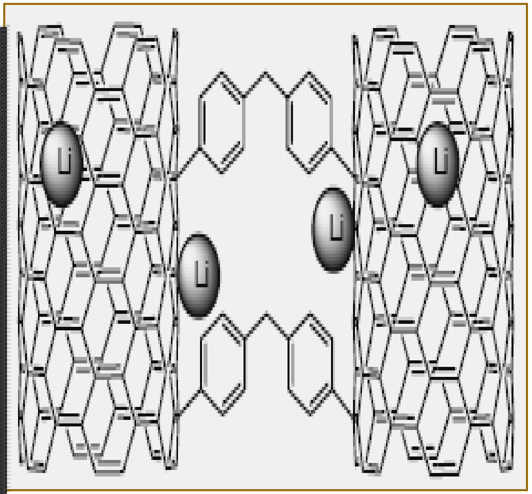


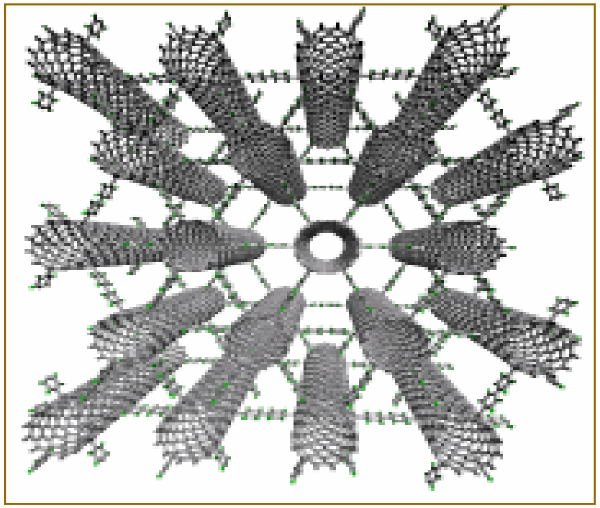


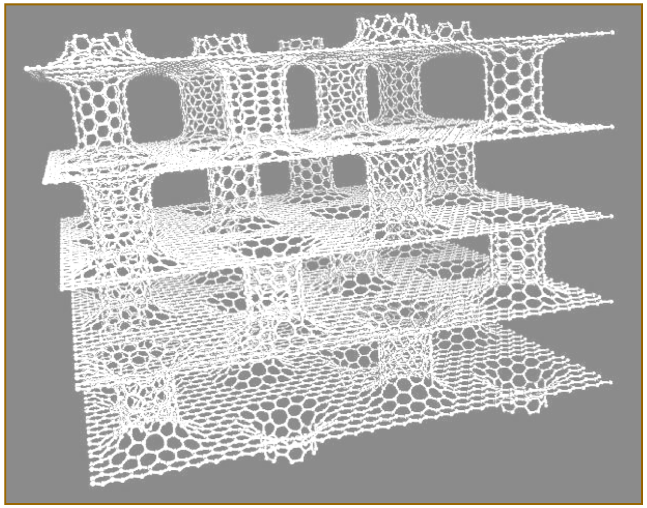
New hydrogen sorbents based on carbon nanomaterials

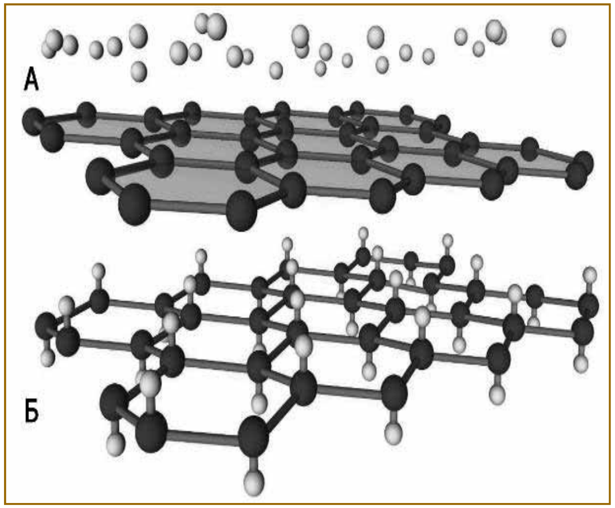




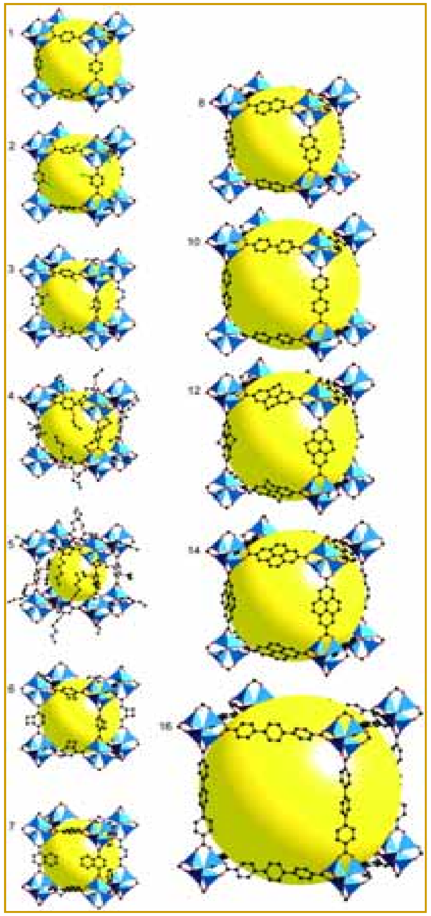


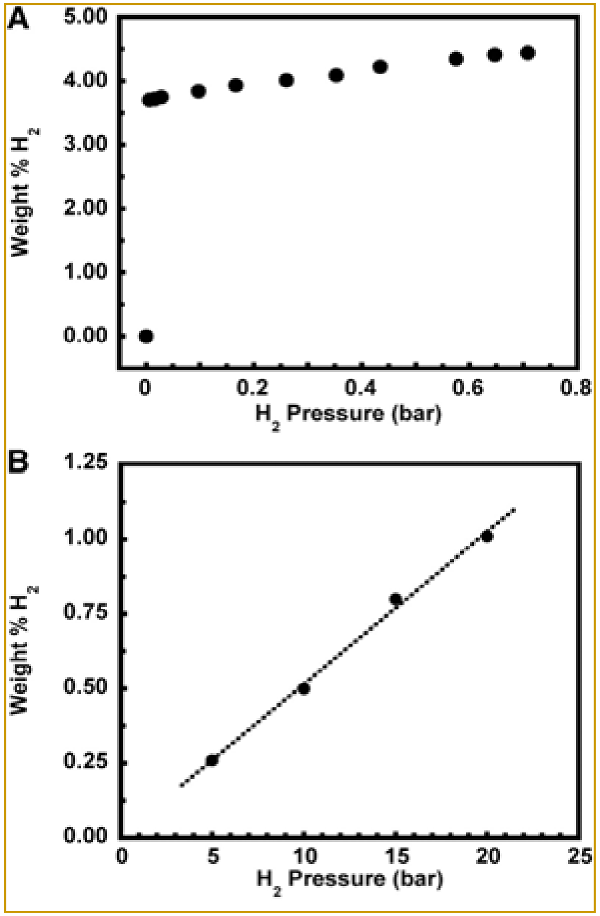


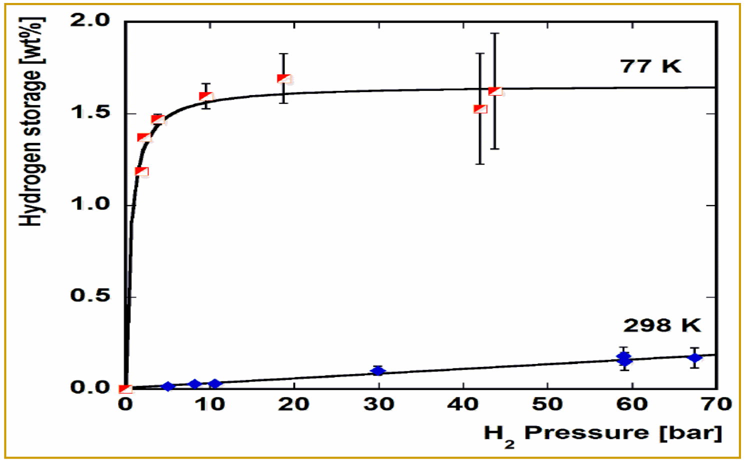




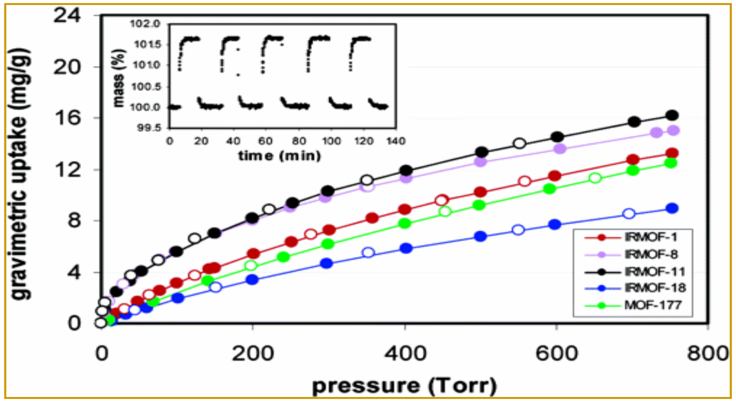
Metal-organic frameworks (MOF)





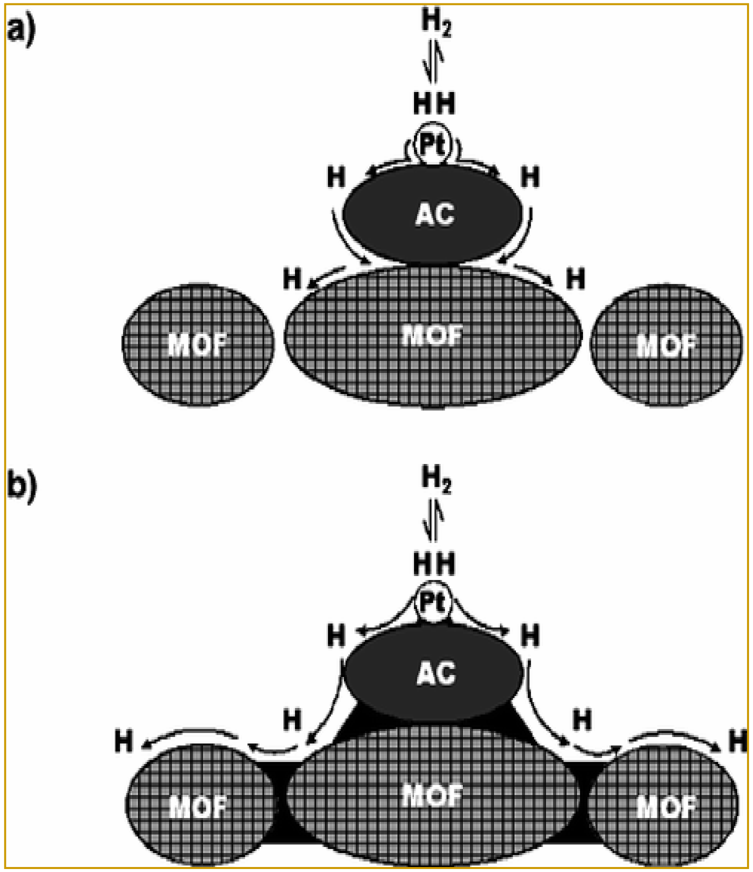


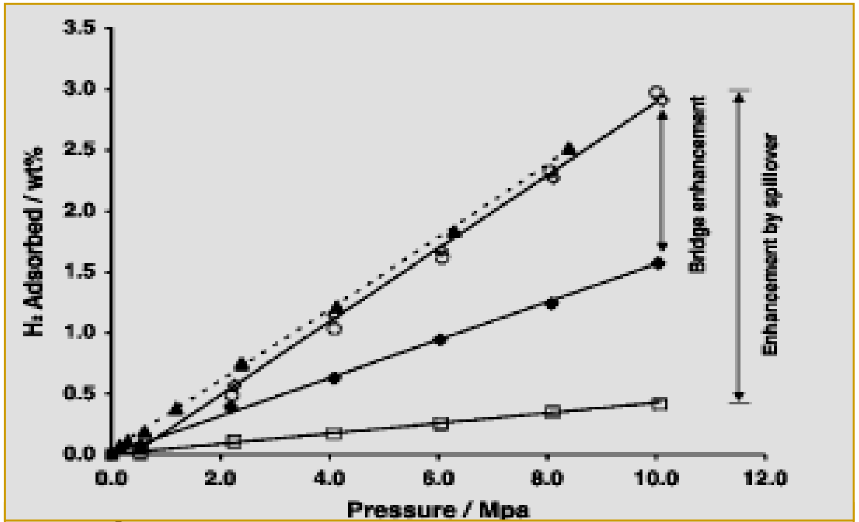
B. Panella, M.Hirsher. *Adv. Mater., 2005*

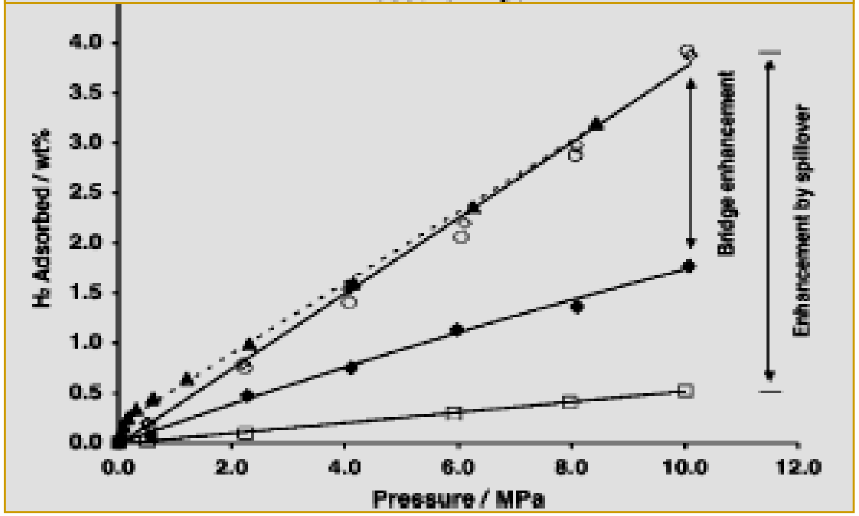


Yaghi Omar M., Univ. of Michigan, USA; Eddaoudi M. et al. *Science.* 2002. V. 295. P. 469; Rosi N.L. et al. *Science.* 2003. V. 300. P. 1127; Chae H.K. et al. *Nature.* 2004. V. 427. P. 523; Rowsell J.L.C. et al. *J. Am. Chem. Soc.* 2004. V. 126. P. 5666.

New hydrogen sorbents based on MOF





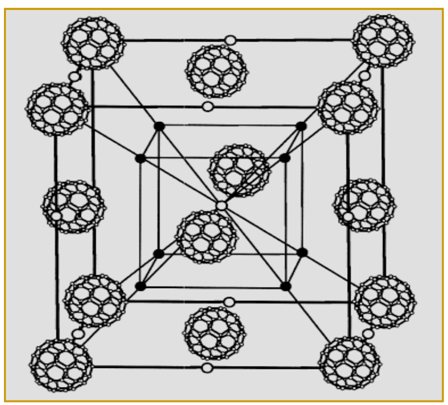


Li Yingwei, Yang Ralph T. *J. Am. Chem. Soc.* 2006. V. 128. P. 726–727.

Reversible organic "hydrides"

Reaction	H contents, (at. H/cm³)·10^{22}	H contents, mass. %
$C_6H_6 + 3\ H_2 \Leftrightarrow C_6H_{12}$	3.35	7.15
$C_7H_8 + 3\ H_2 \Leftrightarrow C_7H_{14}$	2.85	6.15
$C_{10}H_8 + 5\ H_2 \Leftrightarrow C_{10}H_{18}$	4.50	7.25
$C_{60} + 30\ H_2 \Leftrightarrow C_{60}H_{60}$	8.25	7.70
$C_{70} + 35\ H_2 \Leftrightarrow C_{70}H_{70}$	8.25	7.70
$C_{60} + 18\ H_2 \Leftrightarrow C_{60}H_{36}$	5.40	4.50

Fullerite – hydrogen: $C_{60} + x\ H_2 \Leftrightarrow C_{60}H_{2x}$



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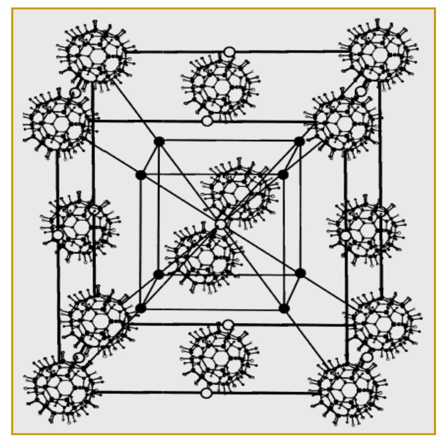
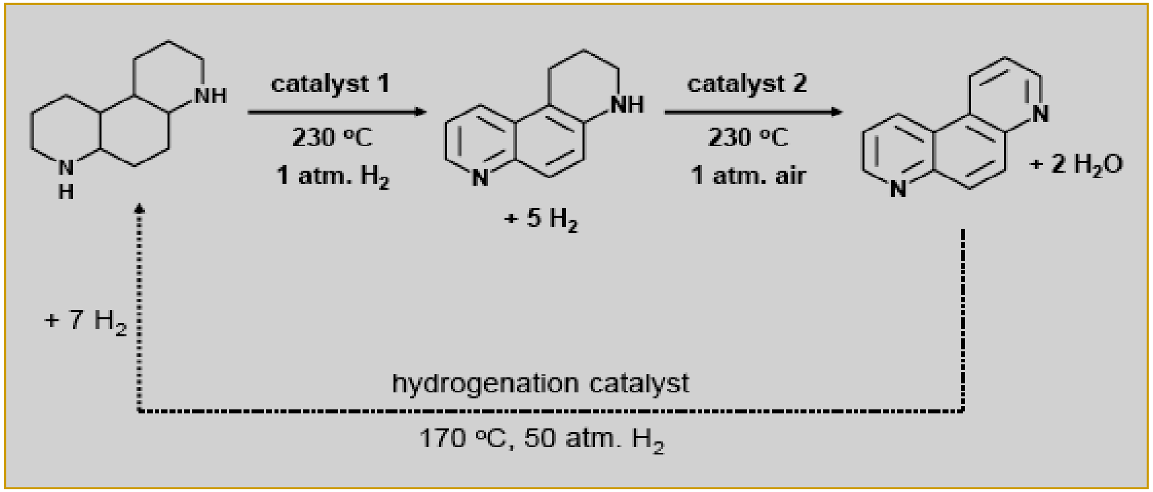
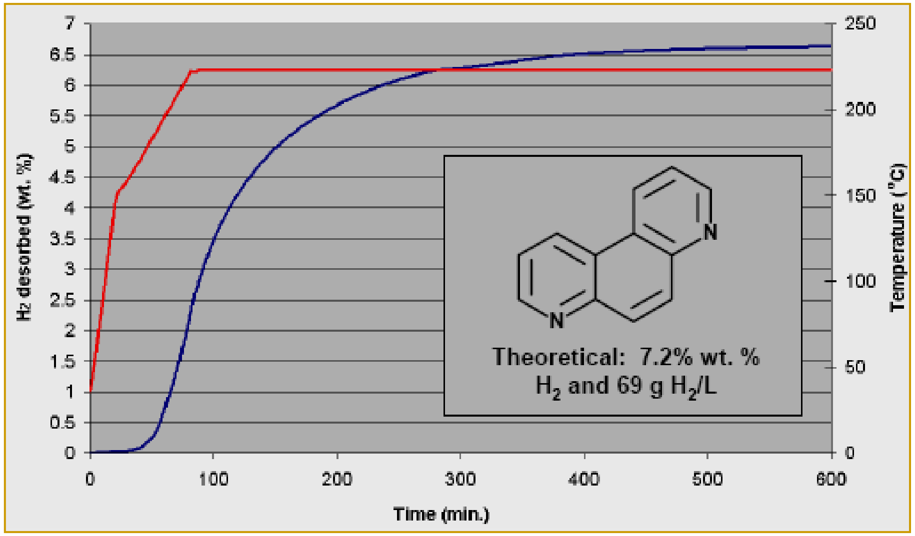


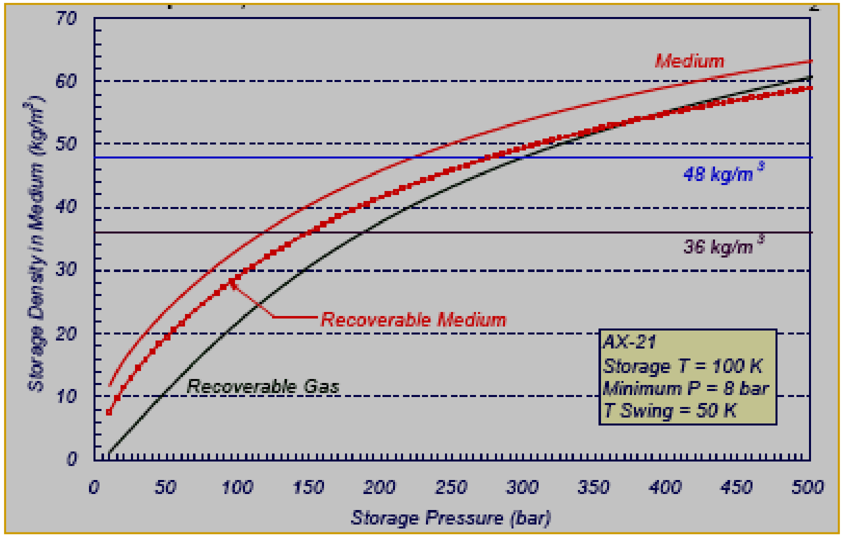
$\{C_{60} + M\} + H_2 \ \underline{\text{1-5 MPa, 570-670 K}}\ \{C_{60}H_x + MH_y\}$

$\{C_{60}H_x + MH_y\}\ \underline{<600\text{ K}}\ \{C_{60}H_x + M\} + 0.5y\ H_2\ \underline{\sim 800\text{ K}}\ \{C_{60} + M\} + 0.5(x+y)\ H_2$

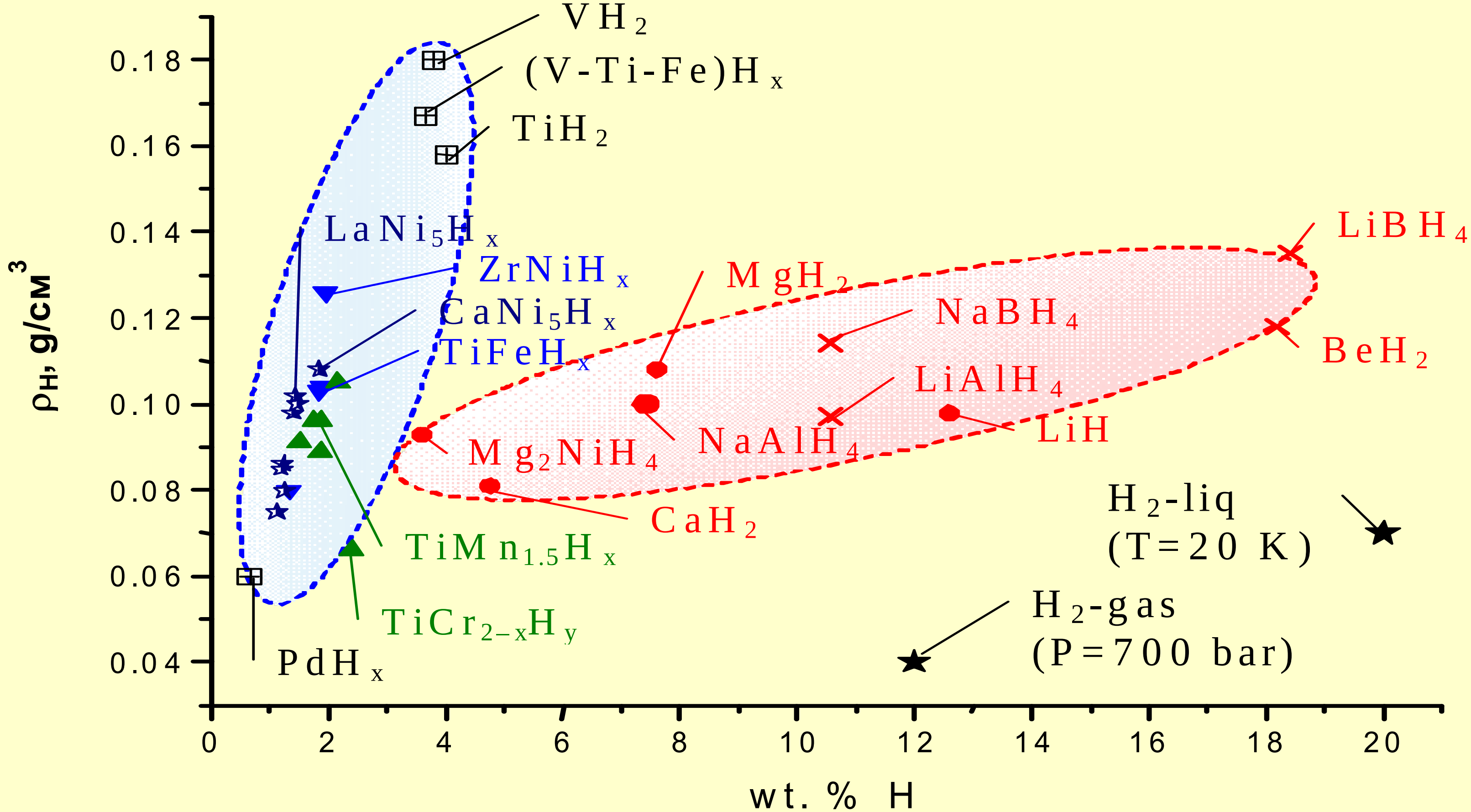
Reversible liquid organic “hydrides”



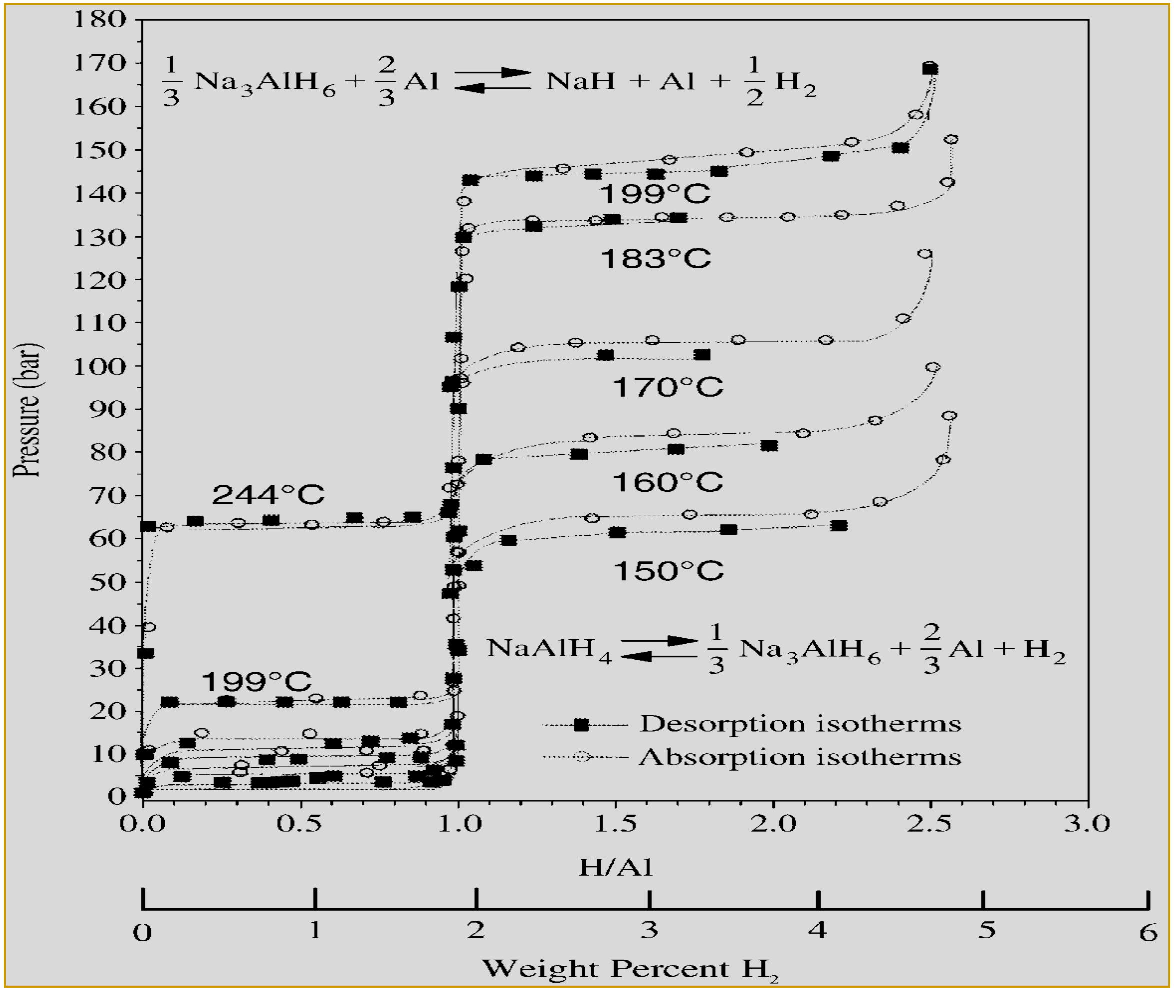




Hydrogen contents in MH storage materials



Metal aluminium hydrides and borohydrides for hydrogen storage



Advances:
- high hydrogen storage capacity,
- availability

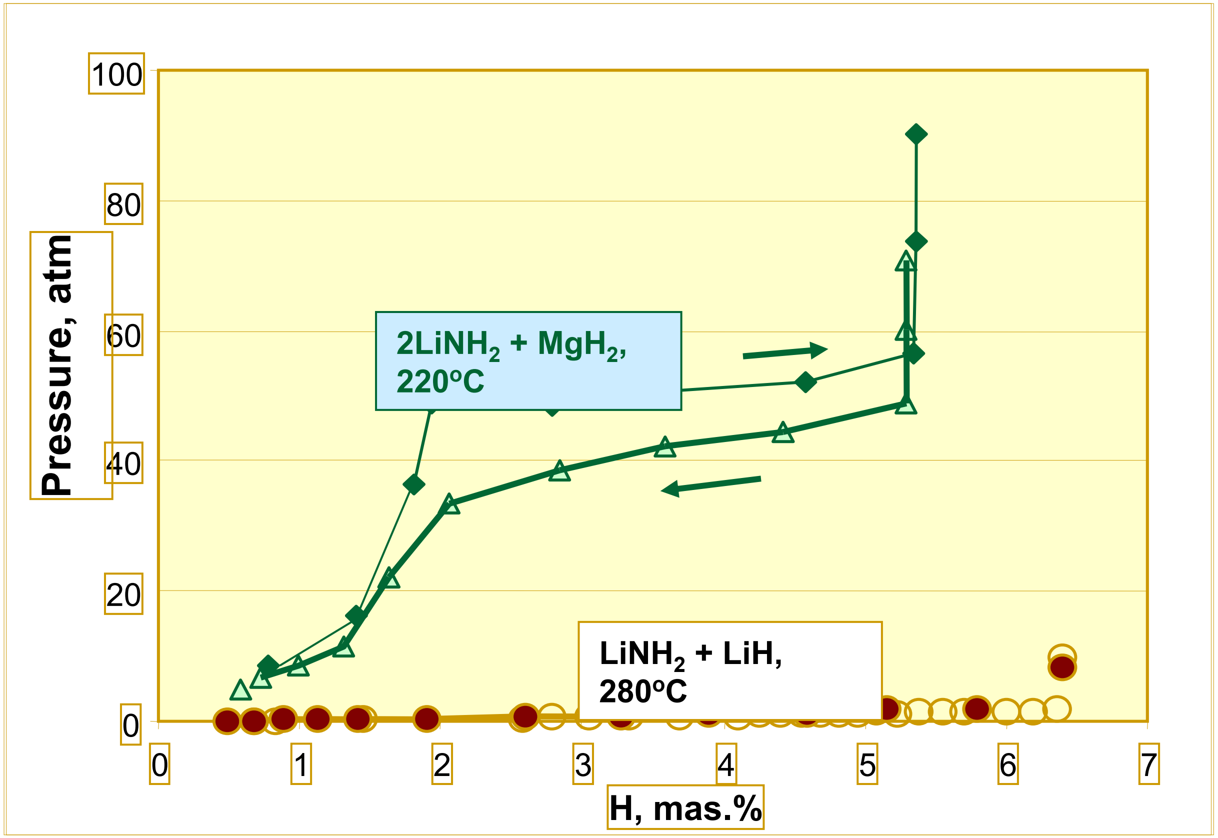
Shortcomings:
- high sensitivity toward water and oxygen,
- poor cyclic stability,
- poor hydrogen sorption and desorption kinetics,
- high cost.

Bogdanović B., Brand R.A., Marjanovic A., Schwickardi M., Tölle J. *J. Alloys Comp.* 2000. V. 302. P. 36–58;

Zaluski L., Zaluska A., Ström-Olsen J. *J. Alloys Comp.* 1999. V. 290. P. 71–78.

Amide-imide systems for hydrogen storage

$2LiNH_2 + MgH_2 \Rightarrow Li_2Mg(NH)_2 + 2H_2 \Leftrightarrow 2LiH + Mg(NH_2)_2$



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Chen P., Xiong Z., Luo J., Lin J., Tan K.L. *Nature.* 2002. V. 420. P. 302.

Ichikawa T., Tokoyoda K., Leng H., Fujii H. *J. Alloys Comp.* 2005. V. 400. P. 245.

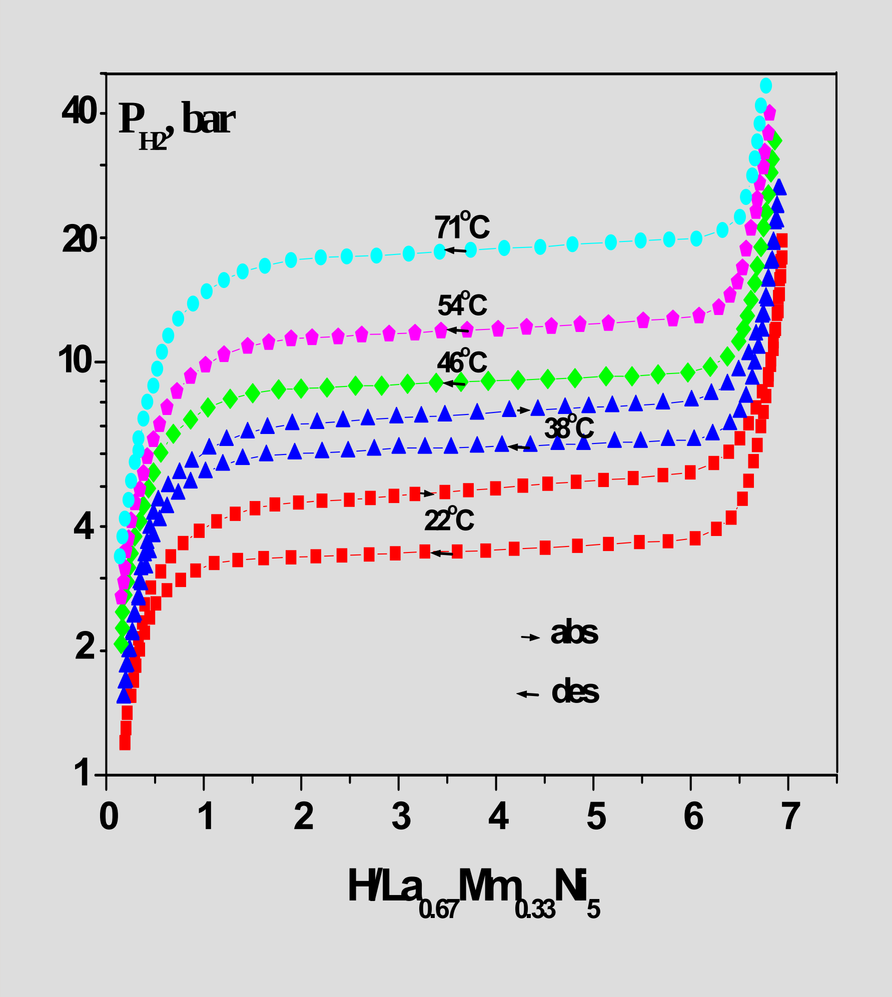
Luo W. *J. Alloys Comp.* 2004. V. 381. P. 284.

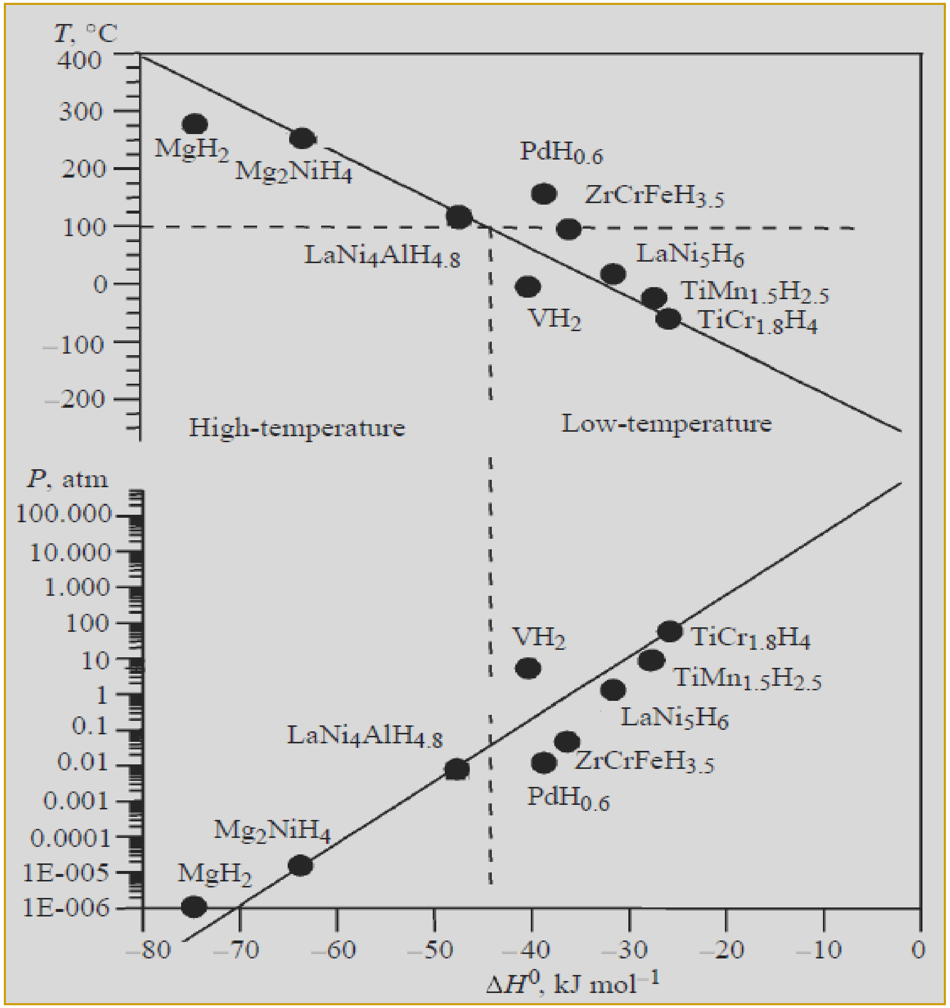
$LiNH_2 + 2LiH \underset{1\ bar}{\overset{300\ ^\circ C}{\Leftrightarrow}} Li_2NH + LiH + H_2 \underset{0.05\ bar}{\overset{300\ ^\circ C}{\Leftrightarrow}} Li_3N + 2H_2$

Hydride-forming metals, intermetallides and alloys for hydrogen storage

Material	Composition	Working interval		H, mass.%
		T, °C	P, atm	
Metals	Mg	300 - 400	1 - 10	7.6
	V	0 - 200	1 - 200	3.6
	Ti	500 - 600	1 - 10	4.0
Intermetallic compounds	AB_5 (A - La, Mm, Ce, Y, Ca; B - Ni, Al, Co, Sn)	0 - 200	0.1 - 150	1.2 - 1.5
	AB_2 (A - Ti, Zr; B - Cr, Mn, Fe)	–70 - 150	0.1 - 250	1.5 - 2.5
	AB (A - Ti, Zr; B - Fe, Ni)	0 - 150	1 - 100	1.7 - 2.0
	A_2B (A - Mg; B - Ni, Cu)	200 - 300	1 - 100	2.5 - 3.7
Alloys	of Mg: Mg-Ni, Mg-Ni-RE	250 - 400	1 - 10	4 - 7
	of V: V-Cr-Mn	0 - 200	1 - 150	1.8 - 3.7
	of Ti: Ti-Al-Ni	200 - 600	1 - 10	3 - 5

Characteristics of reversible metal hydrides





Advances and shortcomings of MH hydrogen storage

ADVANCES:

- high volumetric density,
- acceptable ranges of working temperature and pressure,
- pressure stability at hydrogenation and dehydrogenation,
- easy control of the pressure and release rate,
- compactness and safety of metal-hydride hydrogen accumulators.

SHORTCOMINGS:

- possibility of decomposition due to the hydrogen action,
- high sensitivity toward admixtures,
- problems of heat and mass transfer,
- high enthalpy of hydride formation,
- necessity of external heating and cooling,
- powder sintering (more peculiar to magnesium alloys),
- changes in the alloy microstructure (peculiar to vanadium alloys),
- long time of «charging» and «discharging» of accumulators.

Problems and solution of shortcoming of MH storage systems

Heat and mass transfer problems:

- low heat transfer of powdered MH (0.13–2.3 W/m·K),
- dependence of the heat transfer from the construction of a storage system and working regimes.

Improvements of heat transfer in MH beds:

- introduction of inner heat exchangers with high surface area;
- placing of MH in foam-metal matrices having high heat conductivity.

Problems from fine-dispersed powders:

- increase of the specific volume of metal matrix up to 25%,
- formation of fine-dispersed MH powders (1-10 μm).

Solutions:

- introduction of filters or elaboration of MH-composites,
- apparent density of a MH powder should be no more than 60% of its true density.

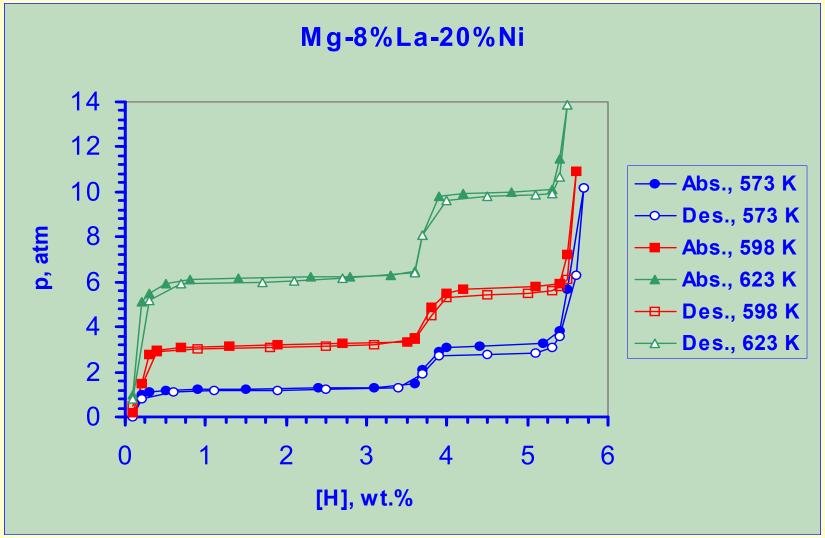
Effect of gas admixtures on hydrogen sorption properties of materials

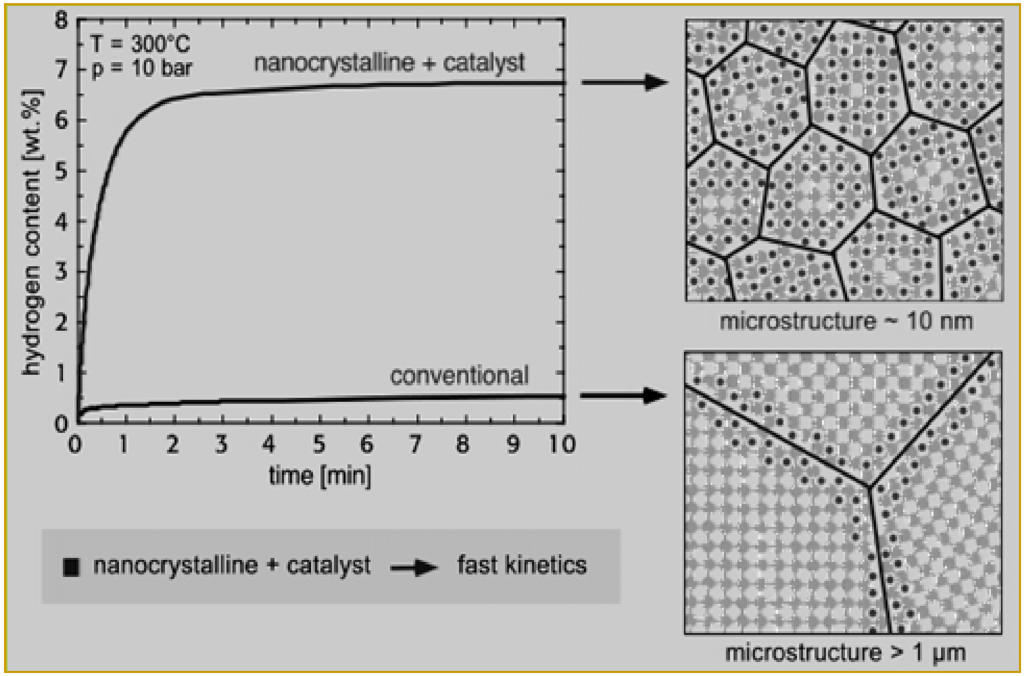
No	Impuritive gases	Sorption properties	Number cycles (impurities – 0.1%)
1	Ar, He, N_2, CH_4, C_2H_6, …	«Inert»	>1000
2	CO_2, (NH_3), …	Chemisorptions	~1000
3	C_2H_4, C_2H_2, (C_3H_6), …	Gas reaction	~1000
4	O_2, H_2O, …	Interaction with metal	~100
5	CO, SO_2, H_2S, ...	«Poisoning»	1-2

- ***Poisoning:*** hydrogen sorption capacity rapidly decreases (CO, SO_2, H_2S,…);
- ***Deceleration***: the sorption rapidly decreases, the hydrogen storage capacity remains the same (CO_2; C_2H_2, C_2H_4,…);
- ***Reaction:*** accompanying by a slow corrosion of the material (O_2, H_2O, …);
- ***Harmless effect:*** the material surface is not damaged, sorption dynamics may be decrease (Ar, N_2, CH_4, C_2H_6, …).

Magnesium and alloys for hydrogen storage

HYDROGEN CONTENTS IN HYDRIDE OF:	*KINETICS CAN BE IMPROVED BY:*
Mg – 7.6 wt.%, **Mg-Ni eutectic –5.8 wt.%,** **Mg-Mm-Ni eut. –5.5 wt.%,** **Mg_2Ni – 3.7 wt.%**	**catalysis,** **ball milling,** **nanocrystalline state**





Preparation of nanostructure alloys of Mg by methods of intensive plastic deformation:

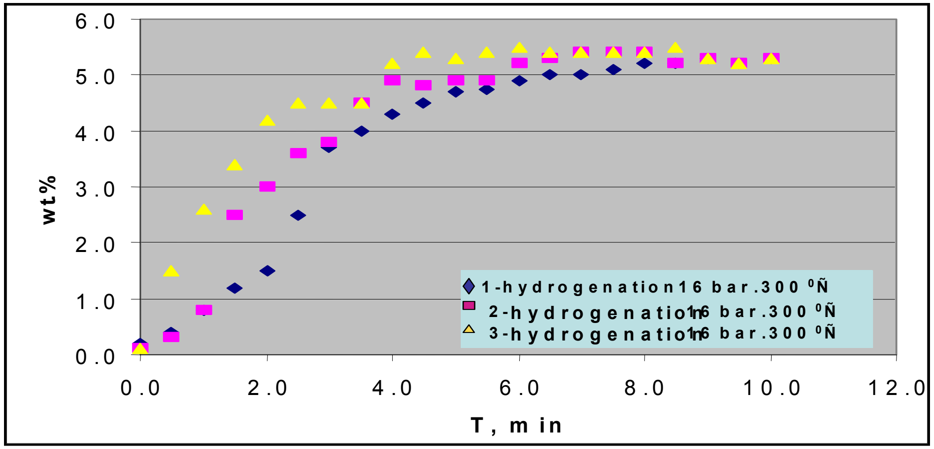
- Equal channel angular pressing (ECAP)
- High pressure torsion (HPT)
- Rapid solidification from melted alloy (RS)
- High energy ball milling (HEBM)

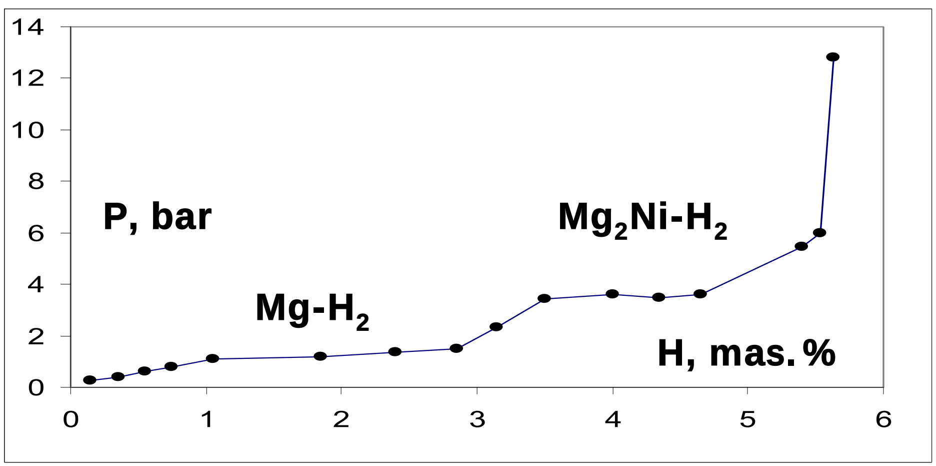
Introduction of catalytic additives:

- Alloying with rare-earth and transition metals
- Ball milling Mg-alloys with MH

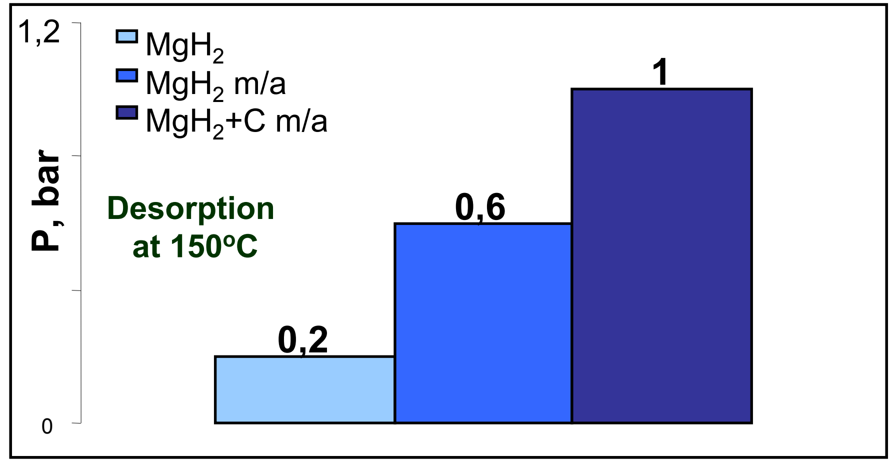
Hydrogen accumulating composites based on magnesium

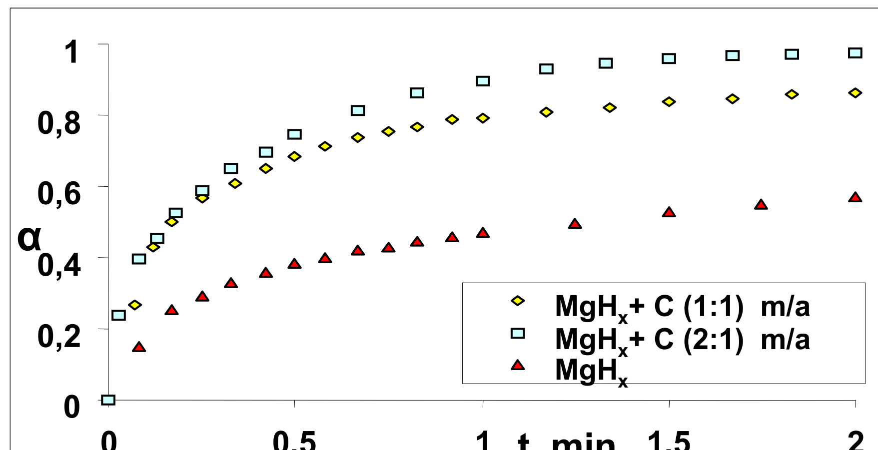
Metal hydride composites on MgH_2



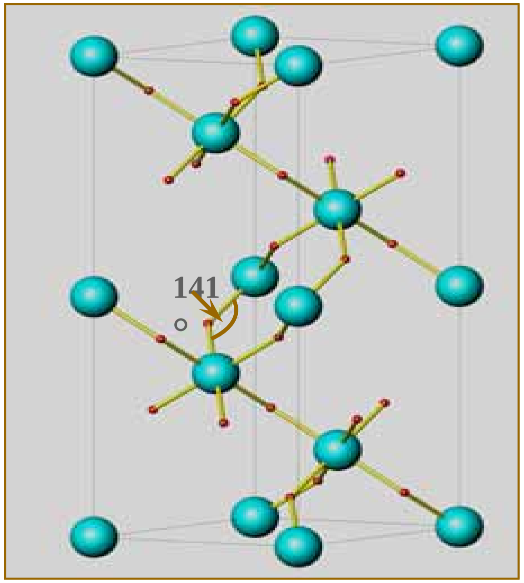


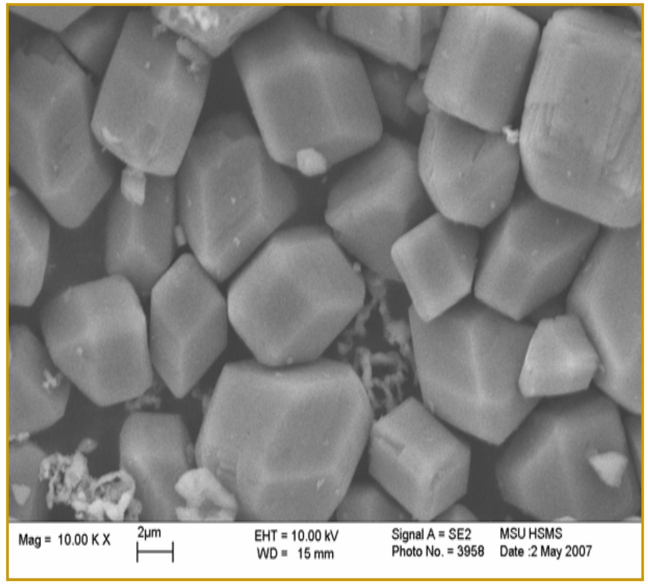
Composites «MgH_2 – carbon»

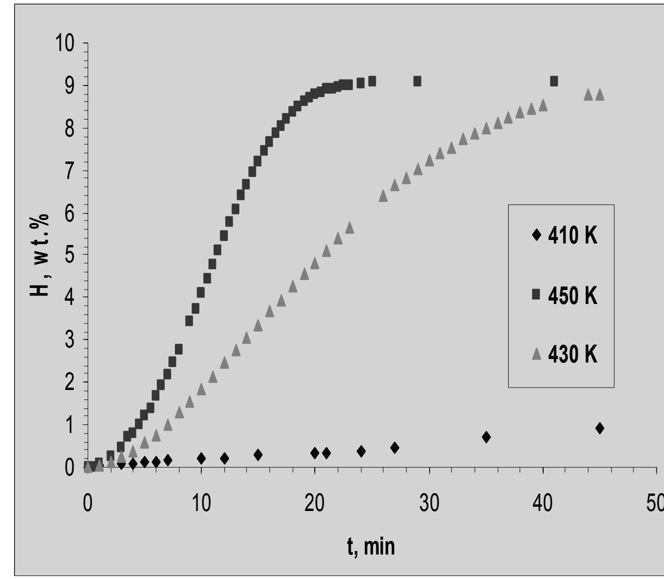




Aluminium hydride for hydrogen storage







Advances: the highest weight and volume hydrogen contents

Shortcomings: difficulty of direct synthesis of the hydride

Probable solution - modification and preparation of nanocomposites:

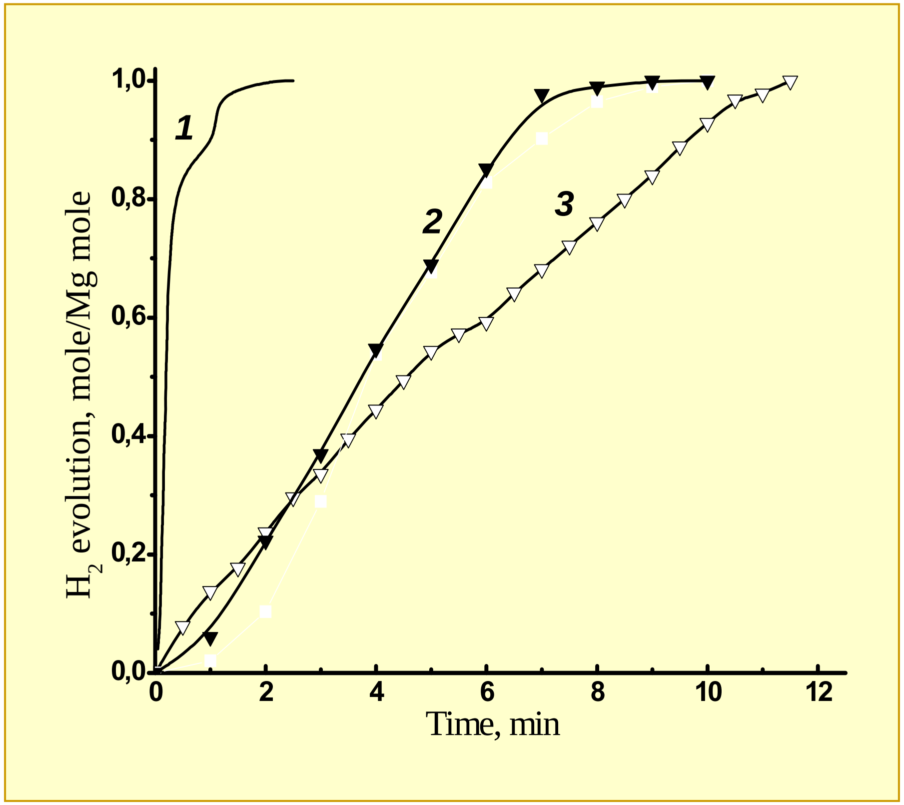
- Ball milling of AlH_3 decreases the decomposition temperature of the hydride and enhances its chemical activity (T_{deg}: 180 →140ºC).
- Additions of LiH to AlH_3 at the ball milling lead to a formation of the $LiAlH_4$ phase and decrease the decomposition temperature (T_{deg} = 112ºC).
- During the ball milling of composites of MgH_2 and AlH_3 thermal stability of hydrides AlH_3 (T_{deg} = 145ºC), γ-MgH_2 (T_{deg} = 280ºC) and α-MgH_2 (T_{deg} = 330ºC) is decreased.
- Addition of TiH_2 at a ball milling catalyzes the decomposition of AlH_3.
- VH_2 doesn't effect on the thermal stability of AlH_3 (T_{deg} = 160–180ºC).
- Lithium amide destabilizes AlH_3 (T_{deg} = 130–150ºC).

Water reacting metals and hydrides as hydrogen sources

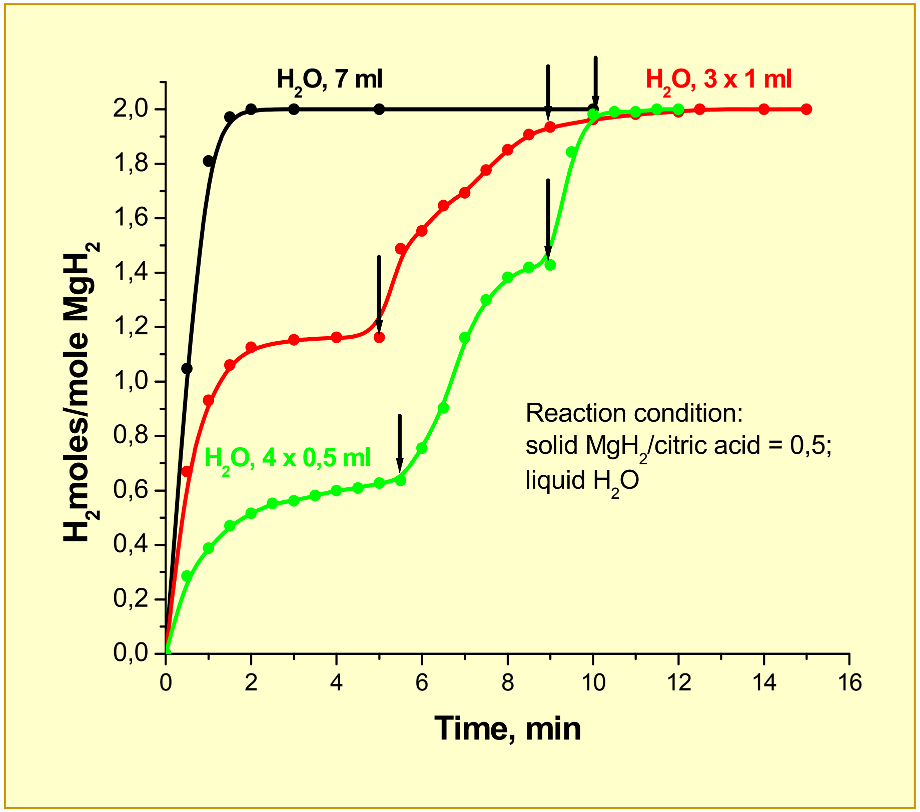
Metals and hydrides	Contents of H, mass. %	Density, g/cm^3	Volume of H_2, m^3/kg of metal or hydride
Mg	-	1,74	0,92
Al	-	2,70	1,23
Si	-	2,33	1,60
Al + LiH			1,28
Si + 2LiH			2,40
LiH	12,5	0,77	2,8
MgH_2	7,6	1,45	1,88
AlH_3	10	1,47	2,24
CaH_2	4,8	1,90	1,06
$NaBH_4$	8,3	1,07	2,48

Remark: **For hydrolysis a considerable excess of water is needed**

Hydrogen generation by acid hydrolysis of magnesium and its hydride

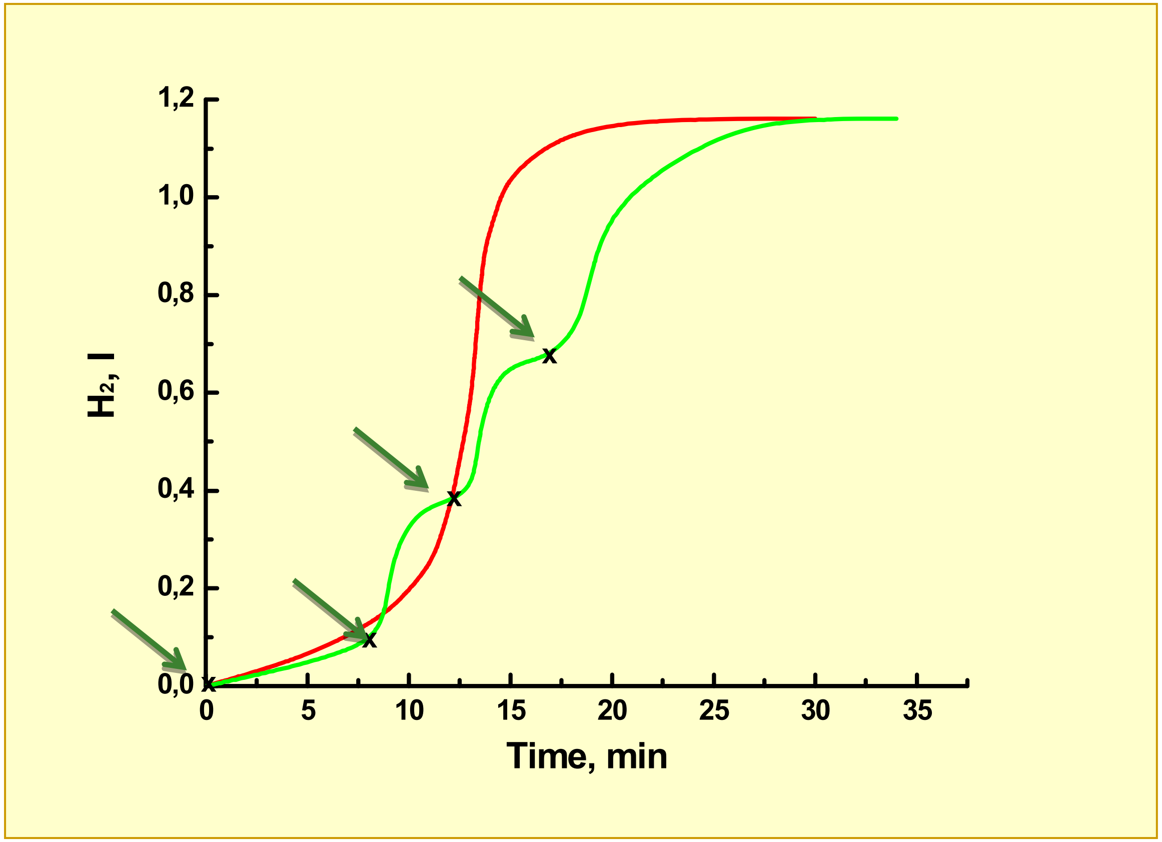


Hydrogen evolution curves at interaction of magnesium with citric acid (3:2 mol.) at one-fold (*1*) and dosed (*2, 3*) water introduction.



Hydrogen release curves at addition of water to the mixture MgH_2 and citric acid.

Hydrogen generation by reaction of activated aluminium with water



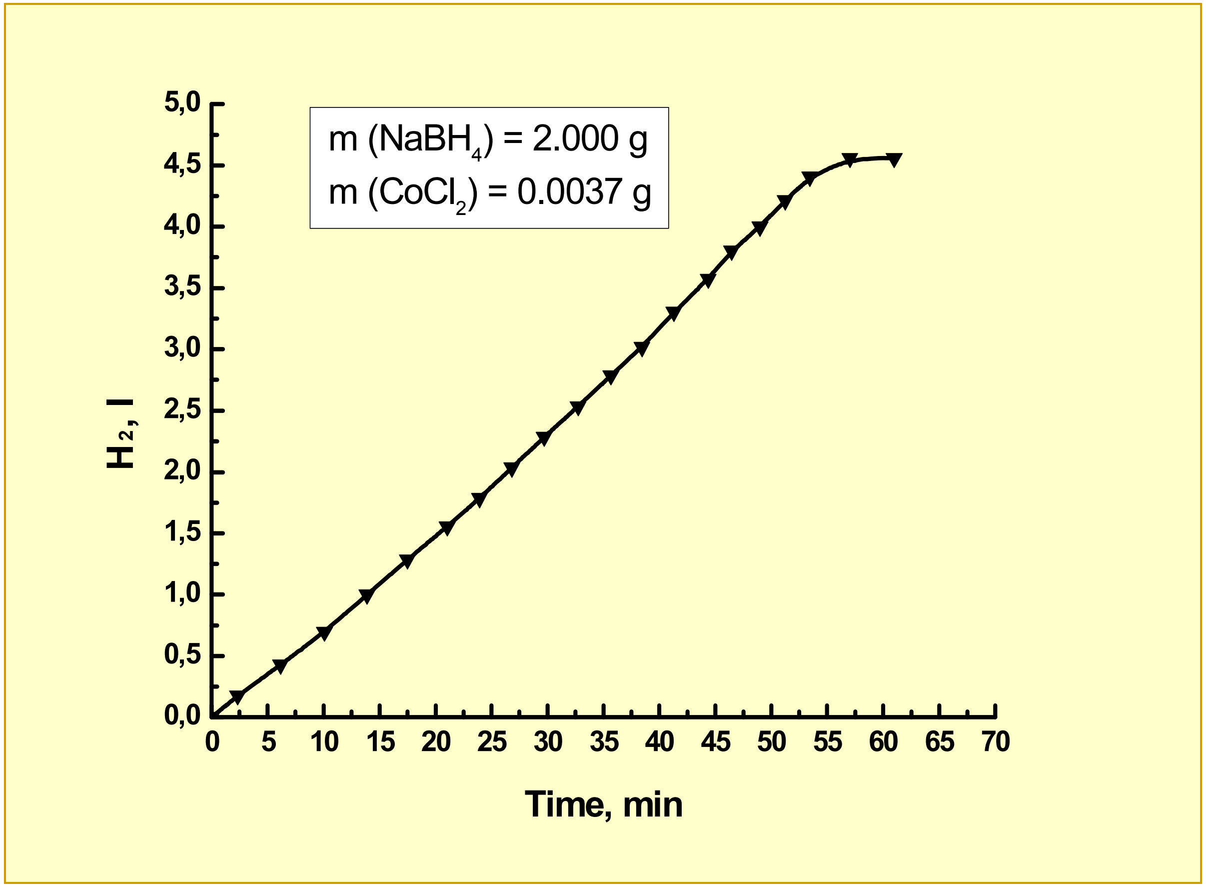
One-fold introduction of water

Dosed (1 ml) introduction of water

The minimum quantity of water, necessary for full hydrolysis, should be in 3 times of more quantity of the activated aluminium (in 1,5 times more stoichiometry).

The volume and weight of a powder, formed at hydrolysis, is approximately in 3 times of more volume and weight of the activated aluminium.

Hydrogen generation by hydrolysis of $NaBH_4$



Curve of hydrogen generation at hydrolysis of 20% solution with $CoCl_2$ additive at 50°C.

Hydrolysis reaction of sodium borohydride by water with $CoCl_2$ additive is accompanied by uniform generation of hydrogen.

$NaBH_4$ can be used for creation of the chemical generator of hydrogen.

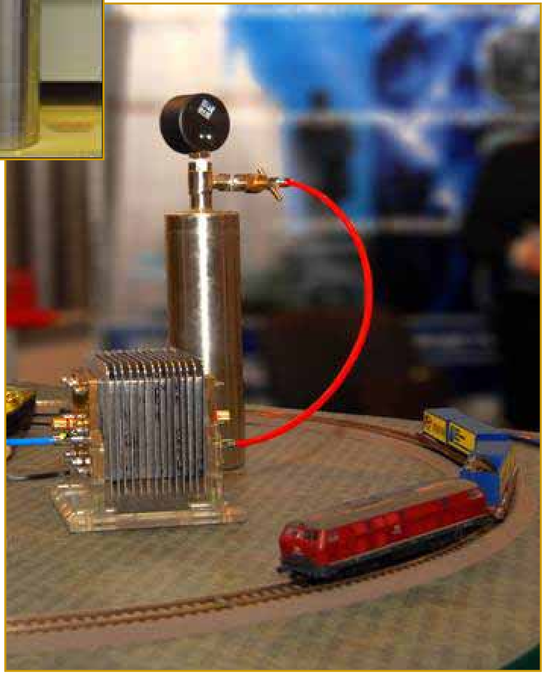
Reversible sources of hydrogen for PEMFC

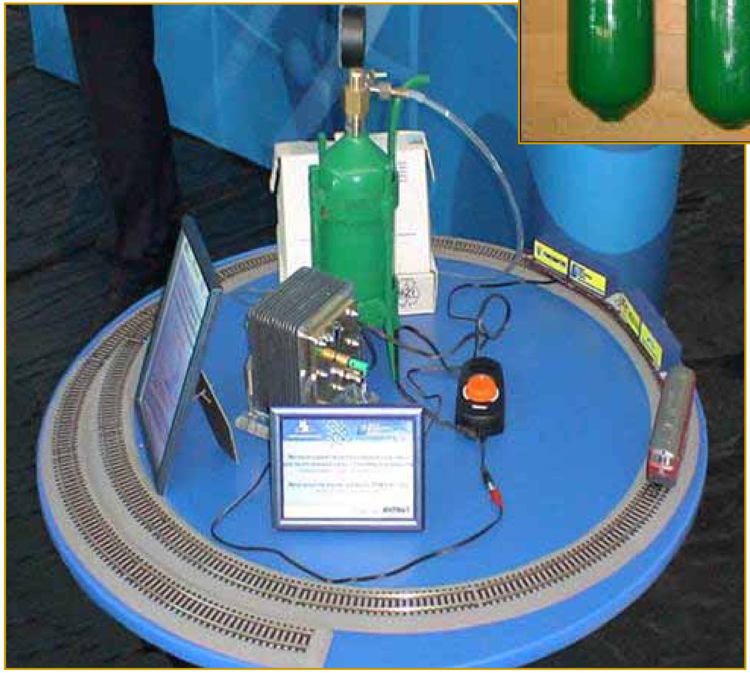
Unit type	Application field	Working material
Accumulators	Charging devices, Stationary setups	Reversible hydrides: La(Mm)Ni_5 – 1.5 wt.% La(Ce)Ni_5 – 1.5 wt.% TiFe – 1.8 wt.% TiZrMnCr – 2.0 wt.% Mg_2Ni – 3.6 wt.% Mg-Mm-Ni – 5.5 wt.%

Hydrogen storage systems for PEMFC

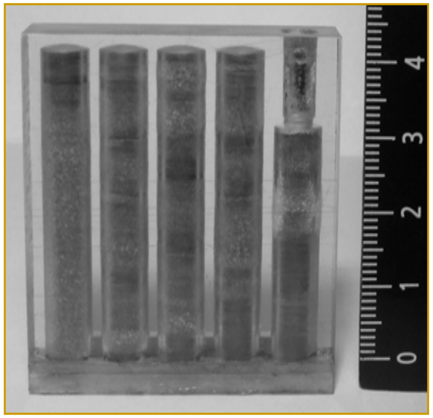


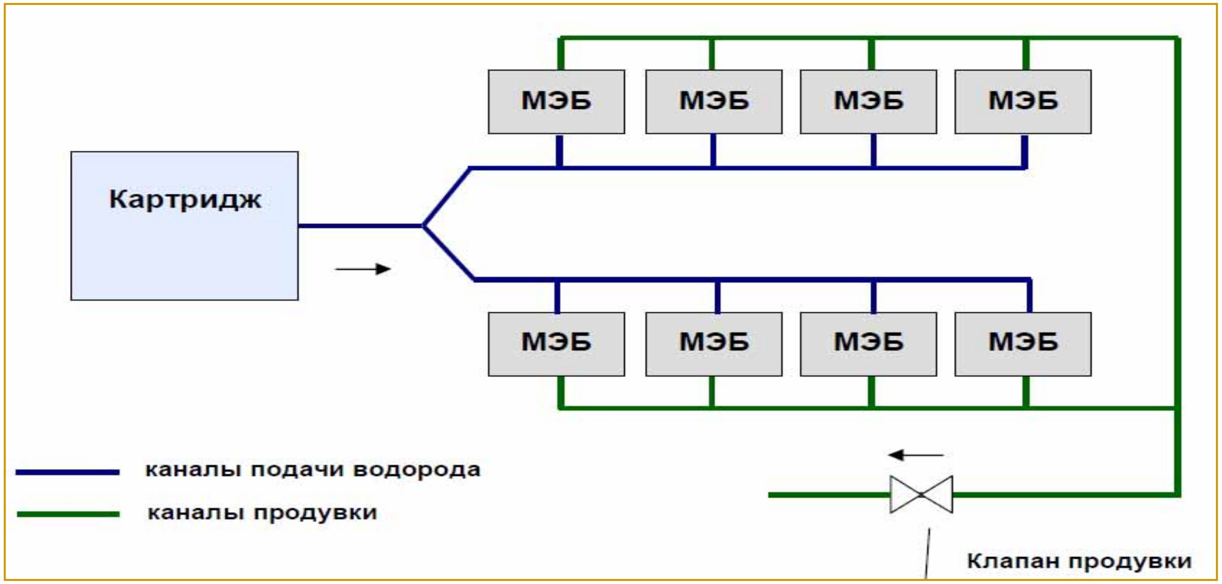
Hydrogen accumulators with a fuel cell





Portable hydrogen cartridge with a fuel cell





Metal-hydride system of refueling of cartridges

Capacity on hydrogen	600 l
The sizes	39x34x16 (cm)
Weight of the device	5.5 kg
Saturation by H_2 at 10 atm	30 mines
Isolation of H_2	3–4 atm
Hydrogen purity	99.999%

Chemical sources of hydrogen for PEMFC

<table>
<tr><th rowspan="2">Unit type</th><th rowspan="2">Application area</th><th colspan="2">Working material</th></tr>
<tr><th>Metal hydrides (termodesorption)</th><th>Metals and hydrides (reacting with water)</th></tr>
<tr><td>Generators cartridge type</td><td>Portable devices, Personal survival systems</td><td>AlH_3 – 10 wt.%
AlH_3+additives – 7-8 wt.%
MgH_2 – 7.6 wt.%
MgH_2+additives –5-7 wt.%
NH_3BH_3 – 18 wt.%

$AlH_3 \Rightarrow Al + H_2$</td><td>Mg – 0.92 l/g
Al – 1.23 l/g
MgH_2 – 1.88 l/g
AlH_3 – 2.24 l/g
$NaBH_4$ – 2.48 l/g

$MgH_2 + H_2O \Rightarrow Mg(OH)_2 + H_2$</td></tr>
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Institute of Problems of Chemical Physics of RAS
Laboratory of Hydrogen Storage Materials

Chernogolovka, Moscow Region,
Russian Federation, 142432
Tel./Fax: +7-496-5221743
E-mail: tarasov@icp.ac.ru