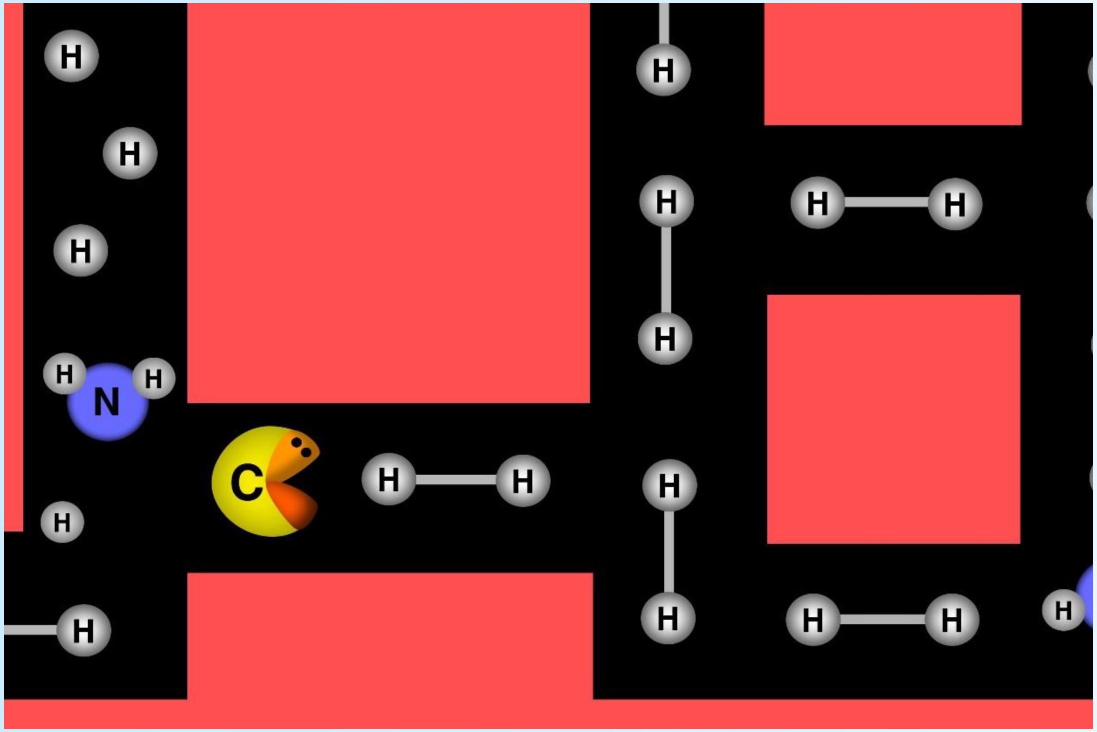
Materials for hydrogen economy: past, current and future



Université catholique de Louvain

Institute of Condensed Matter and Nanosciences
Louvain-la-Neuve, Belgium

Yaroslav Filinchuk

www.filinchuk.com

50th School on Condensed Matter Physics, PNPI, St. Petersburg
14 – 19 March 2016

Université catholique de Louvain

Intermittent Energy Sources

- Wind
- Sun
- Hydro
- Tide
- Wave

⇒ Difficult to integrate to base power

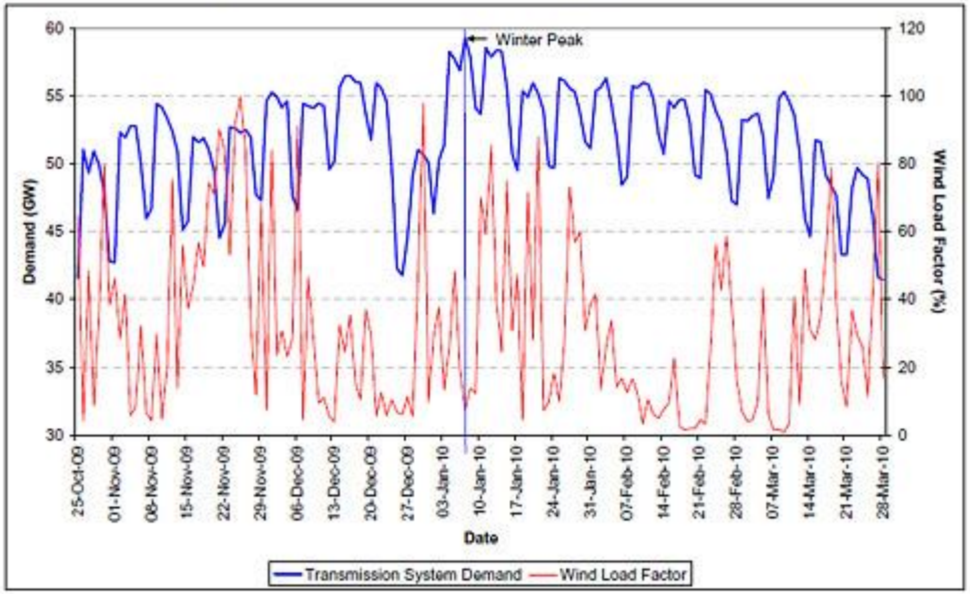
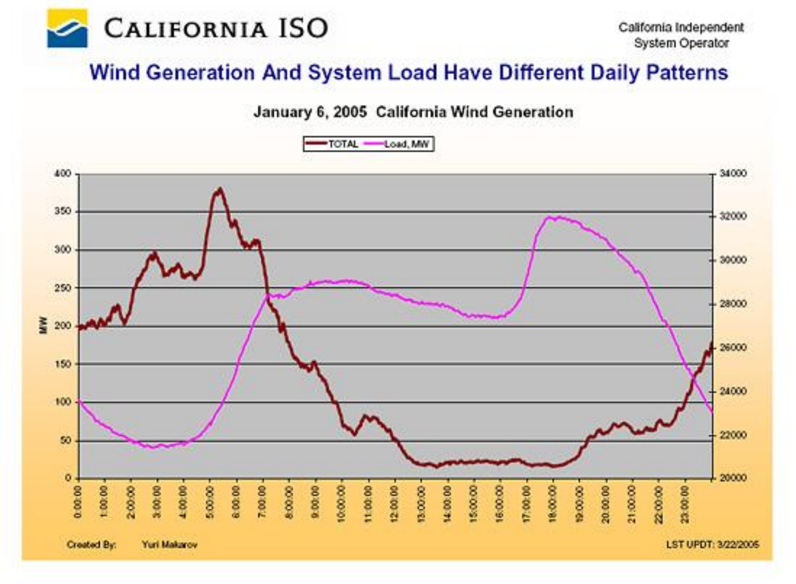


Figure A.30 – 2009/10 Daily Peak and Wind Generation



CALIFORNIA ISO

California Independent System Operator

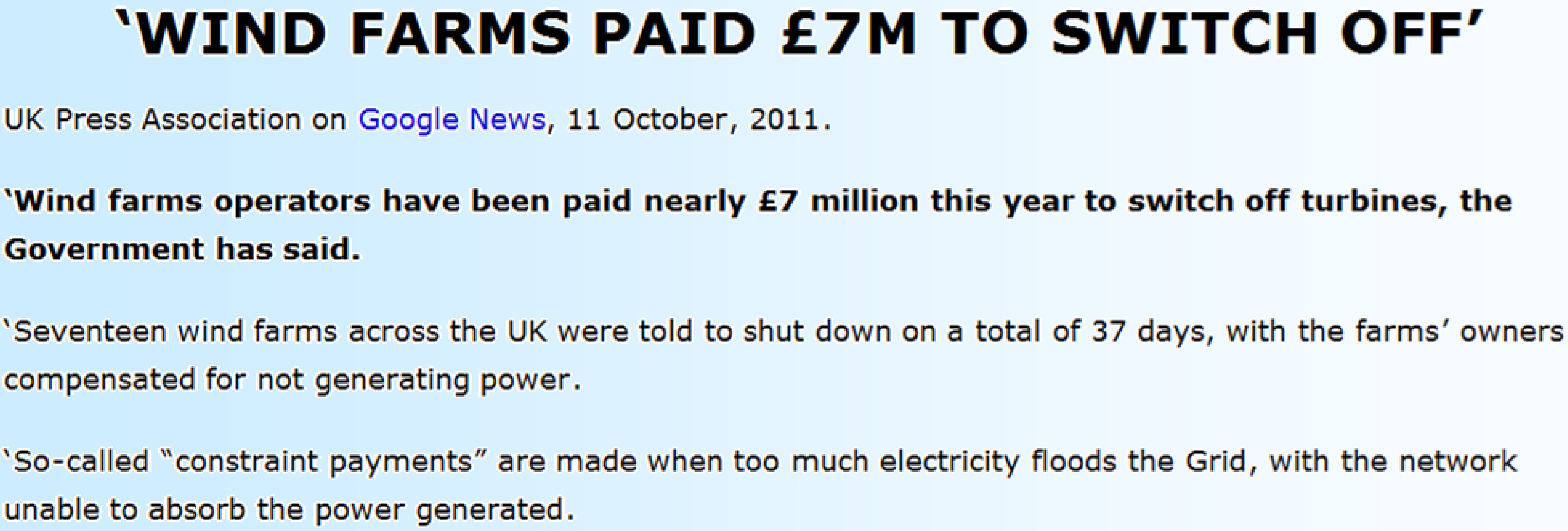
Wind Generation And System Load Have Different Daily Patterns

January 6, 2005 California Wind Generation

Created By: Yuri Makarov

LST UPDT: 3/22/2005

Energy vectors



‘WIND FARMS PAID £7M TO SWITCH OFF’

UK Press Association on Google News, 11 October, 2011.

‘Wind farms operators have been paid nearly £7 million this year to switch off turbines, the Government has said.

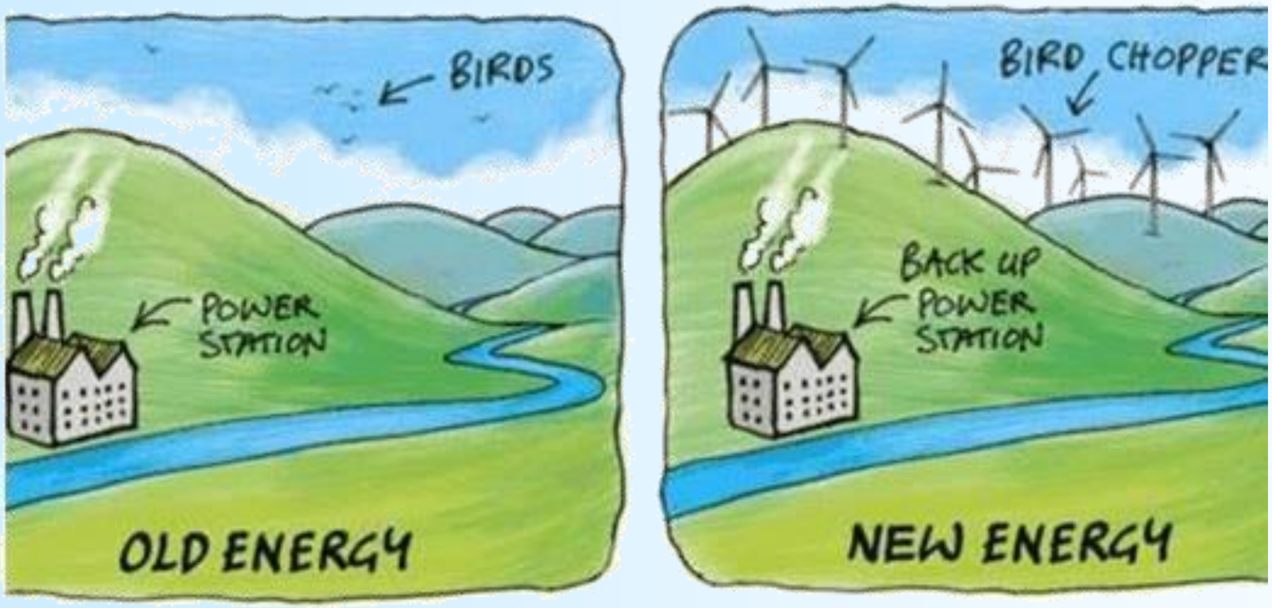
‘Seventeen wind farms across the UK were told to shut down on a total of 37 days, with the farms’ owners compensated for not generating power.

‘So-called “constraint payments” are made when too much electricity floods the Grid, with the network unable to absorb the power generated.

http://www.windbyte.co.uk/windpower.html

We need an energy vector which will transport energy from the production site to the user. Electricity is a good energy vector but it could not be stored in large quantity. Thus, we need another type of energy vector.

Energy vectors



'GREENING' THE LAND

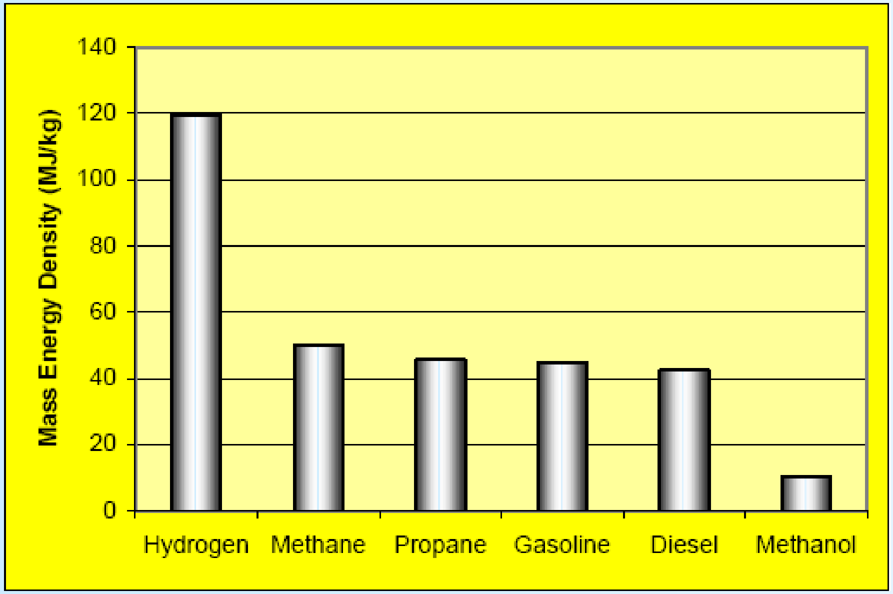
We need an energy vector which will transport energy from the production site to the user. Electricity is a good energy vector but it could not be stored in large quantity. Thus, we need another type of energy vector.

Hydrogen economy

- Hydrogen, in various forms (gas, liquid, hydrides) is used to store and transport energy
- Hydrogen is traded, as now oil
- Reduce dependency on fossil fuels for: ecological, polytical and economical reasons

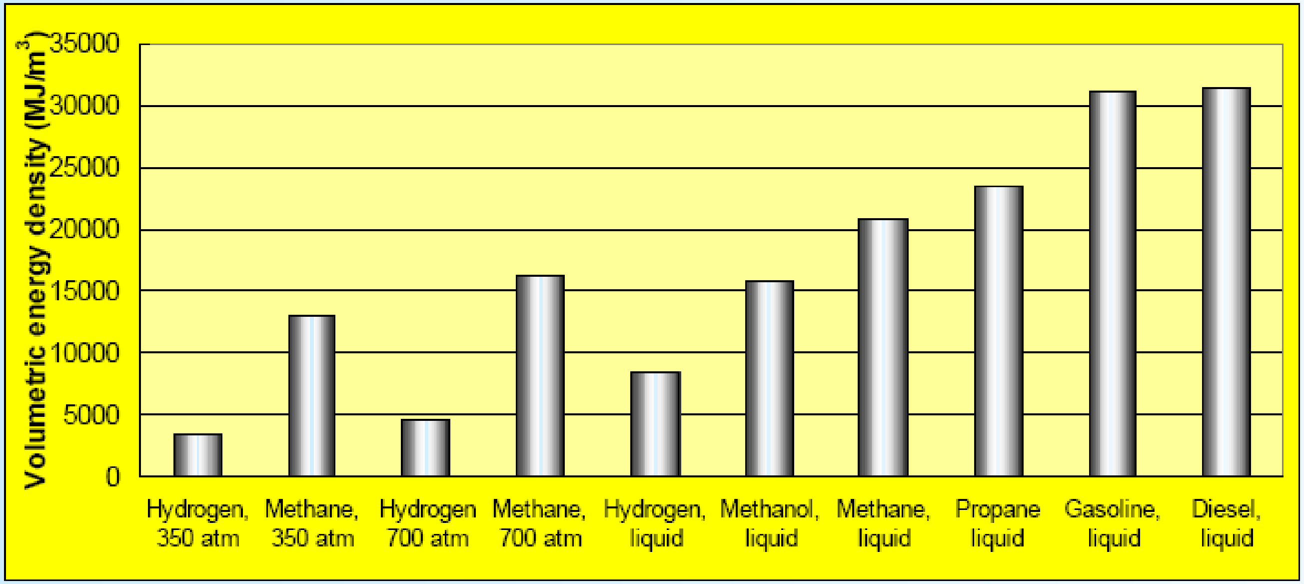
…this has more to do with energy production

Energy density



Lithium-ion batteries up to 1 MJ/kg

For practical applications hydrogen storage density has to be increased



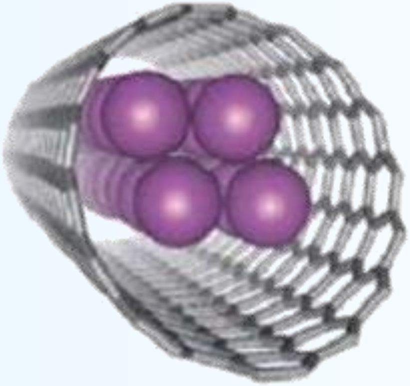
Hydrogen storage is the main issue

Especially for
mobile applications,
e.g. transport

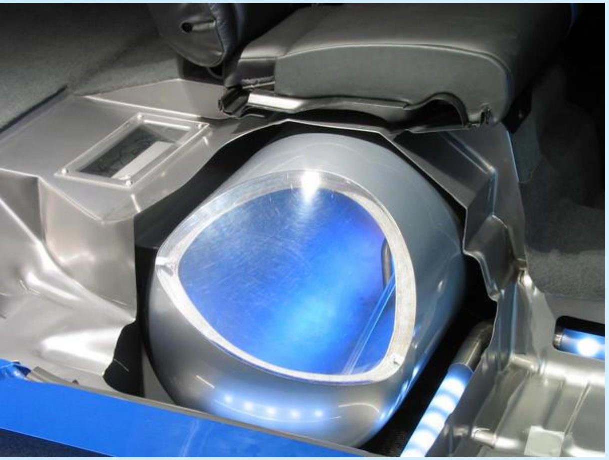
Approaches to storage

- close packing of H atoms (volume density)
- light container (weight density)
- H release, reversibility (thermodynamics)
- low cost and safety (materials science)

Physical adsorption
20 kg H_2/m^3, 4 % wt.
70 bar, 65 K

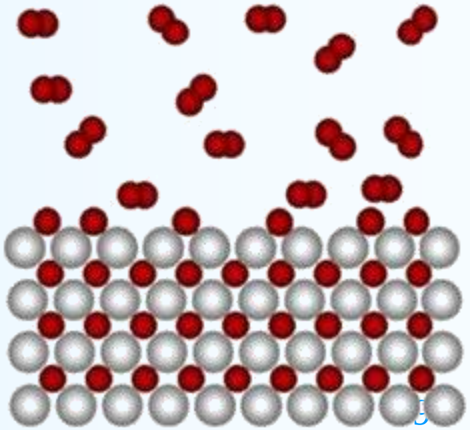


Liquid hydrogen
71 kg H_2/m^3, 100 % wt.
1 bar, 20 K

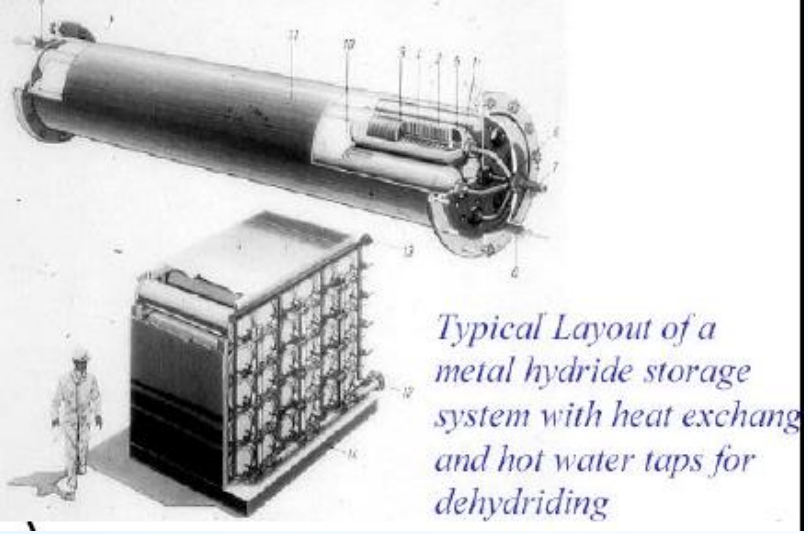


Compressed hydrogen
33 kg H_2/m^3, 13 % wt.
700 bar, 298 K

Chemical absorption
150 kg H_2/m^3, 18 % wt.
1 bar, 298 K



Stationary applications

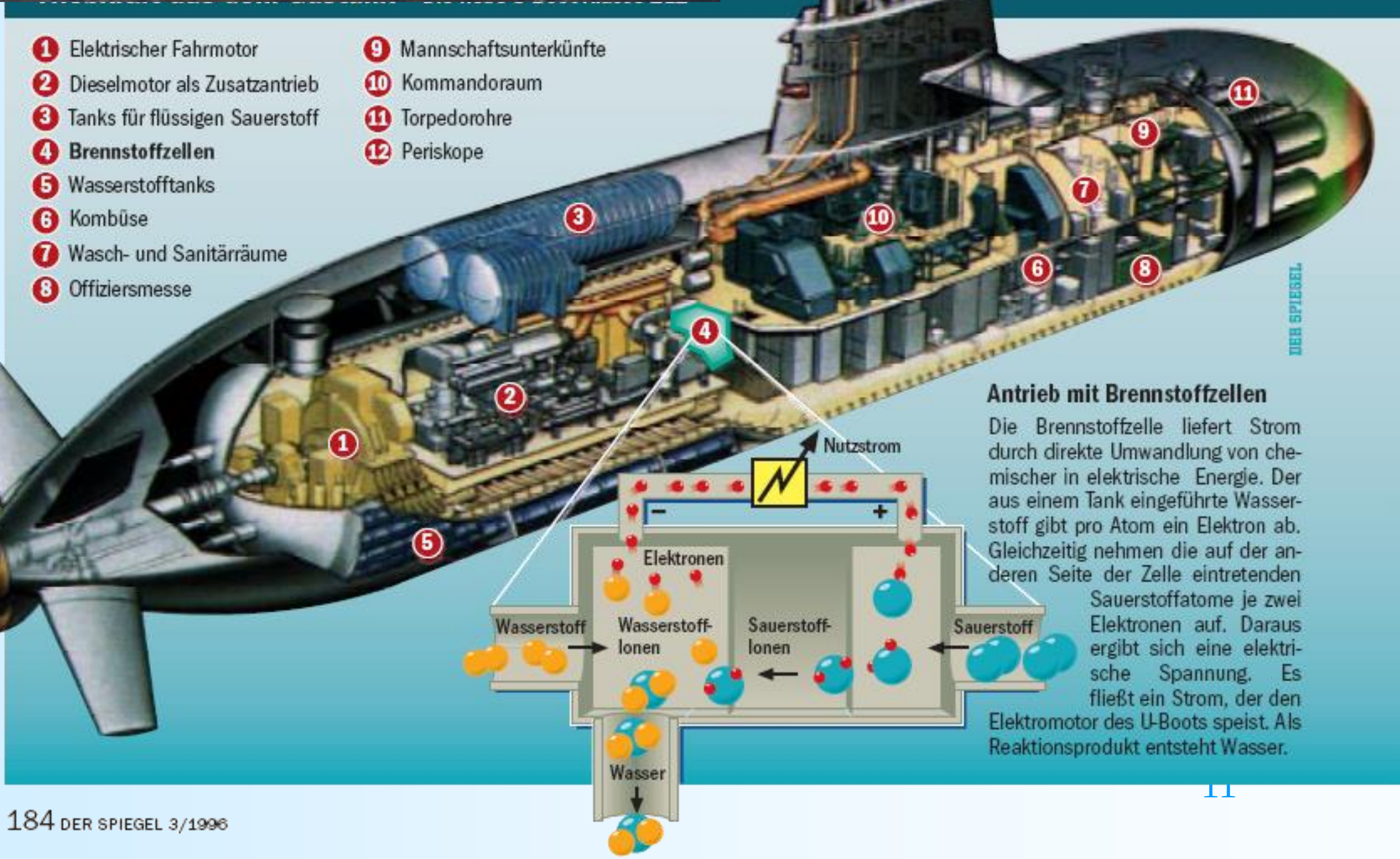

Typical Layout of a metal hydride storage system with heat exchang and hot water taps for dehydriding

Copyright Stan Jirman - stanj@PhotoTrek.ORG

hat;
espeist
rstoff,
ahezu
rfahr-

Milliarden Dollar kostet die Seawolf, das Super-U-Boot der U. S. Navy – das vielfache eines konventionellen Tauchboots.

Mit einem wesentlich besseren Antrieb wollen nun die Ho-

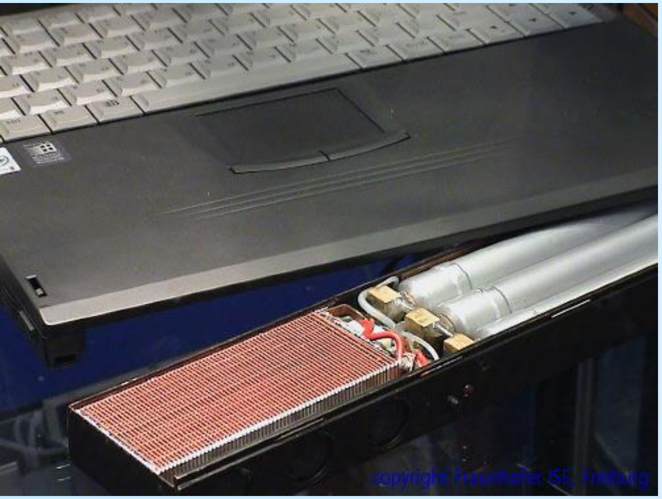


❶ Elektrischer Fahrmotor
❷ Dieselmotor als Zusatzantrieb
❸ Tanks für flüssigen Sauerstoff
❹ **Brennstoffzellen**
❺ Wasserstofftanks
❻ Kombüse
❼ Wasch- und Sanitärräume
❽ Offiziersmesse
❾ Mannschaftsunterkünfte
❿ Kommandoraum
⓫ Torpedorohre
⓬ Periskope

Antrieb mit Brennstoffzellen

Die Brennstoffzelle liefert Strom durch direkte Umwandlung von chemischer in elektrische Energie. Der aus einem Tank eingeführte Wasserstoff gibt pro Atom ein Elektron ab. Gleichzeitig nehmen die auf der anderen Seite der Zelle eintretenden Sauerstoffatome je zwei Elektronen auf. Daraus ergibt sich eine elektrische Spannung. Es fließt ein Strom, der den Elektromotor des U-Boots speist. Als Reaktionsprodukt entsteht Wasser.

Mobile applications



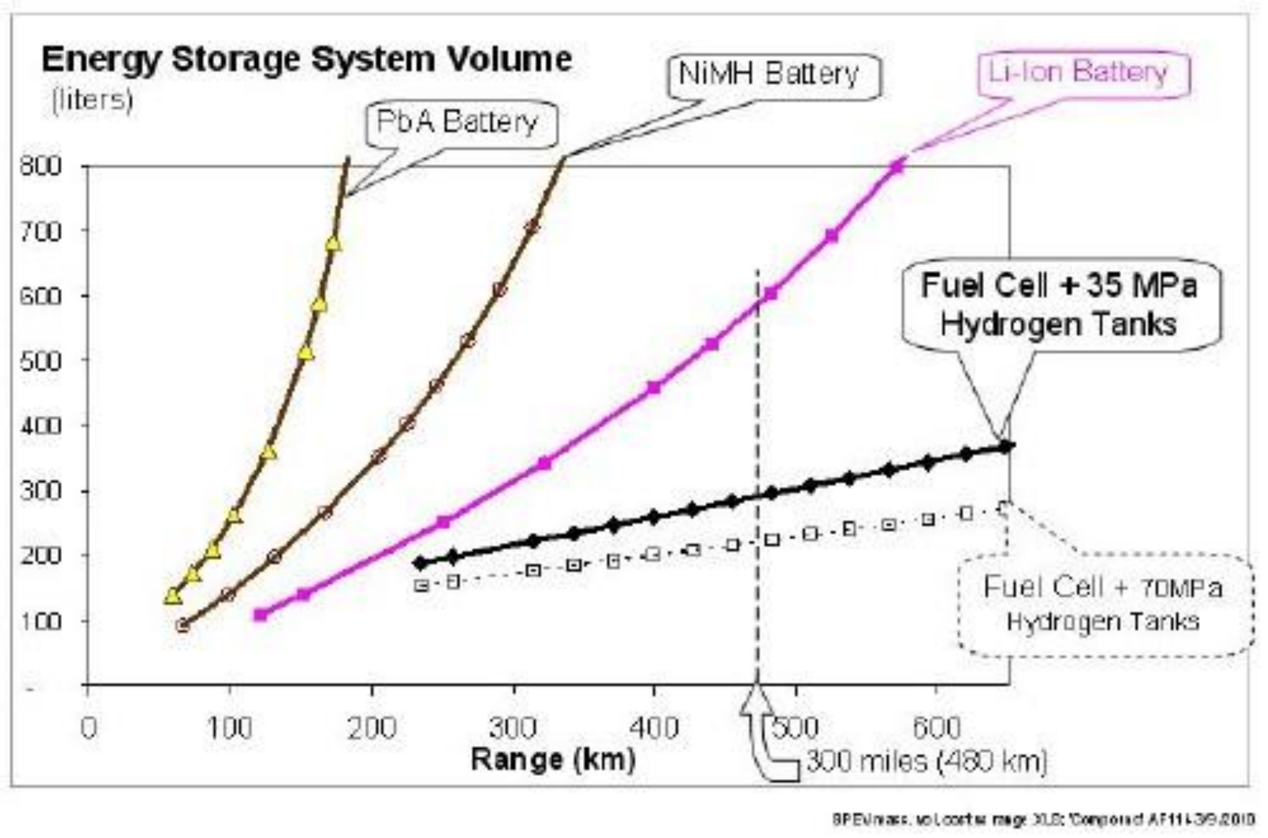
Hydrogen for vehicles

Hydrogen could be used directly in Internal combustion engine (ICE) or with a fuel cell (FC)

ICE:
- Low cost
- Well known engine
- Production of NO_X
- Low efficiency
- Noise

FC:
- High cost
- New type of engine
- Pollution free
- High efficiency
- Silent

Batteries *vs* hydrogen



We should not oppose « batteries » to hydrogen + FC:
both are chemical means of energy storage, used in electrically driven cars

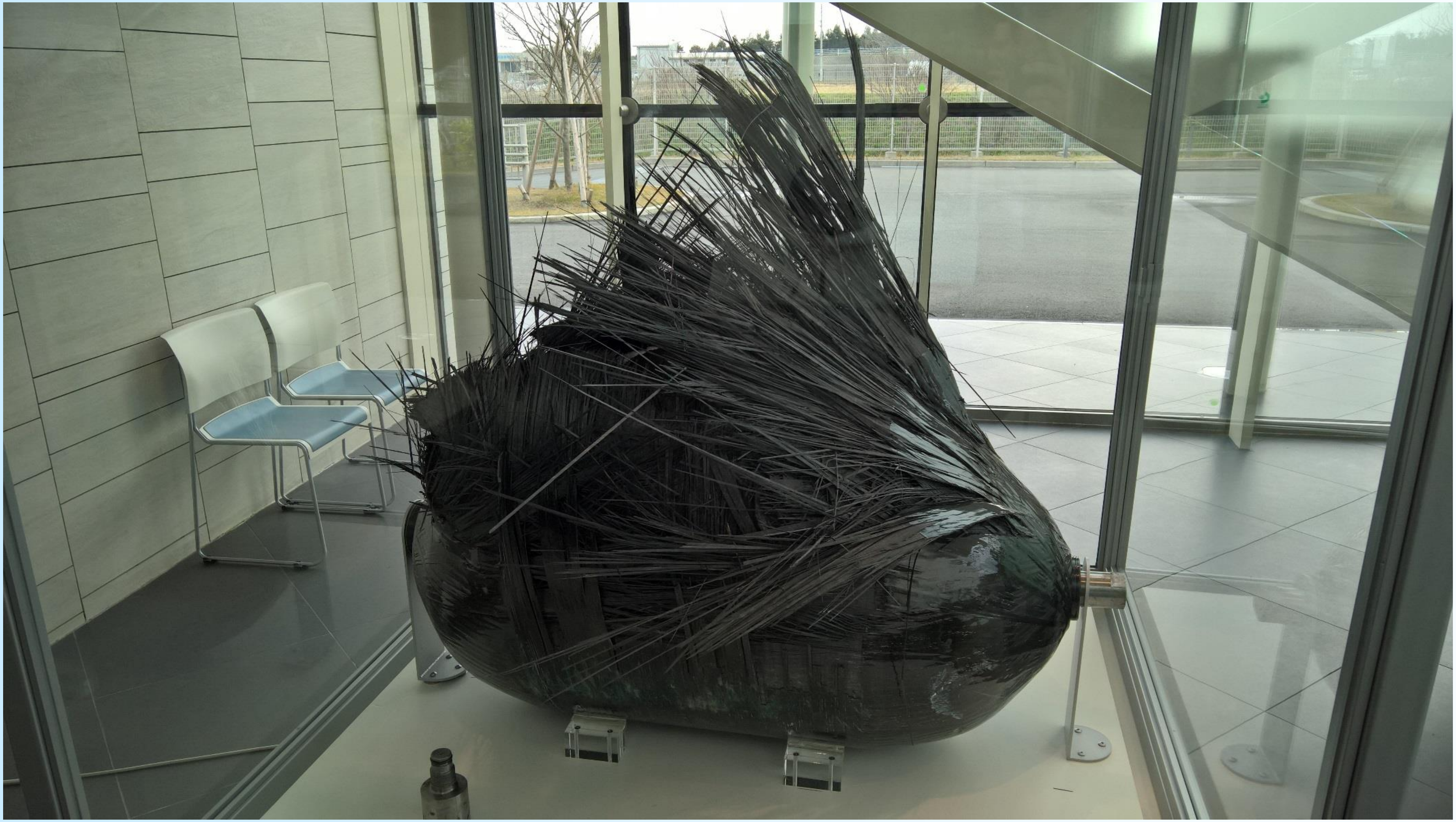
Both revolutionize the cars we know

Hydrogen car

Toyota Mirai, 700 bar, 5 kg H_2, filled by precooled gas

Carbon reinforced fuel tank

Burst test sample, HyTREC facility, Fukuoka, Japan



HyTREC test facility, Fukuoka prefecture

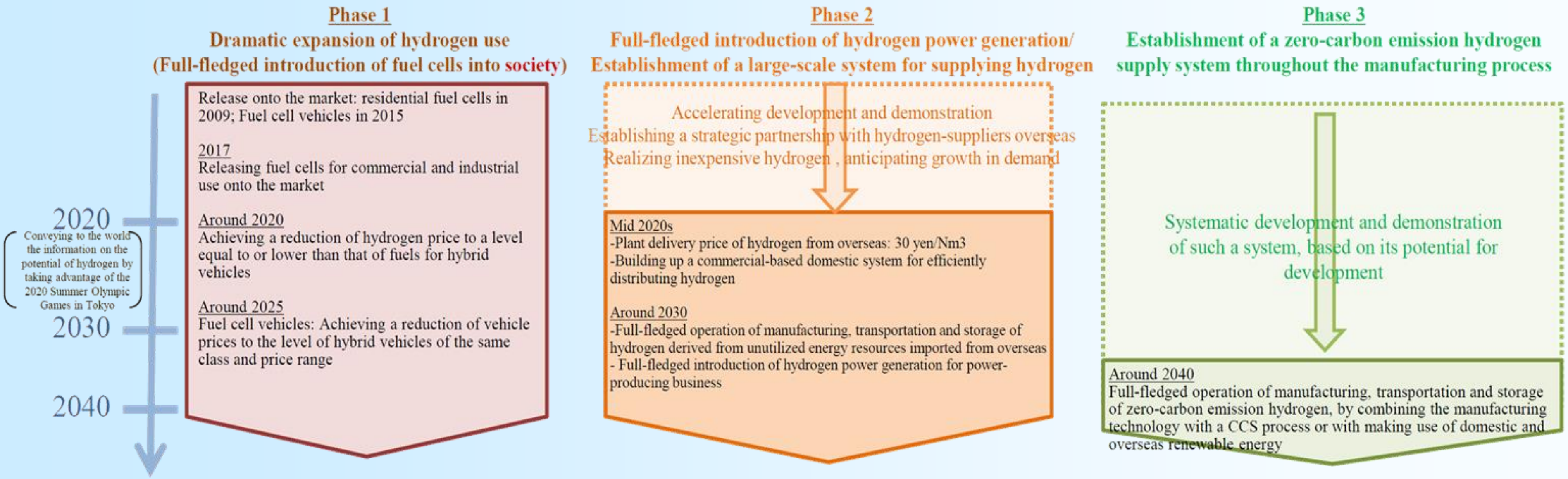
Helps industries to implement hydrogen technologies

Happy driver

HyTREC facility, Fukuoka, Japan

Strategic Road Map for Hydrogen and Fuel Cells

経済産業省
Ministry of Economy, Trade and Industry



Phase 1
Dramatic expansion of hydrogen use
(Full-fledged introduction of fuel cells into society)

Release onto the market: residential fuel cells in 2009; Fuel cell vehicles in 2015

2017
Releasing fuel cells for commercial and industrial use onto the market

Around 2020
Achieving a reduction of hydrogen price to a level equal to or lower than that of fuels for hybrid vehicles

Around 2025
Fuel cell vehicles: Achieving a reduction of vehicle prices to the level of hybrid vehicles of the same class and price range

Phase 2
Full-fledged introduction of hydrogen power generation/
Establishment of a large-scale system for supplying hydrogen

Accelerating development and demonstration
Establishing a strategic partnership with hydrogen-suppliers overseas
Realizing inexpensive hydrogen , anticipating growth in demand

Mid 2020s
-Plant delivery price of hydrogen from overseas: 30 yen/Nm3
-Building up a commercial-based domestic system for efficiently distributing hydrogen

Around 2030
-Full-fledged operation of manufacturing, transportation and storage of hydrogen derived from unutilized energy resources imported from overseas
- Full-fledged introduction of hydrogen power generation for power-producing business

Phase 3
Establishment of a zero-carbon emission hydrogen supply system throughout the manufacturing process

Systematic development and demonstration of such a system, based on its potential for development

Around 2040
Full-fledged operation of manufacturing, transportation and storage of zero-carbon emission hydrogen, by combining the manufacturing technology with a CCS process or with making use of domestic and overseas renewable energy

2020
Conveying to the world the information on the potential of hydrogen by taking advantage of the 2020 Summer Olympic Games in Tokyo
2030
2040

Market scale of the equipment and infrastructure businesses related to hydrogen and fuel cells in Japan
Approx. 1 trillion yen in 2030 → Approx. 8 trillion yen in 2050

Market scale: 7.46 Billion EU in 2030, 59.7 Billion EU in 2050

Hydrogen programs in the Western world

Japan: implementation of the strategic plan, on all levels
Run by the government + regional initiatives

EU: trying to lunch to the markets. Research is limited only to high TRLs within Fuel Cell Hydrogen Joint Undertaking (FCH JU).
Run by big industry that is also defining the policy

USA: slow recovery after halting the hydrogen program by Obama's administration. Centres of excellentce operated by the DOE
Mostly academic + initiatives of some states (California)

Hydrogen landscape is defined by

Cheap oil: less motivation

Big public and polytical attention to Li-ion batteries

Large investment made into the compressed hydrogen gas

These are constraints of today!

Fundamental drivers of hydrogen economy

High energy density

Much cheaper and much safer than Li-ion batteries

Raw materials are less critical

Residential systems

H2One, Toshiba

Kyushu Resort Hotel

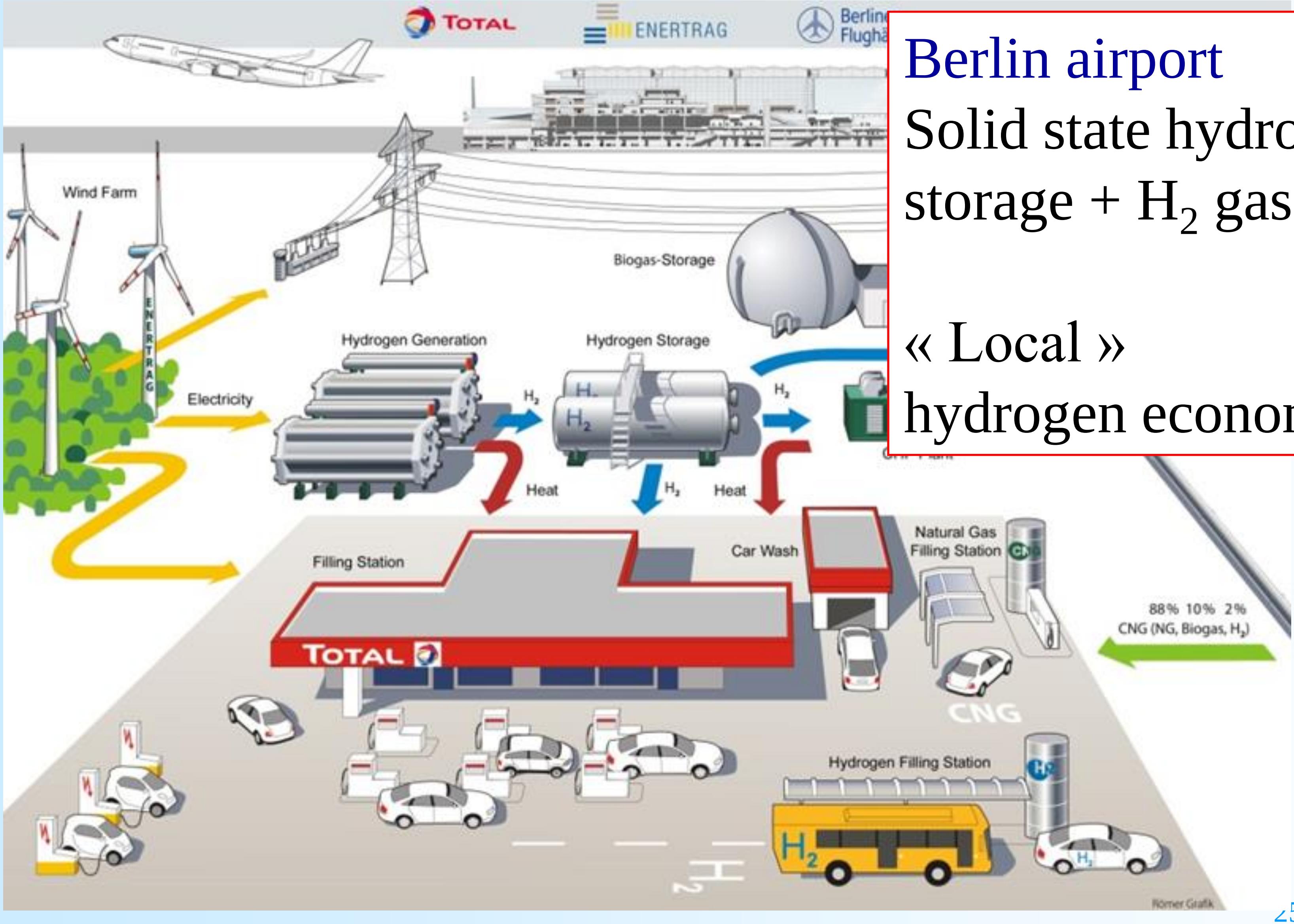
one-week's supply of electricity and hot water for 300 people using CO_2-free hydrogen energy

Enhancing the electrical grid

MYRTE, Corsica

$Sun \longrightarrow H_2 \longrightarrow$ electricity to the grid on demand

Large scale stationary systems



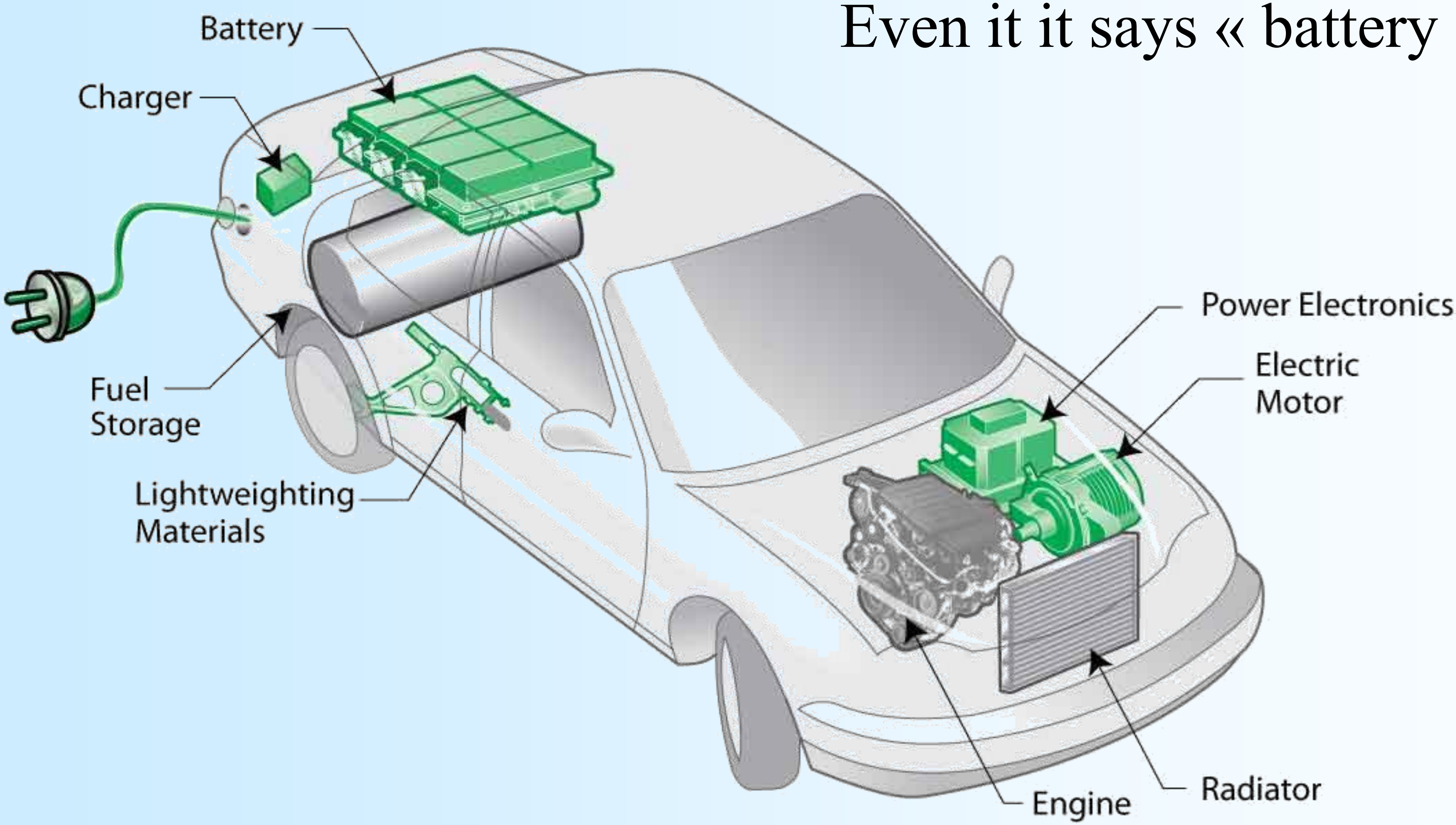
Berlin airport

Solid state hydrogen storage + H_2 gas

« Local » hydrogen economy

Hybrid cars: run on hydrogen

Even it it says « battery »



Commercial hydrogen cars from 3 manufacturers

Kyushu University, Japan

Japanese vision of the future

Renewable energy + H-storage + distribution

Hydrogen storage: main classes

Intermetallic solid solutions & compounds: $LaNi_5$-H, FeTi-H, Mg_2FeH_6

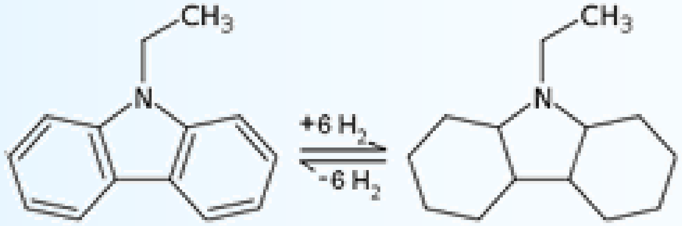
Amides: $LiNH_2 + 2LiH \leftrightarrow Li_3N + H_2$

Alanates: $NaAlH_4 \leftrightarrow NaH + Al + H_2$
(Ti-catalyzed reversibility)

Borohydrides: $LiBH_4 + MgH_2 \leftrightarrow MgB_2 + LiH + H_2$
(reactive hydride composite)

Catalyzed hydrolysis: $NaBH_4 + H_2O \rightarrow NaBO_2 + H_2$

Liquid organic hydrogen carriers



Solid-state hydrogen storage

DOE goal: 5.5 wt. % H_2 for the complete system

Metallic hydrides *d*- or *f*-metal based	Complex hydrides Light: $Z = 1\text{-}14$	Porous systems MOFs & carbons
Too heavy	Too stable, non-reversible	Interact weakly with H_2
M-H accumulators Future: stationary use	Aimed for mobile applications	

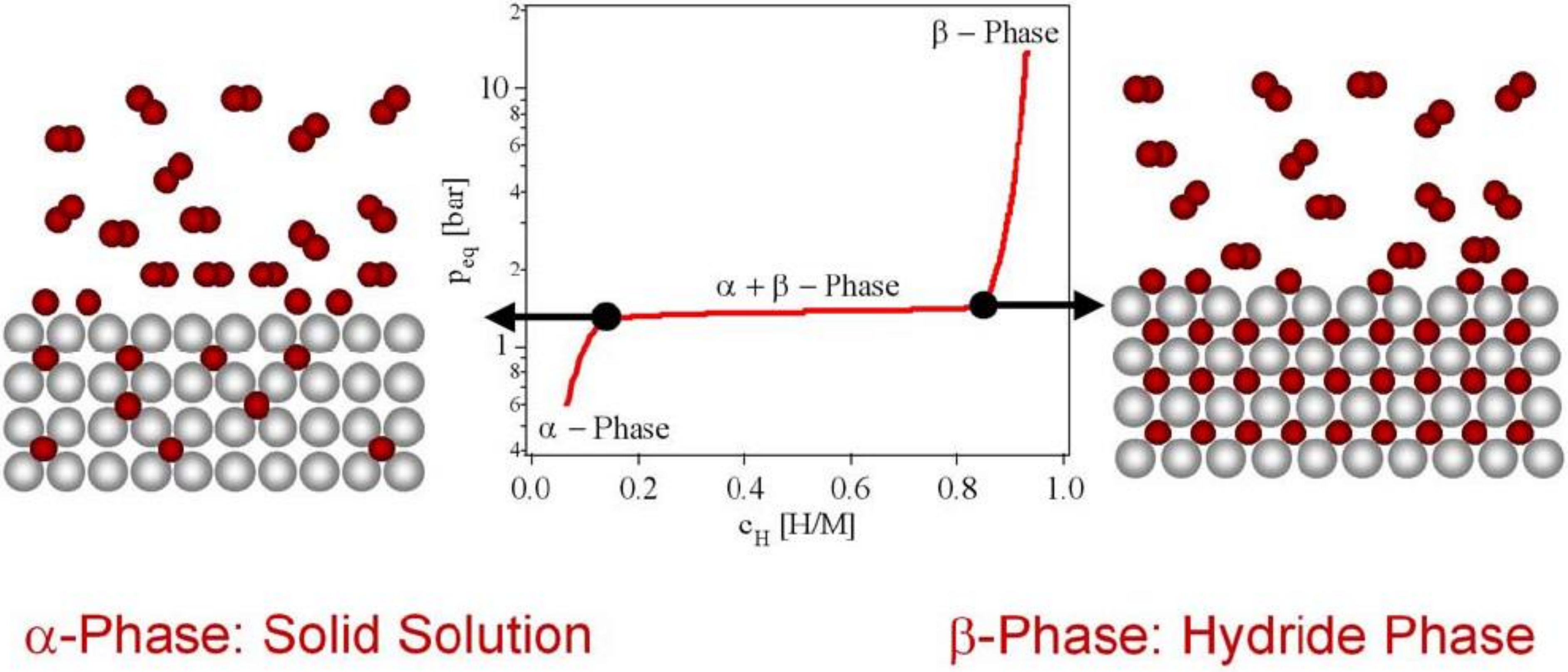
Different bonding:

interstitial H

covalent M-H (M = B, N, Al…)

physisorbed H_2

Metallic hydrides



Schlapbach & Züttel, *Nature*, 414, 353-358, 2001

p_{eq} at RT

10^{-24}	1.7	3400	bar
LaH_3	$LaNi_5H_{6.7}$	$NiH_{0.8}$	

$$\Delta G = \Delta H - T\Delta S$$
$$RT \ln (p_{eq}) = \Delta H - T\Delta S$$

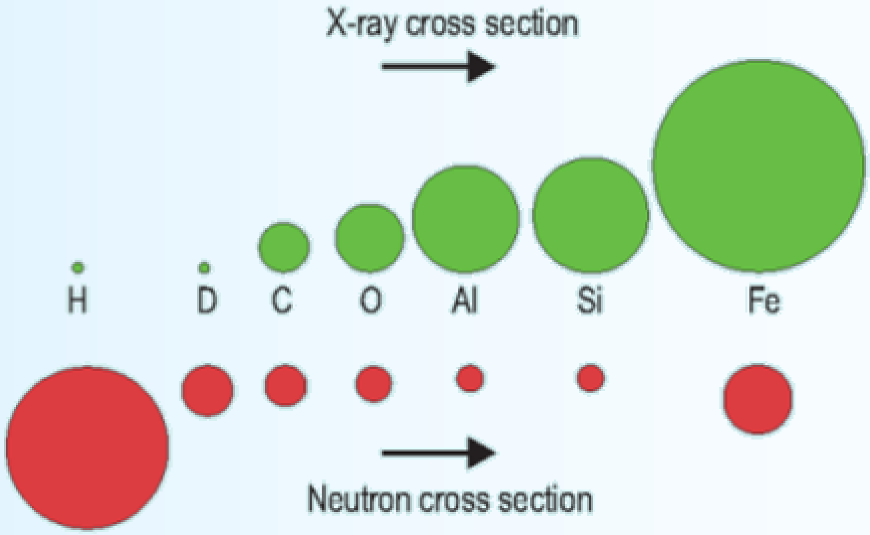
Hydrogen in metals

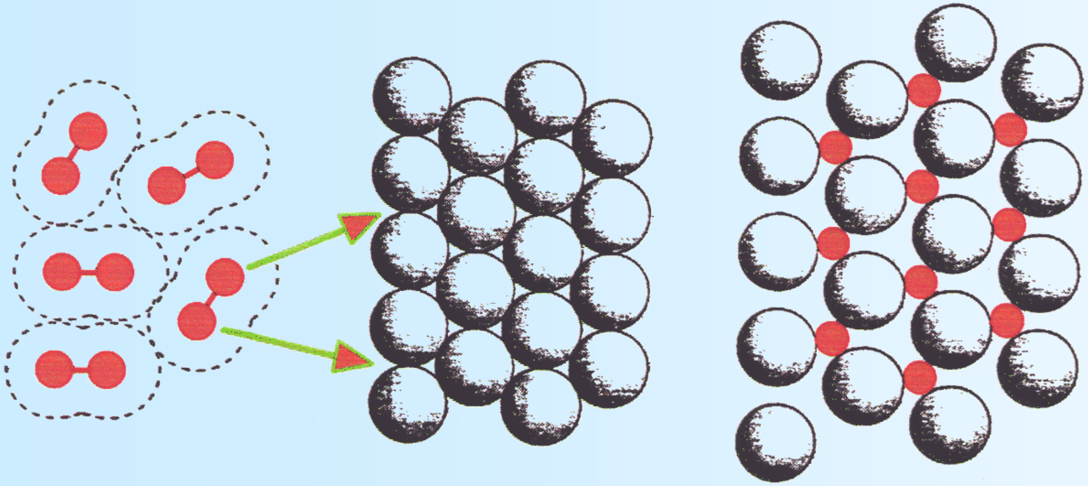
$LaNi_5H_6$

« Geometric » model

(Westlake, 1983)

- atoms are rigid spheres
- "interstitial" hole size > 0.38Å
- H-H > 2.1 Å (H-H blocking)

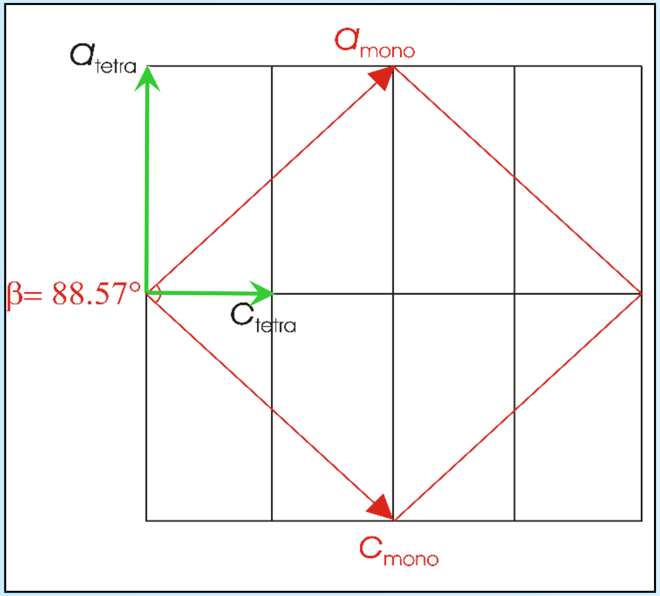




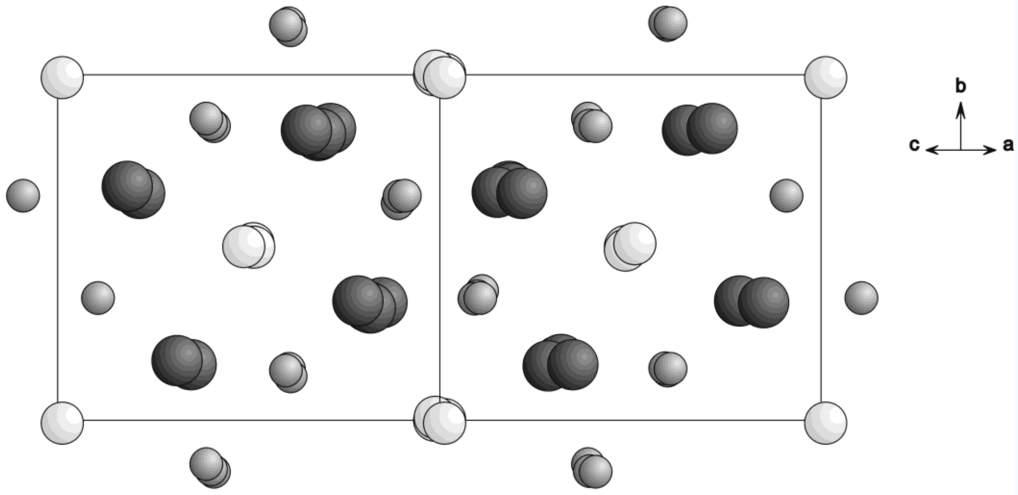
Actually, there is a rich chemistry of M-H interactions

Synchrotron: real structure

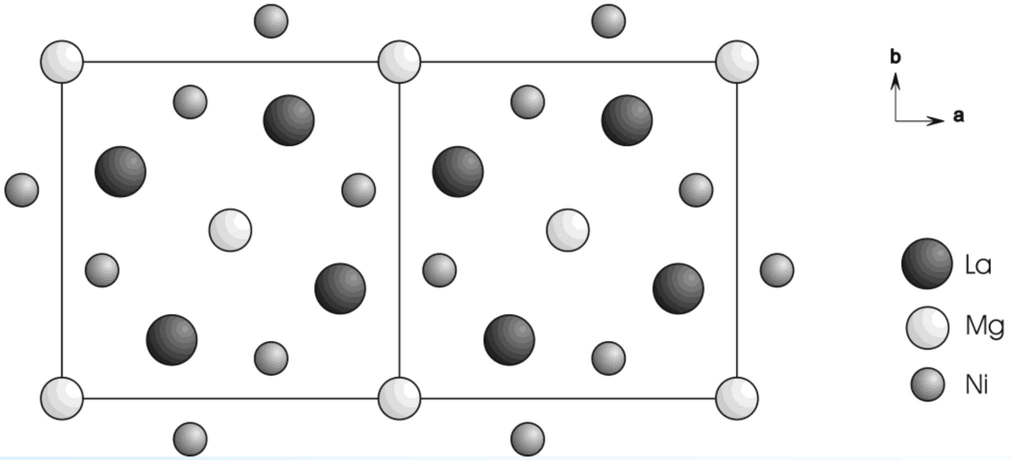
$La_2MgNi_2–D_2$



La_2MgNi_2	$La_2MgNi_2H_8$
Tetragonal	**Monoclinic**
7.64 3.94 Å	11.84 7.82 11.96 Å 92.78 °



Metal atom shifts < 0.65 Å

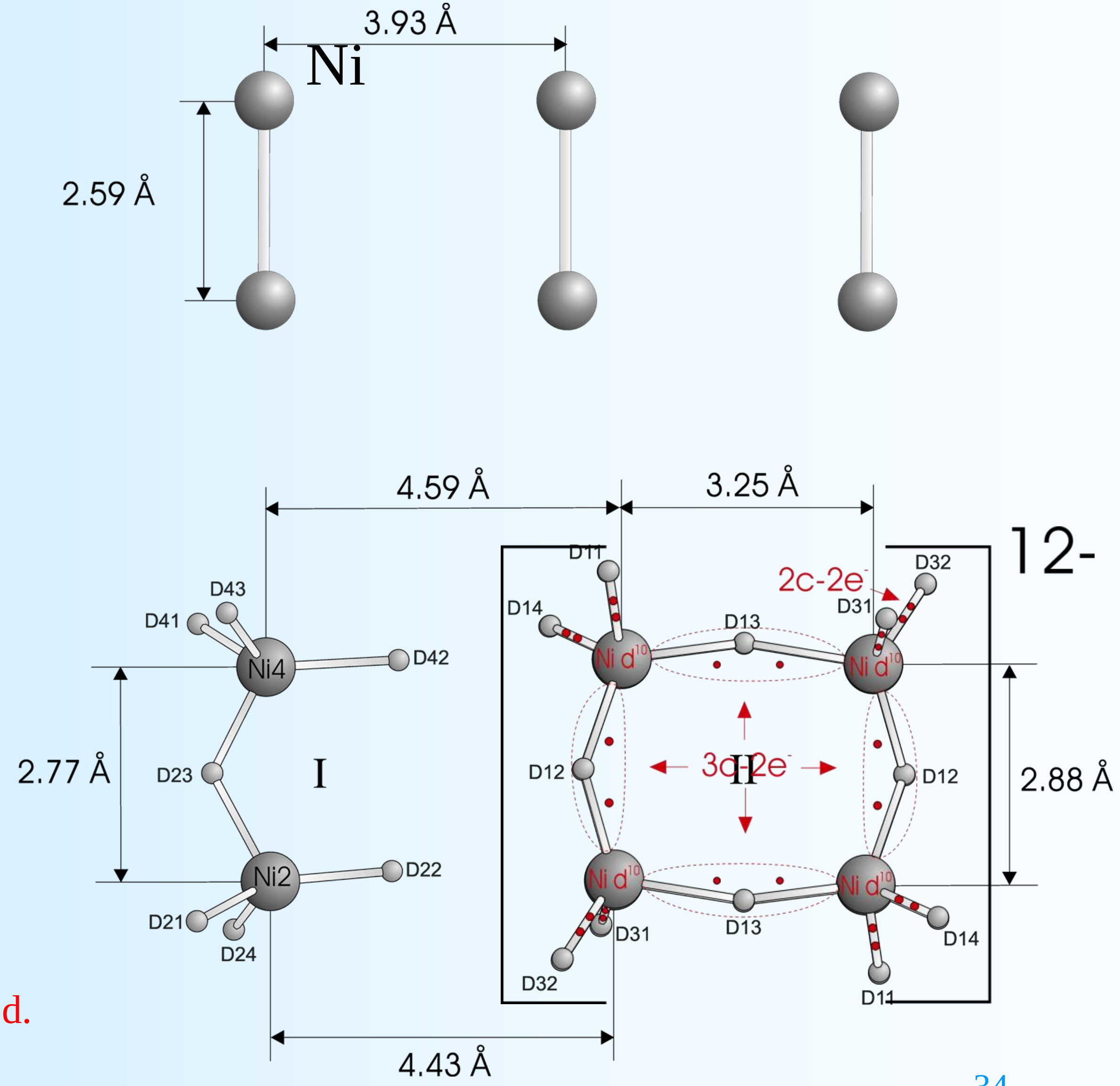


Metal-hydride complexes $[Ni_2H_7]^{7-}$ & $[Ni_4H_{12}]^{12-}$

La_2MgNi_2

$\downarrow H_2$

$La_2MgNi_2H_8$

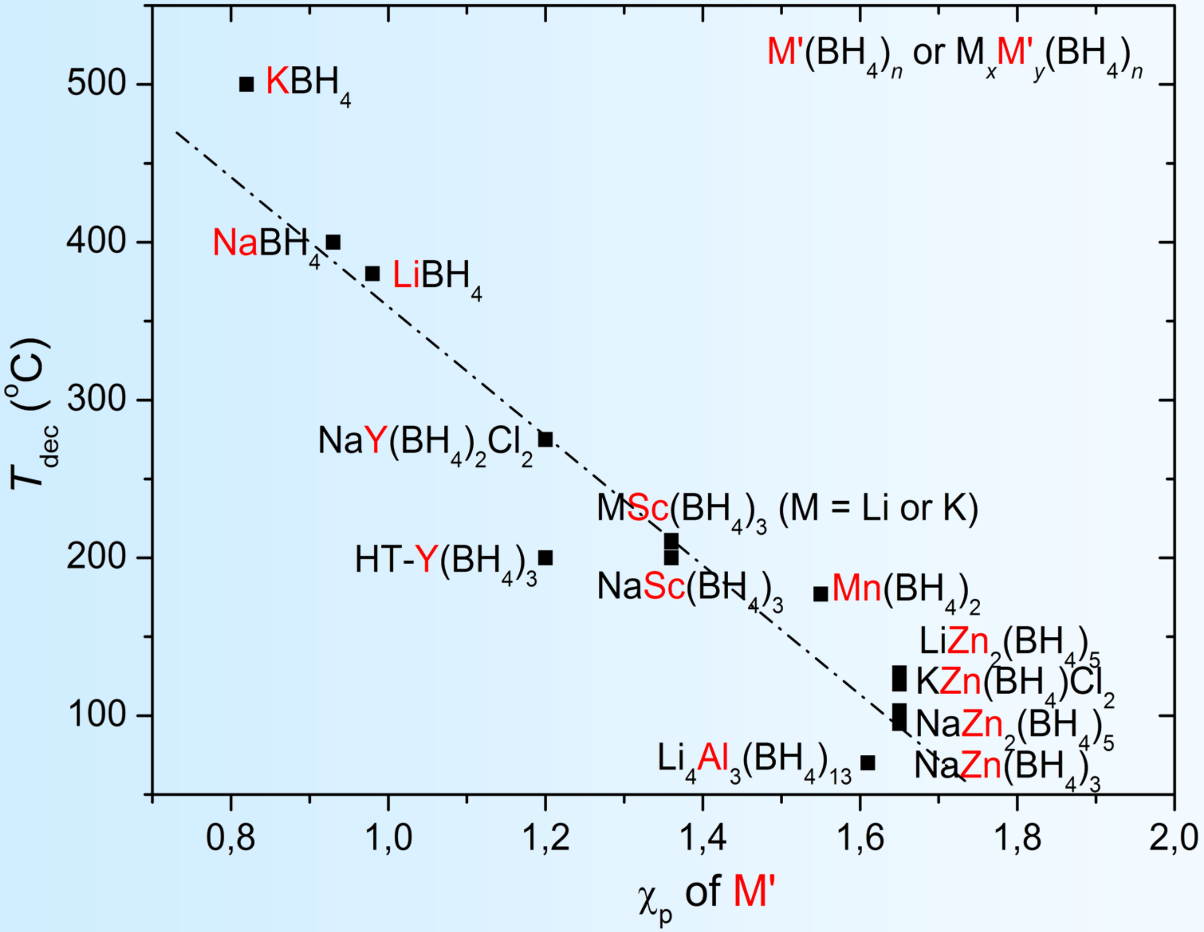


Chotard *et al.*, Angew. Chem. Int. Ed. 45 (2006) 7770

$M(BH_4)_n$

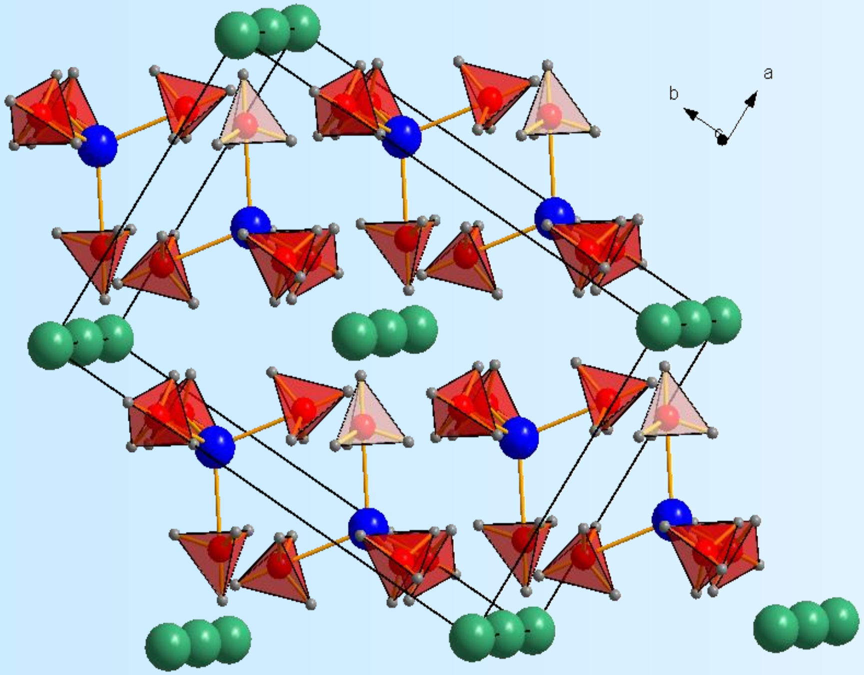
Metal borohydrides: composition - stability

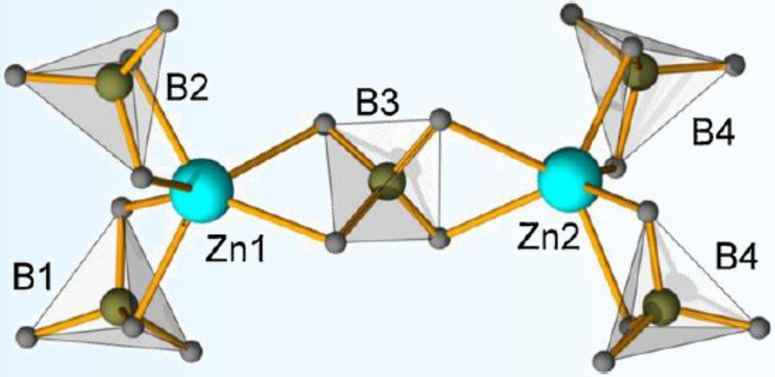
T_{dec} depends on the electronegativity of the complex-forming metal



Rude *et al.*, Phys. Status Solidi A 208 (2011) 1754

$M[M'_n(BH_4)_m]$ Bimetallic borohydrides: 2 bonding schemes





- $[Sc(BH_4)_4]^-$ is a complex anion
  - Na is a countercation

- $[Zn_2(BH_4)_5]^-$ is a complex anion
  - Li is a countercation

Černý *et al.*, JPCC, 114 (2010) 1357

Ravnsbæk *et al.*, Angew. Chem. Int. Ed., 48 (2009) 6659

$K[Zn(BH_4)Cl_2]$

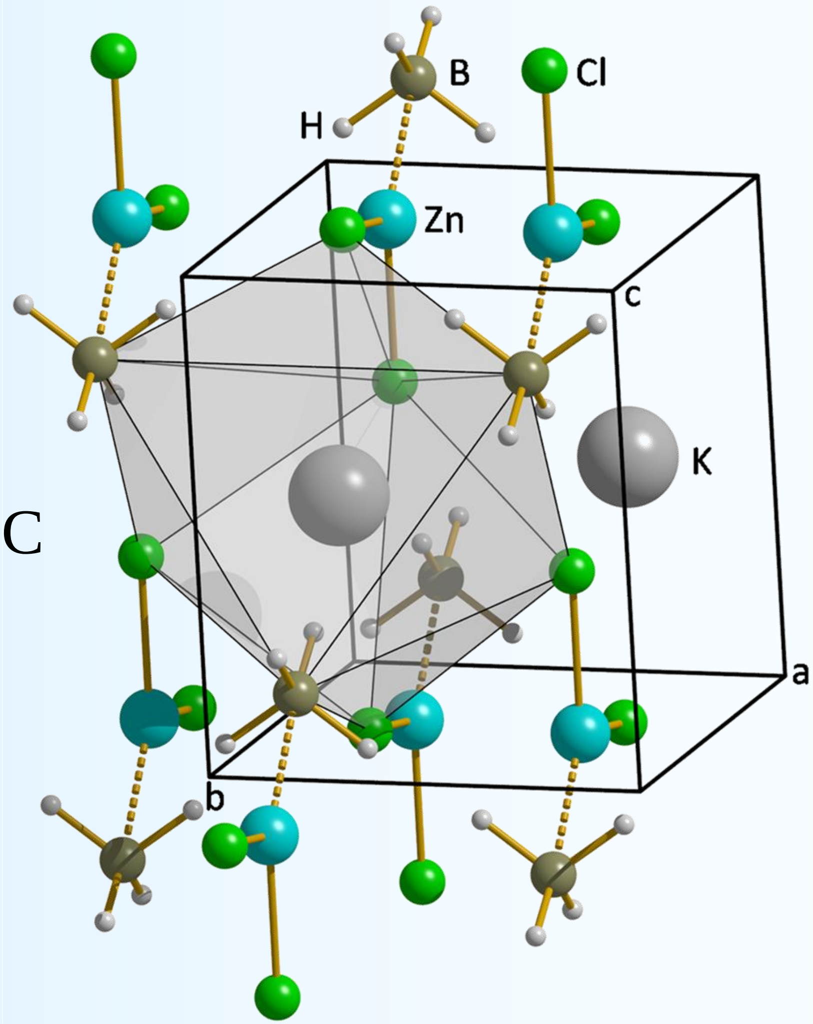
Combined use of BH_4 and Cl ligands

Complex anion

$[Zn(BH_4)Cl_2]^-$

These compounds decompose at ~100°C

- controlled charge transfer to BH_4



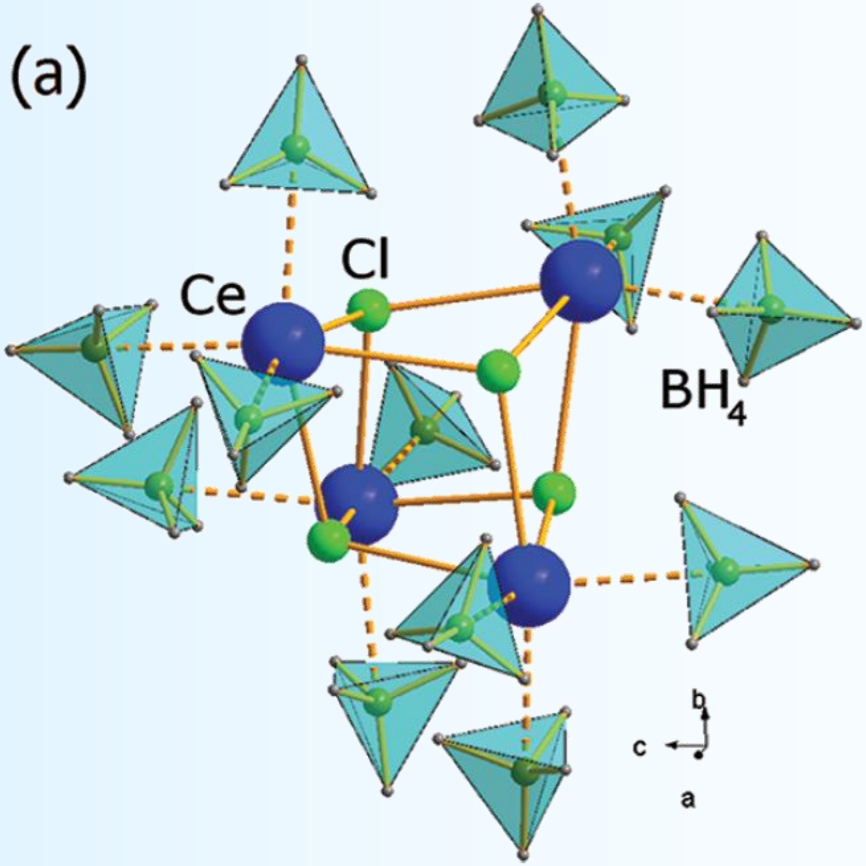
Ravnsbæk *et al.*, Eur. J. Inorg. Chem., (2010) 1608

$LiCeCl(BH_4)_3$

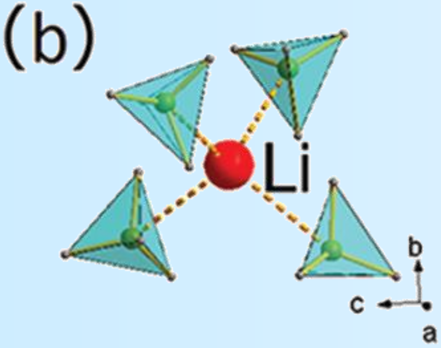
Polynuclear complexes

Complex anion

$[Ce_4Cl_4(BH_4)_{12}]^-$



Li-ion conductor at room T



Li disorder: XRD + NPD + DFT

Ley *et al.*, Chem. Mater., 24 (2012) 1654

Li-ion in Hydrides

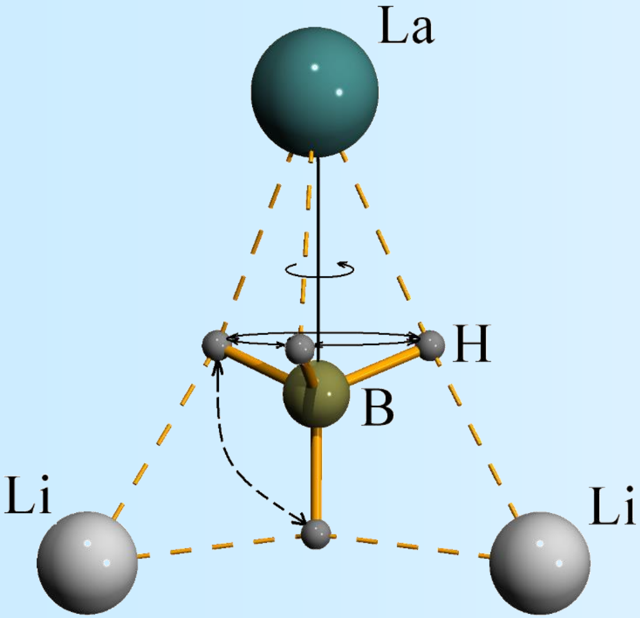
Paddle-wheel mechanism

$LiCeCl(BH_4)_3$ is a good Li-ion conductor

Ley *et al.*, Chem. Mater., 24 (2012) 1654

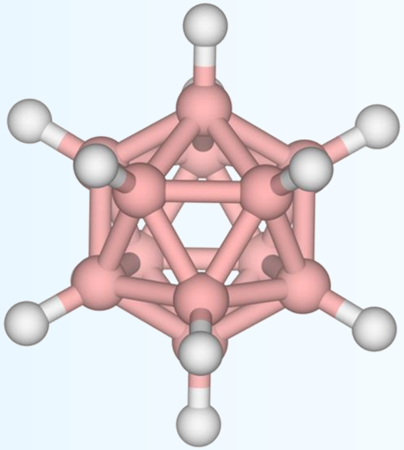
NMR data are governed by a combined effect of two types of motion. They suggest that the **Li ion jumps** and the **reorientational jumps of BH_4** groups in $LiLa(BH_4)_3Cl$ may be correlated.

Skripov *et al.*, JPCC, 117 (2013) 14965

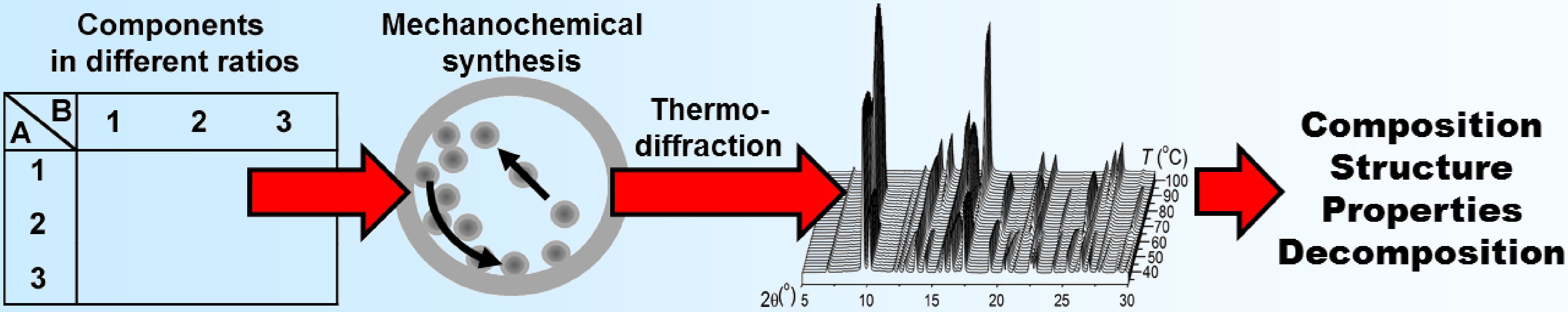


$(Li,Na)_2B_{12}H_{12}$ reaches 0.79 S/cm at 550 K

He *et al.*, Chem. Mater., (2015) 5483



Synthetic screening & fast characterization



Components in different ratios

Mechanochemical synthesis

Thermo-diffraction

Composition
Structure
Properties
Decomposition

Angew. Chem. Int. Ed. **2012**, 51, 3582.

T : 70-80 °C

$2\ KCd(BH_4)_3 \rightarrow K_2Cd(BH_4)_4 + Cd(BH_4)_2$

$Cd(BH_4)_2 \rightarrow Cd + B_2H_6 + H_2$

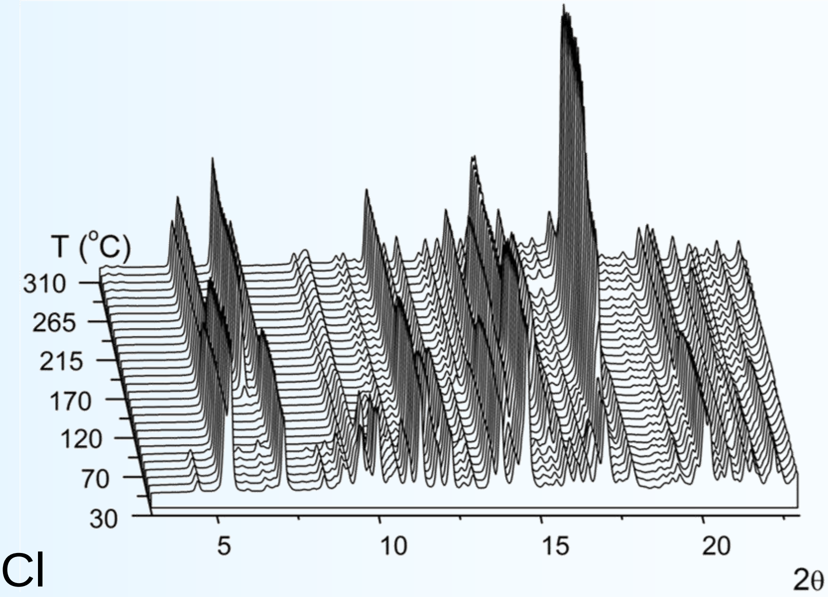
T : 80 – 90 °C

$K_2Cd(BH_4)_4 \rightarrow Cd + B_2H_6 + H_2 + KBH_4$

T : 160 – 170 °C

$KCdCl_3 + 2\ KBH_4 \rightarrow Cd + B_2H_6 + H_2 + 3KCl$

$KCdCl_3 + 3KCl \rightarrow K_4CdCl_6$

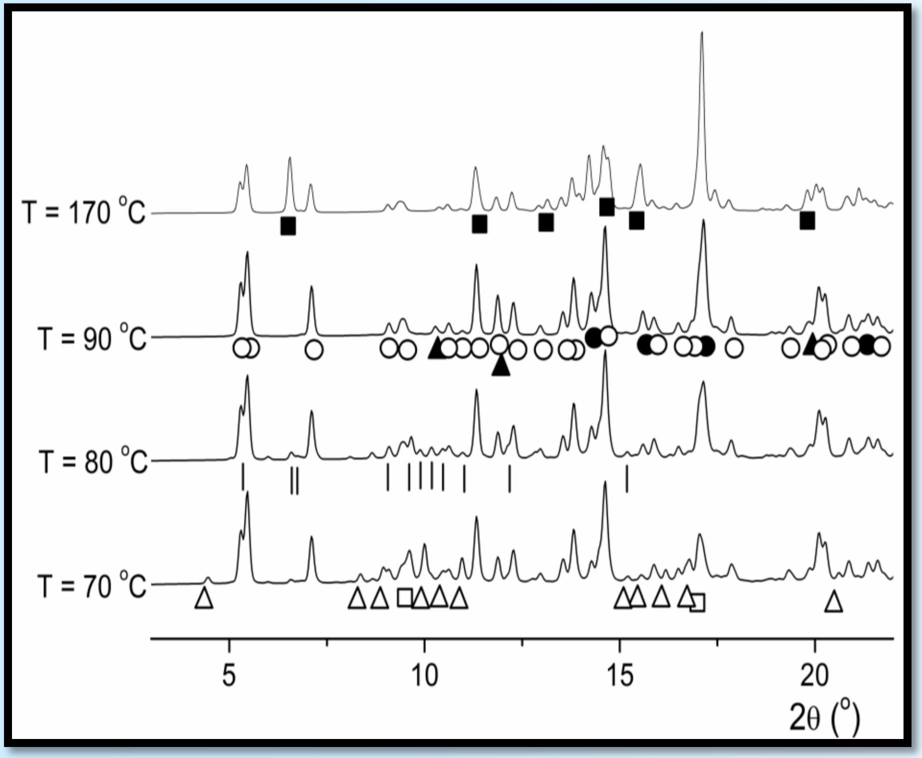


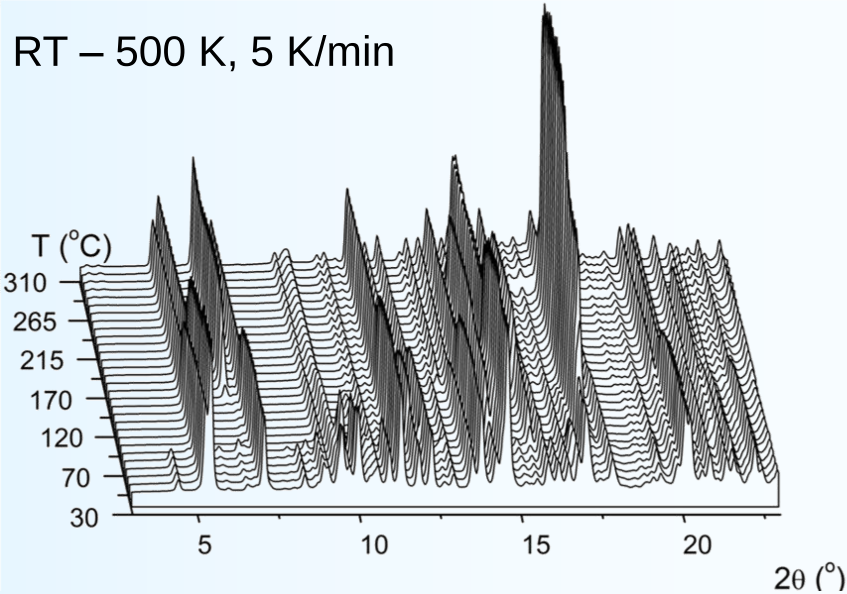
New structures from mixtures of unknown phases

“Decomposition-aided indexing” + solution from difference curves

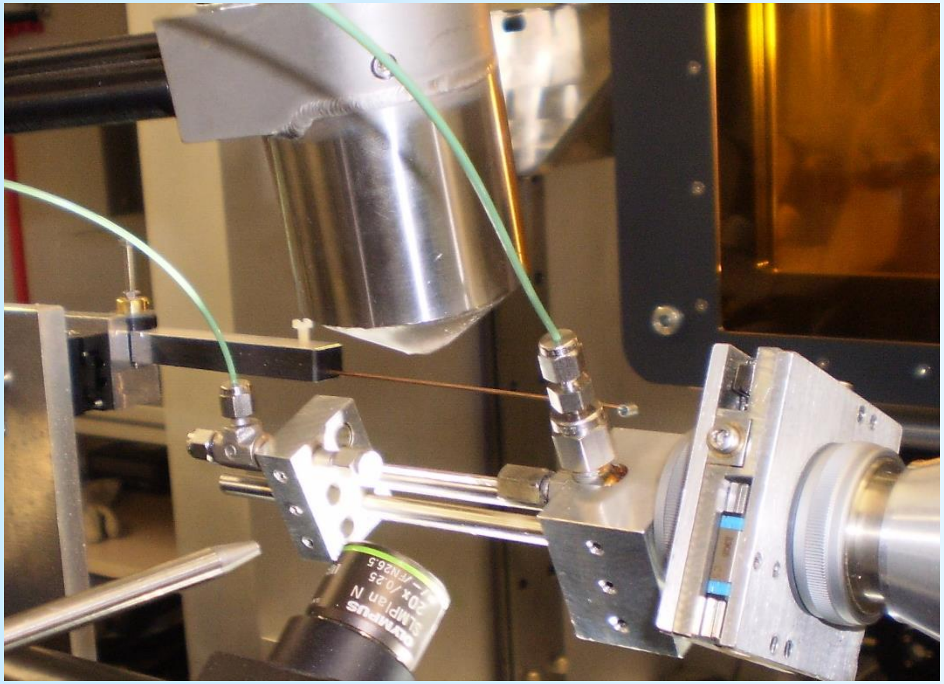
Z. Kristallogr. 2011, 226, 882-891.

	□ Cd(BH$_4$)$_2$	△ KCd(BH$_4$)$_3$	| K$_2$Cd(BH$_4$)$_4$	○ KCdCl$_3$	● Cd	▲ KBH$_4$	■ K$_4$CdCl$_6$
70 °C	**2.4 wt%**	**12.7 wt%**	**7.9 wt%**	**74.6 wt%**	**2.4 wt%**	0 wt%	0 wt%
80 °C	0 wt%	0 wt%	**14.7 wt%**	**76.8 wt%**	**8.5 wt%**	0 wt%	0 wt%
90 °C	0 wt%	0 wt%	0 wt%	**79.8 wt%**	**14.4 wt%**	**5.8 wt%**	0 wt%
170 °C	0 wt%	0 wt%	0 wt%	**74.6 wt%**	**23.8 wt%**	0 wt%	**29.6 wt%**

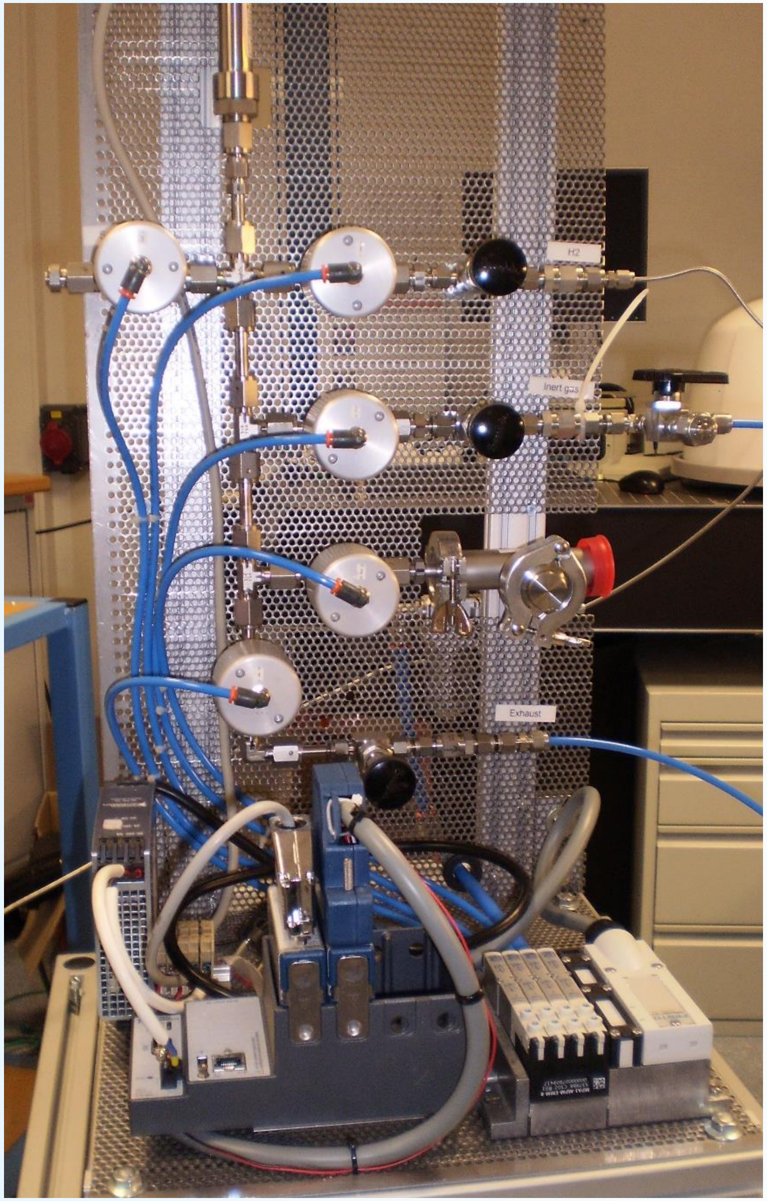




Automated gas dosing



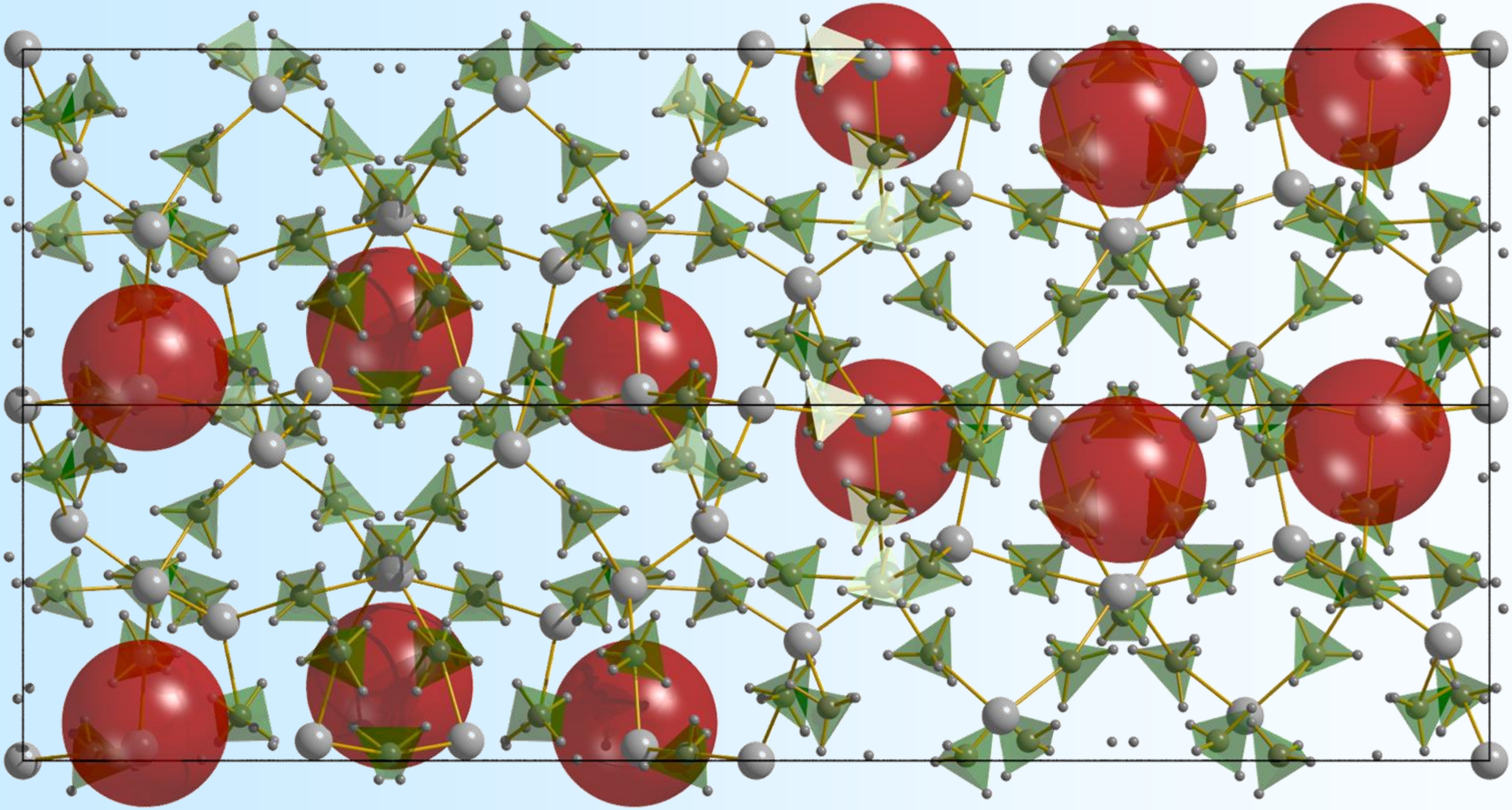
Lab: Mo rotating anode, focusing mirror, IP detector, gas + cooler/heater



Synchrotrons: SNBL/ESRF, MS/SLS(PSI), ID15/ESRF, I11/Diamond
Neutrons: NIST, HRPT/SINQ(PSI), E9/Berlin

$Mg(BH_4)_2$

Less ionic – the first porous borohydride

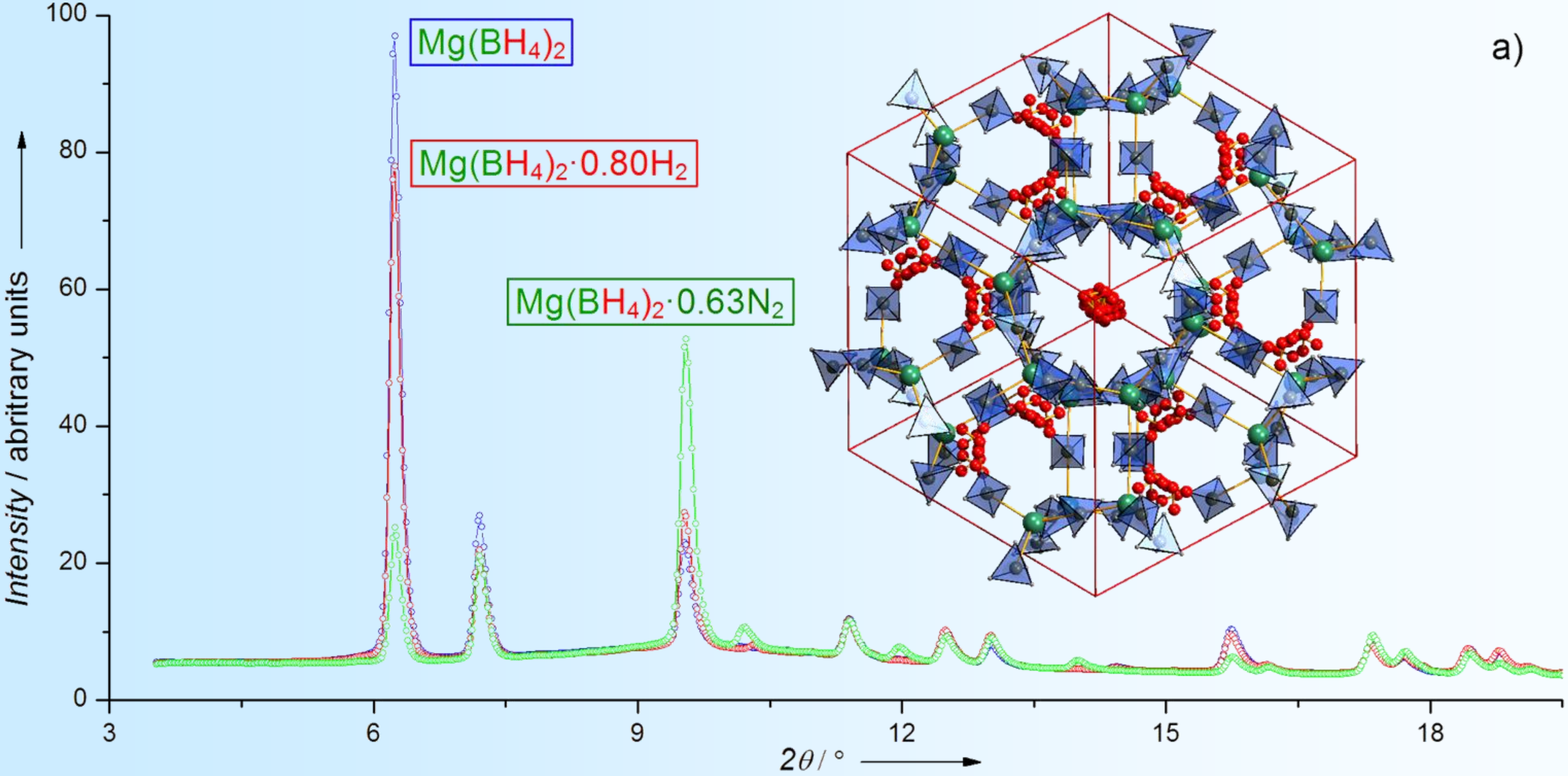


α-phase, the unoccupied voids are shown as large spheres
They account for 6.4% of the space

Filinchuk *et al*., Chem. Mater., 21 (2009) 925

γ-$Mg(BH_4)_2$ and γ-$Mn(BH_4)_2$

The first open-pore hydrides



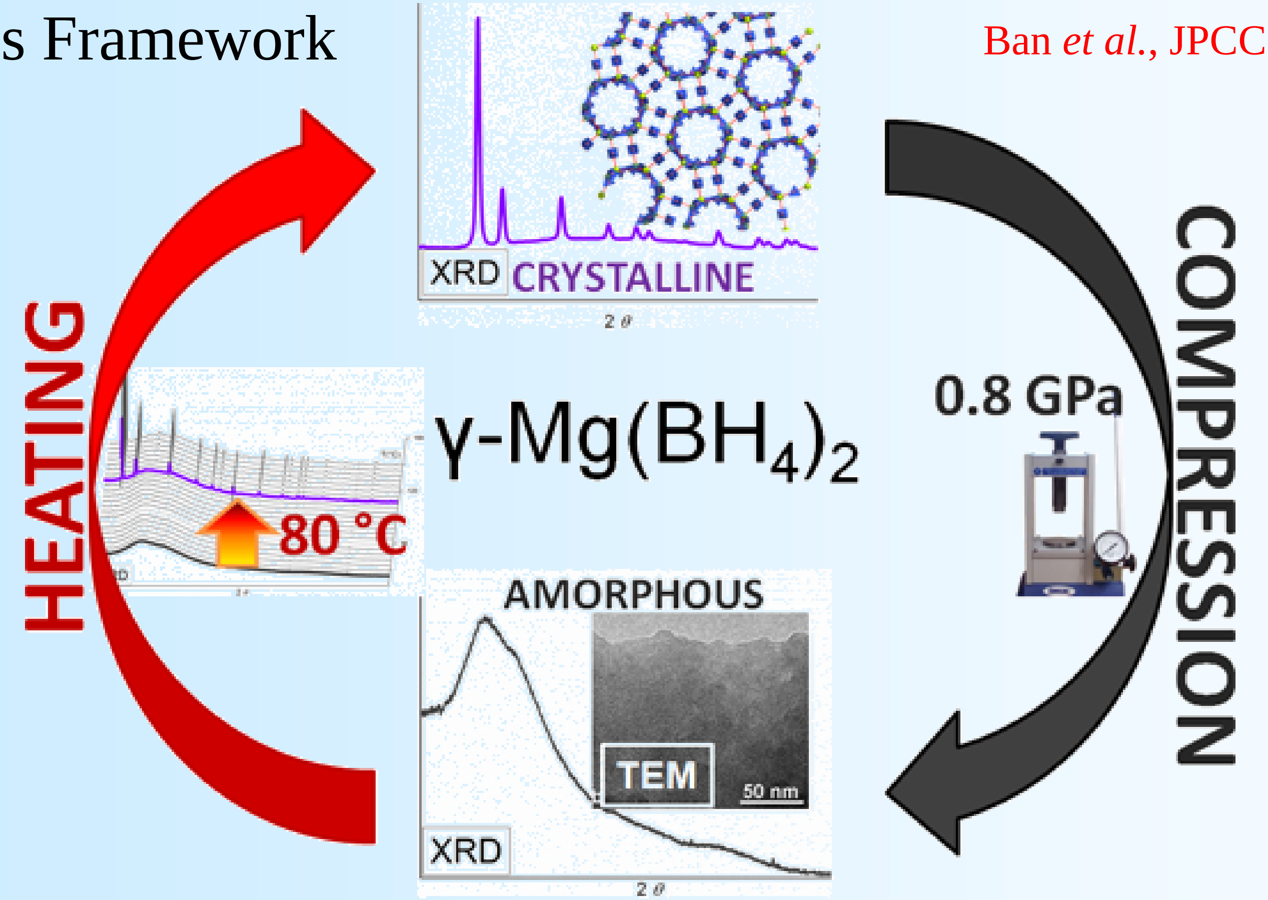
Filinchuk *et al.*, Angew. Chem. Int. Ed., 50 (2011) 11162
Richter *et al.*, Dalton Trans., 44 (2015) 3988

γ-$Mg(BH_4)_2$

Reversible transition porous ↔ dense

Porous Framework

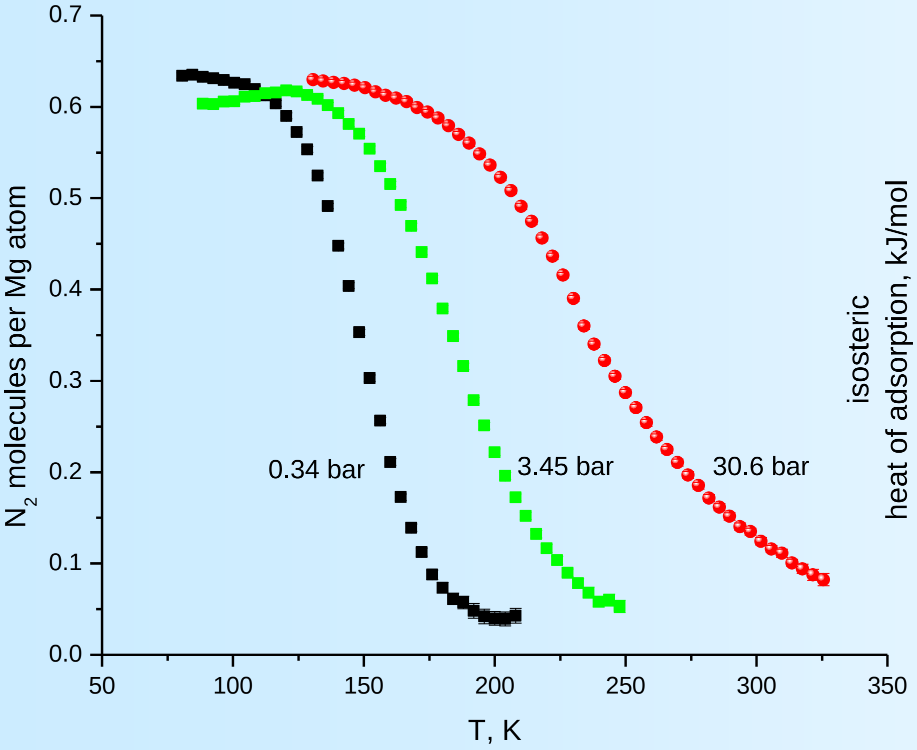
Ban *et al.*, JPCC, 118 (2014) 23402

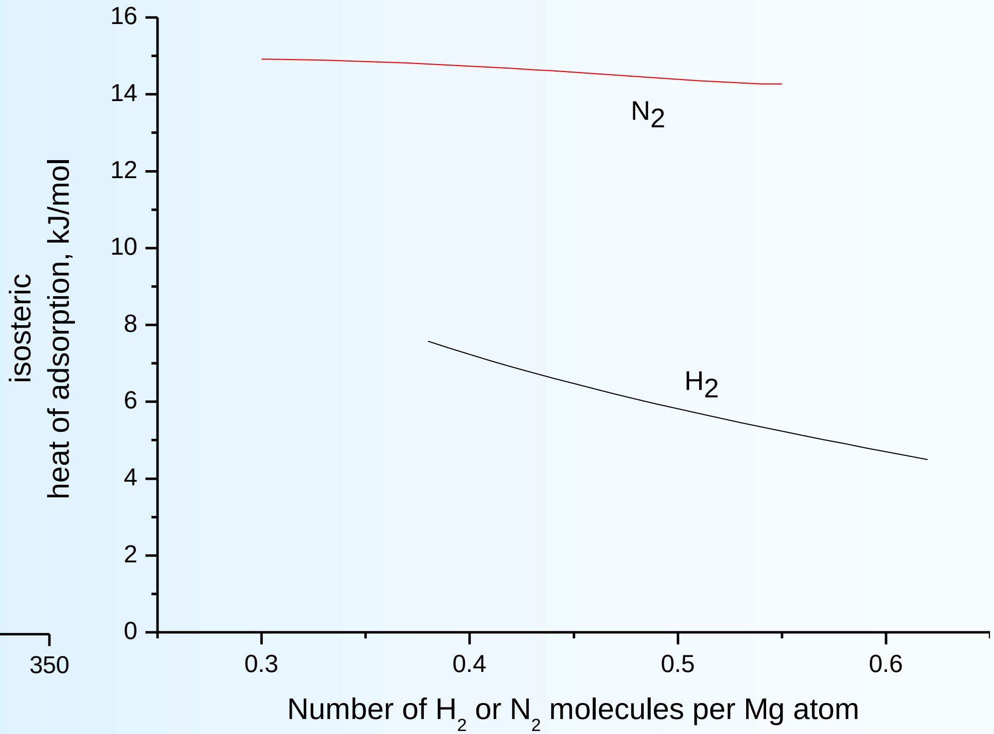


Pressure-collapsed, amorphous: **ultra-dense hydride, 145 g H / litre**

γ-$Mg(BH_4)_2$

Heats of adsorption from diffraction





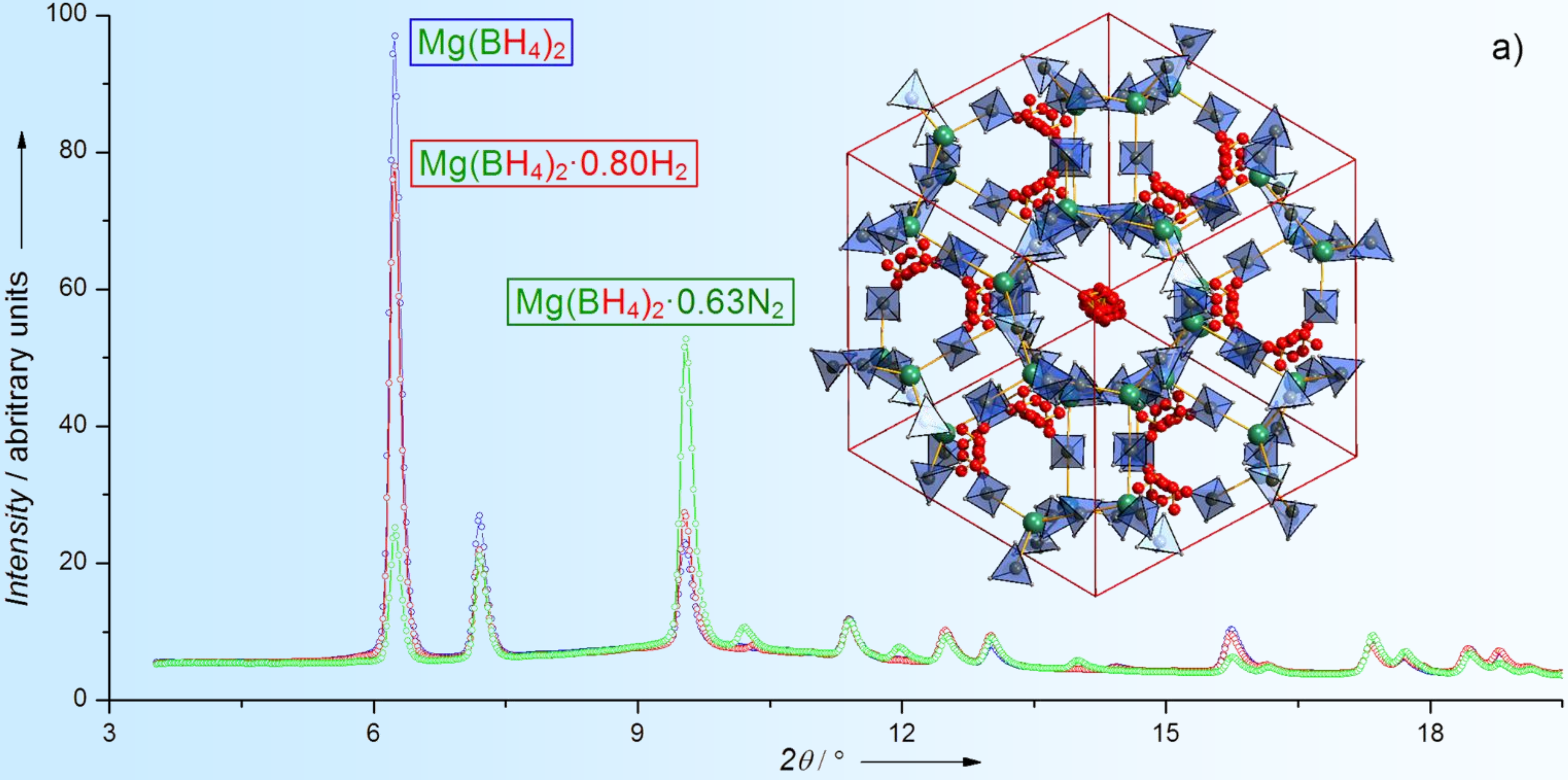
$$\ln \frac{P_1}{P_2} = \frac{\Delta h}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

– derived from Clausius-Clapeyron equation

Group of Michel Hirscher: confirms 3 wt % H_2, 5.8 kJ/mole H_2

γ-$Mg(BH_4)_2$

The first open-pore hydride: gas loading



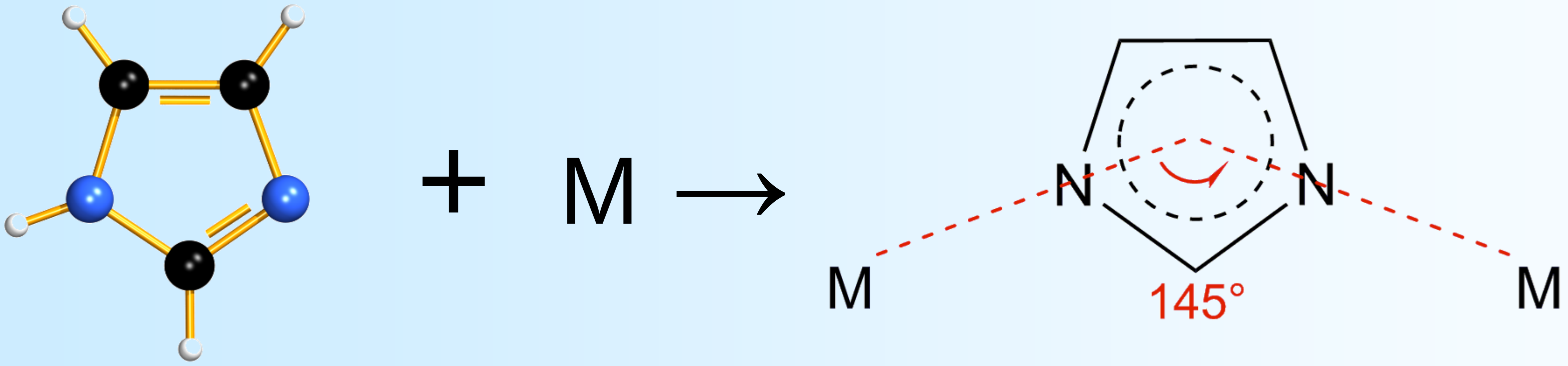
Filinchuk *et al.*, Angew. Chem. Int. Ed., 50 (2011) 11162

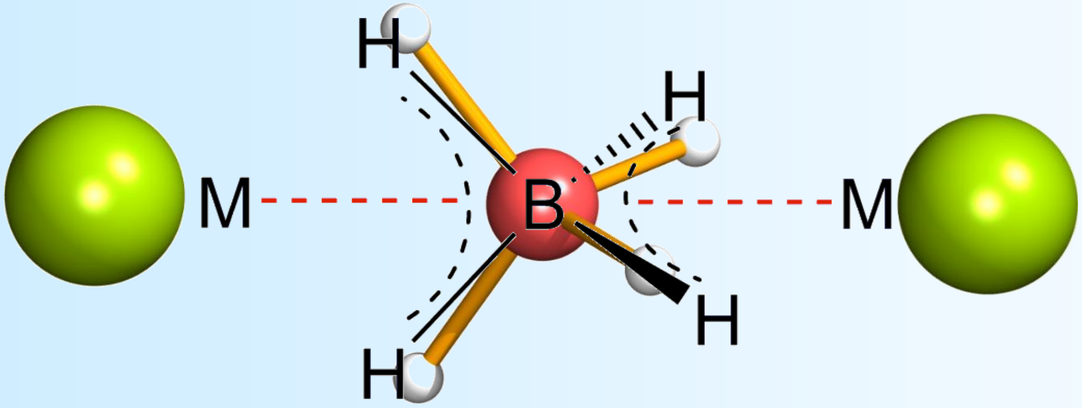
BH$_4$-Im

Combining hydride and classical ligands

Imidazole

Imidazolates (ZIFs)





BH_4^- is coordinated linearly via edges

Filinchuk *et al.*, Angew. Chem. Int. Ed., 50 (2011) 11162

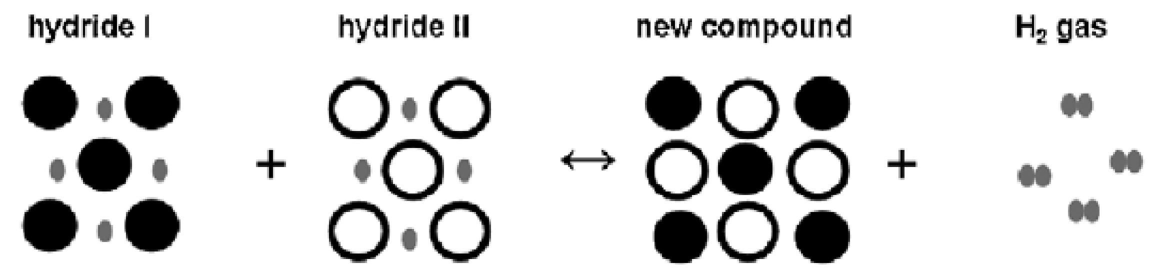
BH_4-Im

Imidazolates-borohydrides

- ✓ The hybrid hydrides are designed and obtained for the first time
- ✓ High BH_4 dynamics may allow for higher reactivity
- ✓ We are going for porous Im-BH_4 frameworks, using substituted imidazolates
  New compositions are obtained with methyl- and benzimidazolates

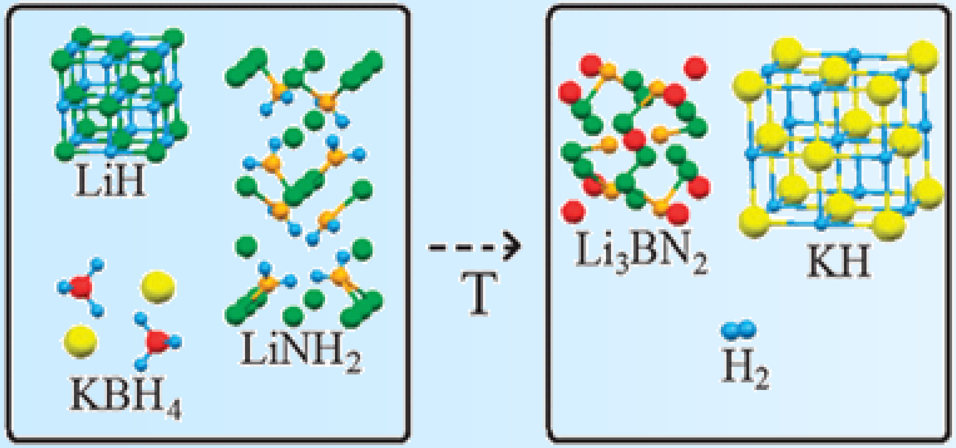
Porosity can allow for reactions inside the pores !

Reactive hydride composites

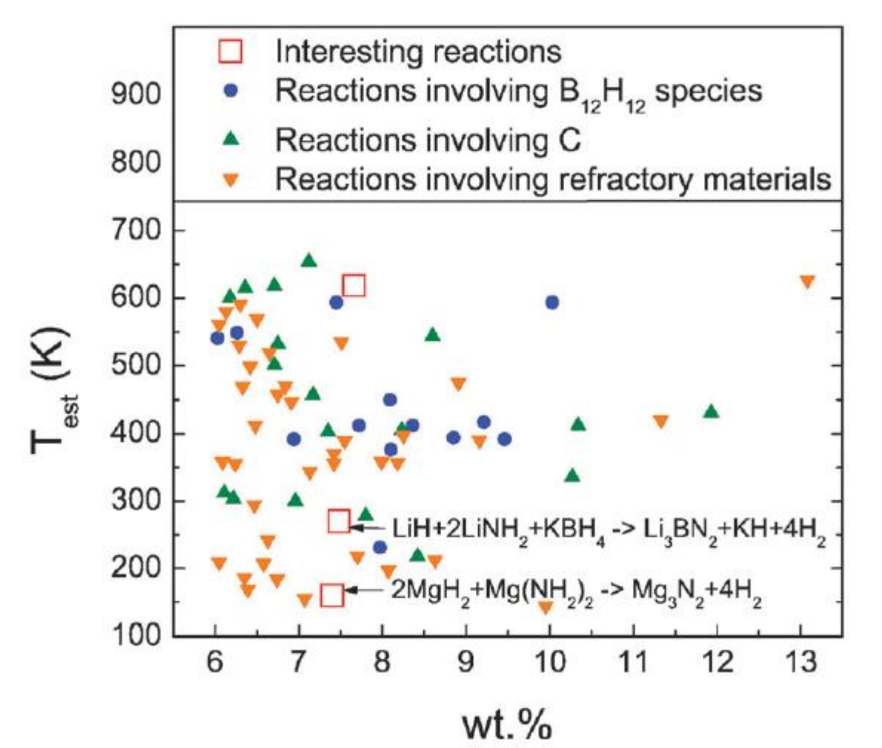


reversible

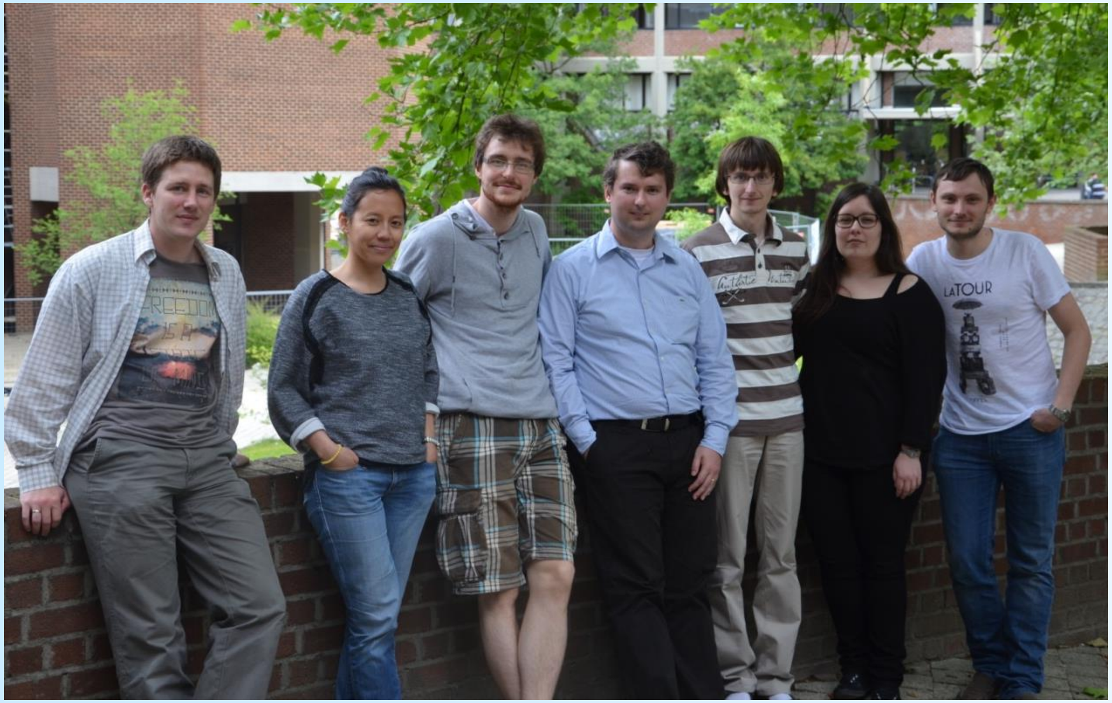
$$15 \leq \Delta U_0 \leq 75 \text{ kJ mol}^{-1} \text{ H}_2$$



Kim *et al.*, PCCP, 13 (2011) 7218



Acknowledgements



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IMP RAS: **Alexander Skripov**
GM: **Scott Jorgensen**
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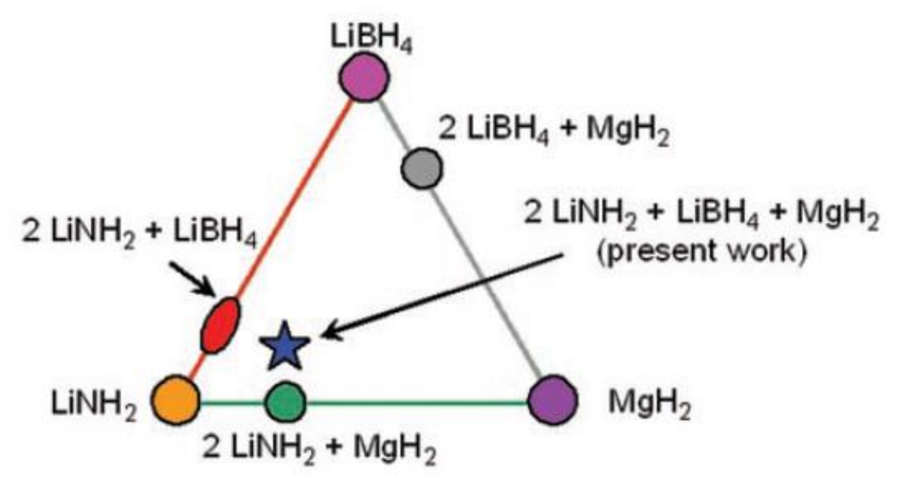
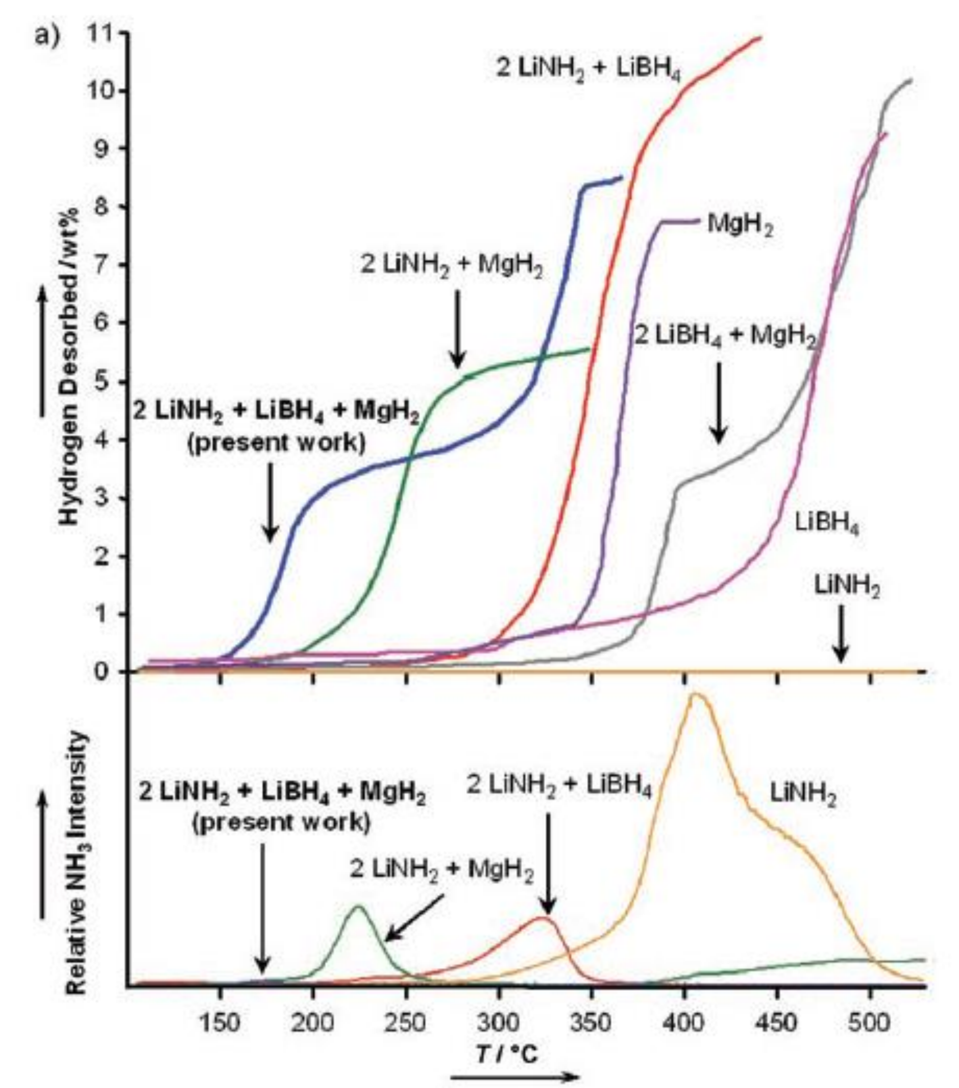
COST Action MP1103

Facilities

H_2FC/IFE, SNBL/ESRF,
NIST, SINQ, HMI,
SLS/PSI

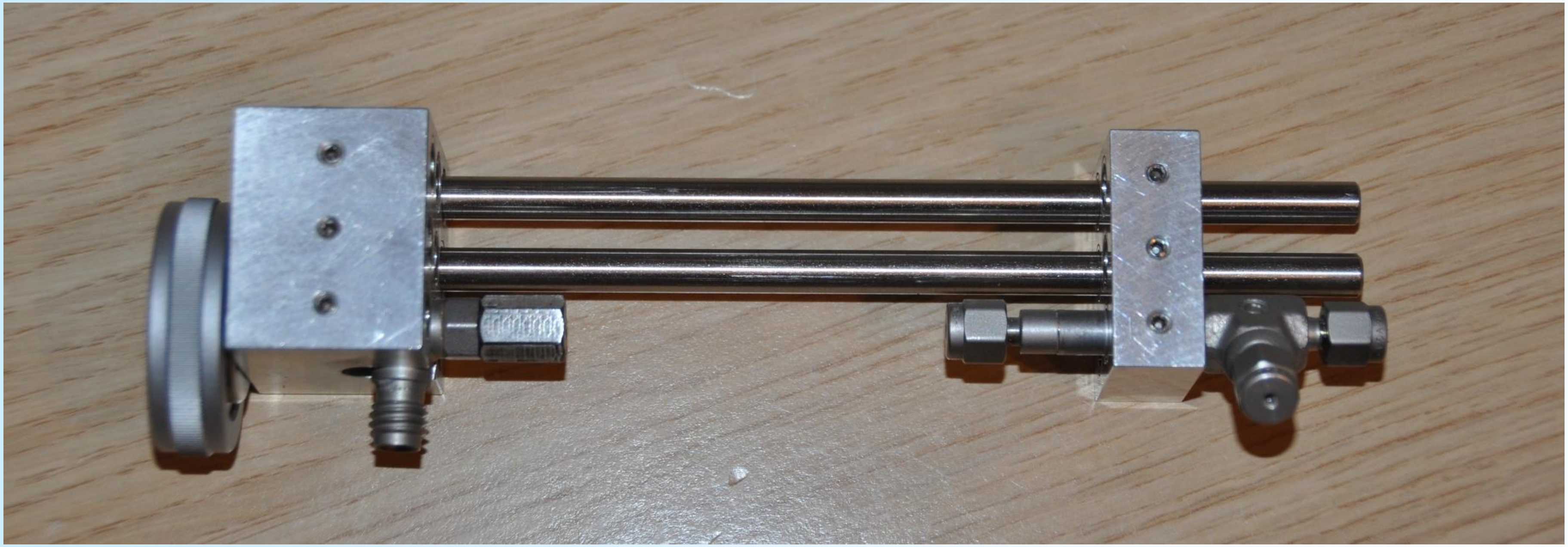
Reactive hydride composites: practice





Yang *et al*.,
Angew. Chem., Int. Ed.
47 (2008) 882

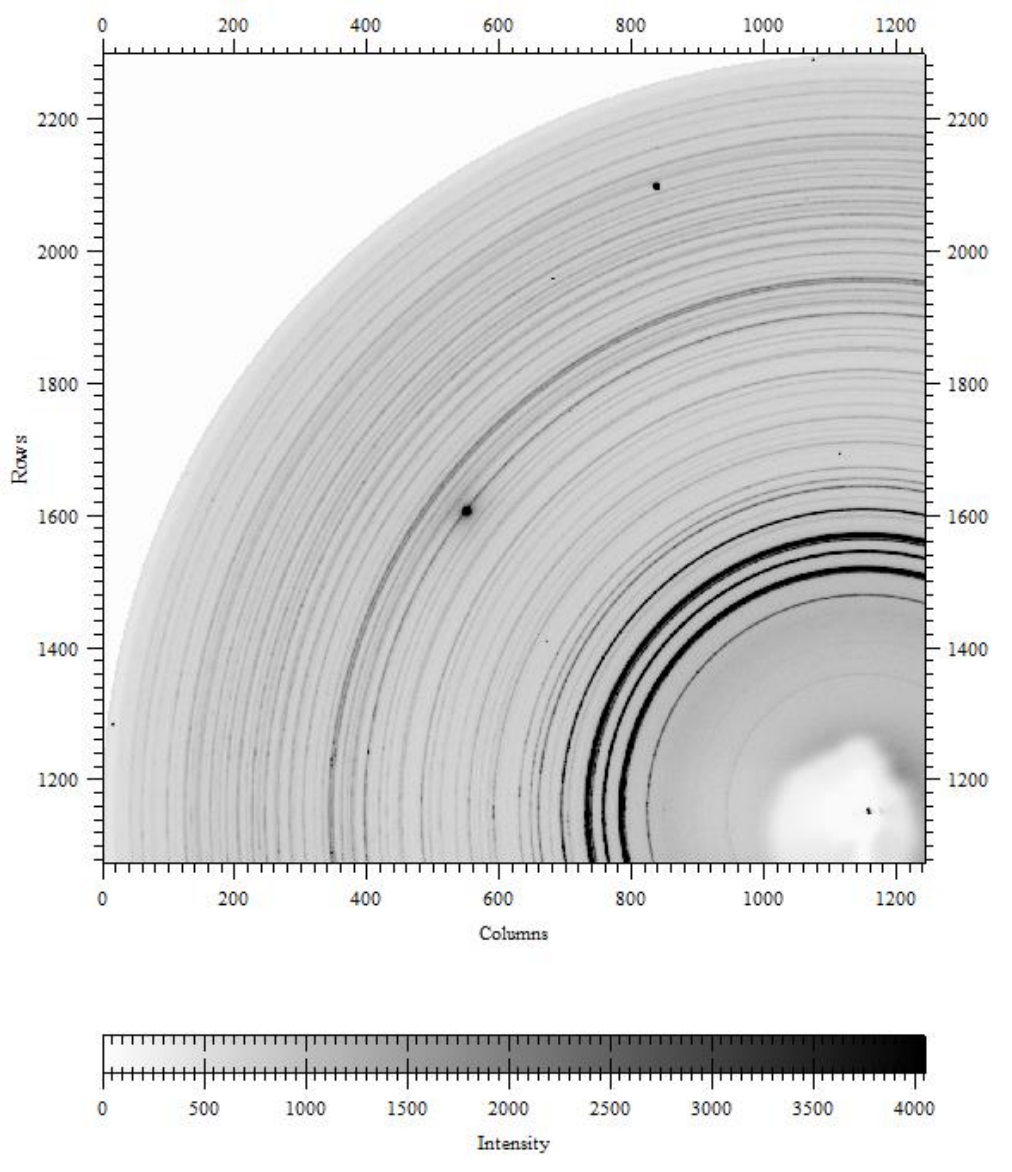
Gas cells – sapphire tube



- Short mount – fits into Lab setups
- Left + right handed threads to avoid capillary twisting

Jensen *et al.*, J. Appl. Cryst, 43 (2010) 1456

Single-crystal sapphire tube

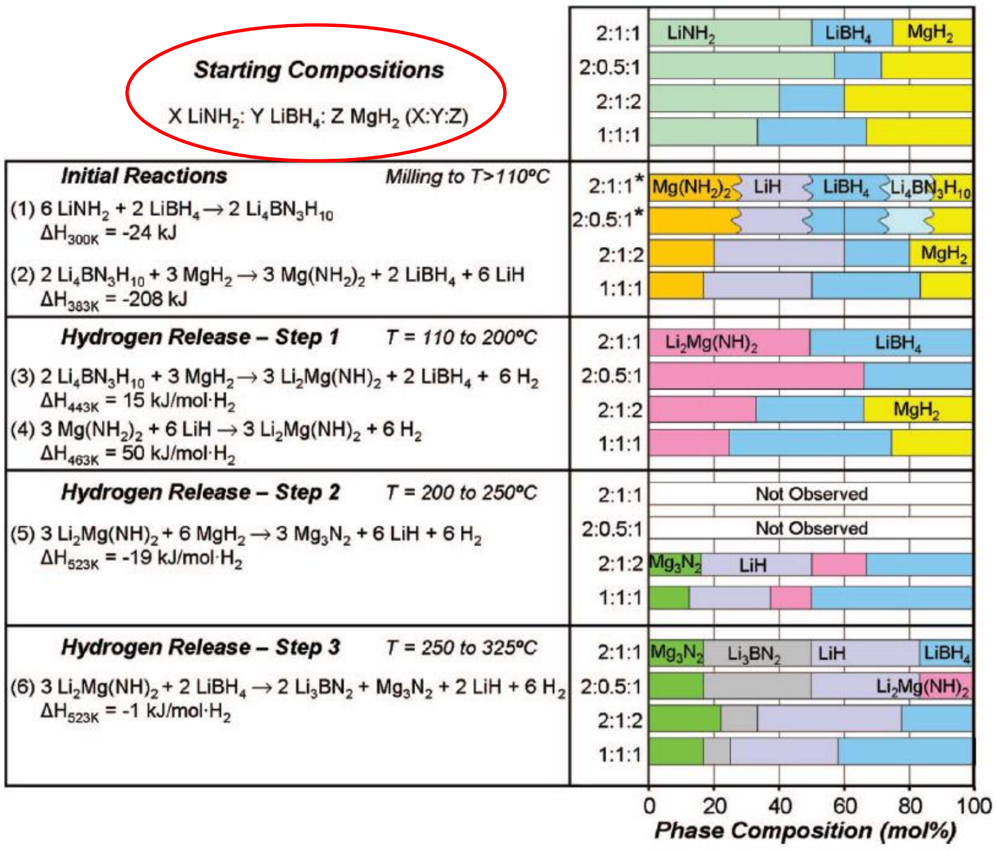


- Background-free
- Inert
- Robust

- Expensive
- Absorbing X-rays

Suitabe for
a very high-P systems
or for
highly reactive samples

Reactive hydride composites: practice



Starting Compositions

X $LiNH_2$: Y $LiBH_4$: Z MgH_2 (X:Y:Z)

Initial Reactions — *Milling to T>110°C*

(1) $6\ LiNH_2 + 2\ LiBH_4 \rightarrow 2\ Li_4BN_3H_{10}$
$\Delta H_{300K} = -24$ kJ

(2) $2\ Li_4BN_3H_{10} + 3\ MgH_2 \rightarrow 3\ Mg(NH_2)_2 + 2\ LiBH_4 + 6\ LiH$
$\Delta H_{383K} = -208$ kJ

Hydrogen Release – Step 1 — *T = 110 to 200°C*

(3) $2\ Li_4BN_3H_{10} + 3\ MgH_2 \rightarrow 3\ Li_2Mg(NH)_2 + 2\ LiBH_4 + 6\ H_2$
$\Delta H_{443K} = 15$ kJ/mol·H_2

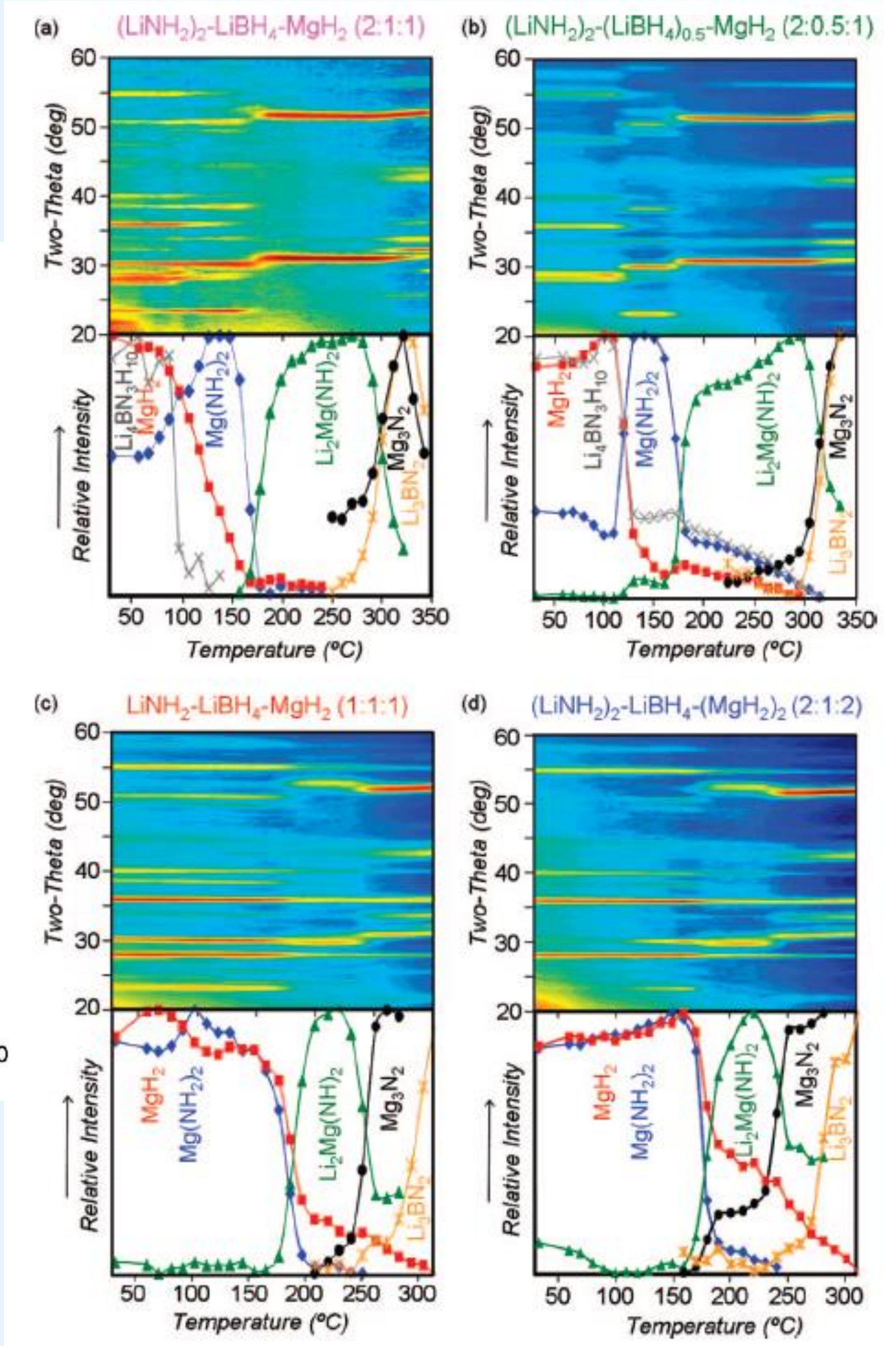
(4) $3\ Mg(NH_2)_2 + 6\ LiH \rightarrow 3\ Li_2Mg(NH)_2 + 6\ H_2$
$\Delta H_{463K} = 50$ kJ/mol·H_2

Hydrogen Release – Step 2 — *T = 200 to 250°C*

(5) $3\ Li_2Mg(NH)_2 + 6\ MgH_2 \rightarrow 3\ Mg_3N_2 + 6\ LiH + 6\ H_2$
$\Delta H_{523K} = -19$ kJ/mol·H_2

Hydrogen Release – Step 3 — *T = 250 to 325°C*

(6) $3\ Li_2Mg(NH)_2 + 2\ LiBH_4 \rightarrow 2\ Li_3BN_2 + Mg_3N_2 + 2\ LiH + 6\ H_2$
$\Delta H_{523K} = -1$ kJ/mol·H_2



Sudik *et al.*, JPCC 113 (2009) 2004

Ammonia, amidoboranes etc.


H C H
H B Al N
B Li
N
H B N
C Al Li
H B N
H B N
C Al Li
H B N

Al-H(N),B

Why Al^{3+} ?

- ✓ Given its high polarizing power defined by the exceptional charge-to-radius ratio Al^{3+} stands on its own in the bimetallic $MAl(BH_4)_n$, $MAl(NH_2)_n$ and $MAl(NH_2BH_3)_n$ series
- ✓ The activation of neutral molecules, namely ammonia and ammonia borane, requires highly polarizing cation
- ✓ Low weight, high natural abundance
- ✓ Chemistry of Al complexes with B- and N-based hydrides has been explored only recently.

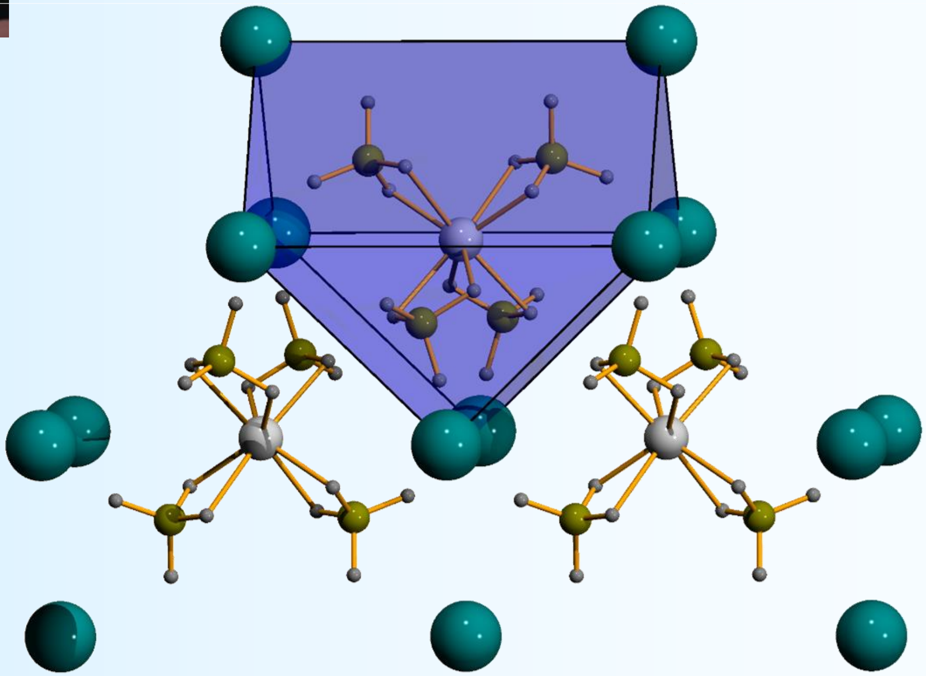
Al-H(B)

Started as a way to stabilize $Al(BH_4)_3$

$AlCl_3 + 3LiBH_4 \rightarrow Al(BH_4)_3 + 3LiCl$

$Al(BH_4)_3 + MBH_4 \rightarrow M[Al(BH_4)_4]$

No chlorine anions: higher H-content!



M = K

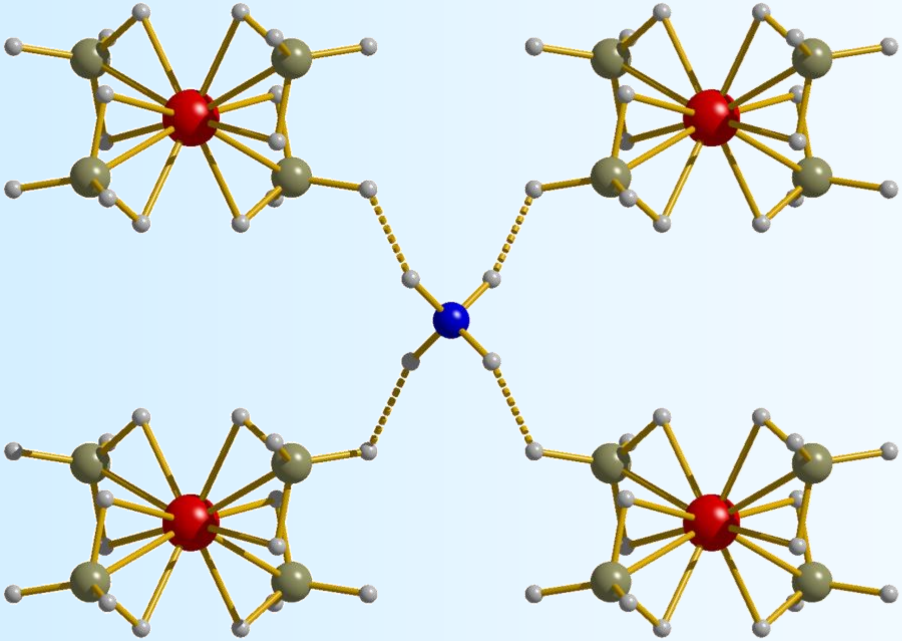
Dovgaliuk *et al.*, JPCC, 118 (2014) 145

Knight, et *al.*, JPCC, 117 (2013) 19905

Al-H(B)

NH_4-Al-BH_4

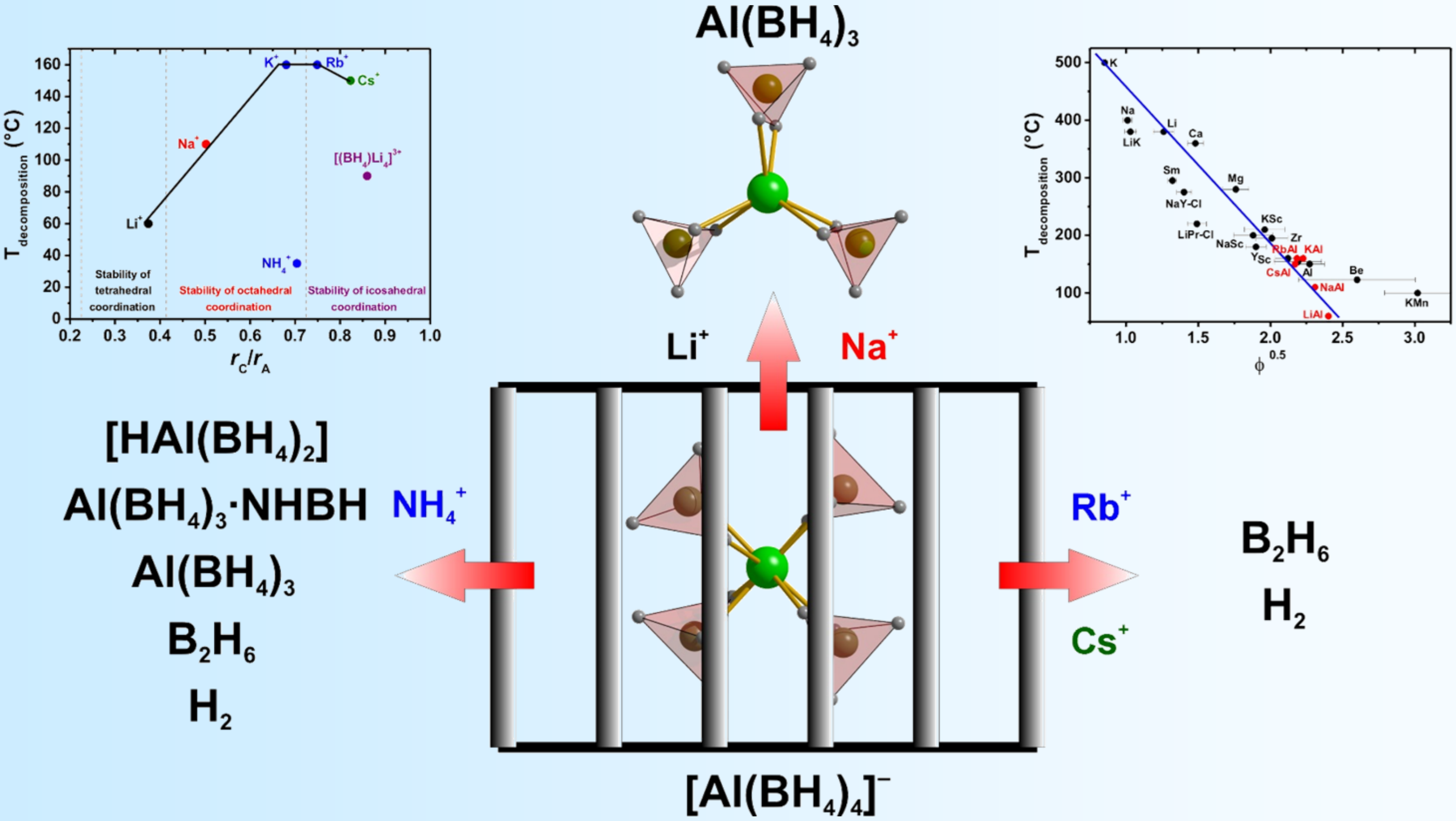
$Al(BH_4)_3 + NH_4BH_4 \rightarrow NH_4[Al(BH_4)_4]$



$NH_4[Al(BH_4)_4] \rightarrow Al(BH_4)_3 \cdot NHBH + 3H_2$ at 35 °C

Al-H(B)

Versatile source of H for RHCs



$Al(BH_4)_3$

Li^+ Na^+

$[HAl(BH_4)_2]$

$Al(BH_4)_3 \cdot NHBH$

$Al(BH_4)_3$

B_2H_6

H_2

NH_4^+

Rb^+

Cs^+

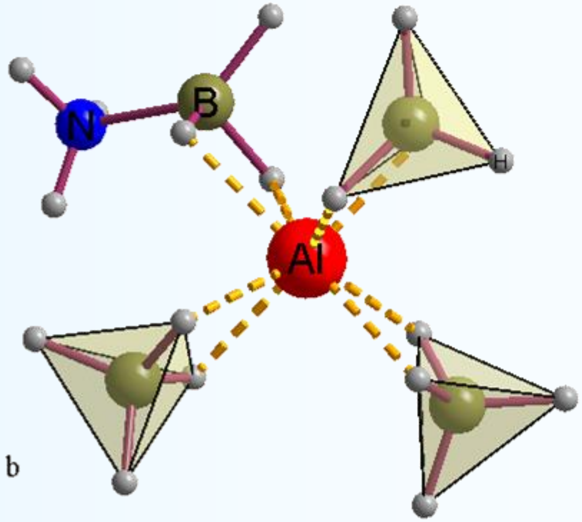
B_2H_6

H_2

$[Al(BH_4)_4]^-$

Molecular complexes

$Al(BH_4)_3 + NH_3BH_3 \rightarrow Al(BH_4)_3 \cdot NH_3BH_3$



Stabilizes the very unstable $Al(BH_4)_3$

AB is coordinated via the boron side

Dovgaliuk et al., *Chem. Mater*. 2015, 27, 768-777.

Al-H(B)

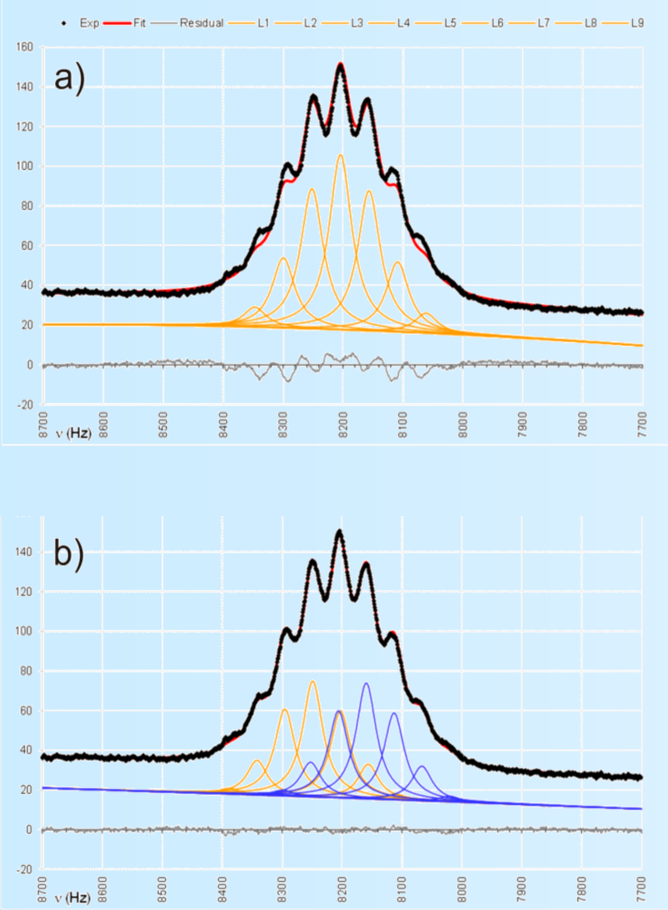
Mild & endothermic dehydrogenation

Gravimetric, volumetric and MS studies indicate release of pure H_2 @ 70 °C

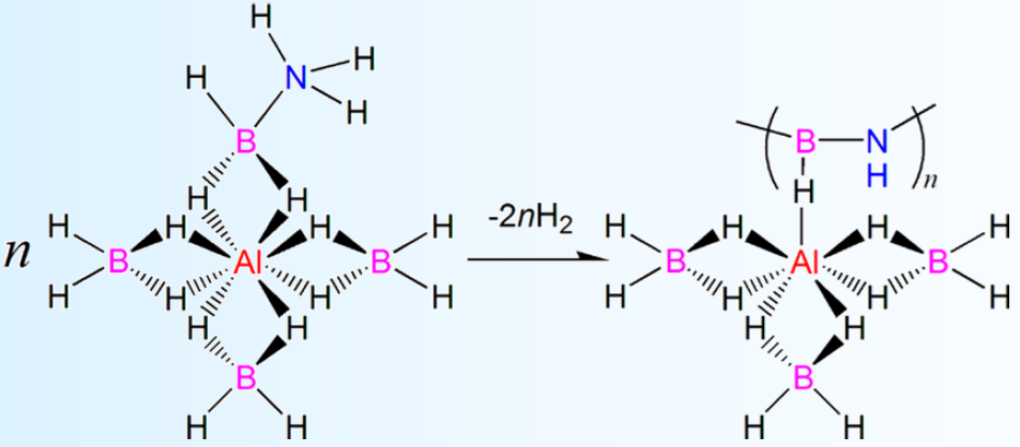
$$Al(BH_4)_3{\cdot}NH_3BH_3 \rightarrow Al(BH_4)_3{\cdot}NHBH + 2H_2$$

^{27}Al NMR spectrum deconvolution

Dovgaliuk et al., *Chem. Mater*. 2015, 27, 768-777.



~~$[Al(BH_4)_4]^-$ with 8 equivalent H atoms~~



$Al(BH_4)_3{\cdot}NHBH$ with 6H + 1 H atoms around Al

Al-H(B)

Tuning the $AlL_3 \cdot R\text{-}NH_2BH_3$ system

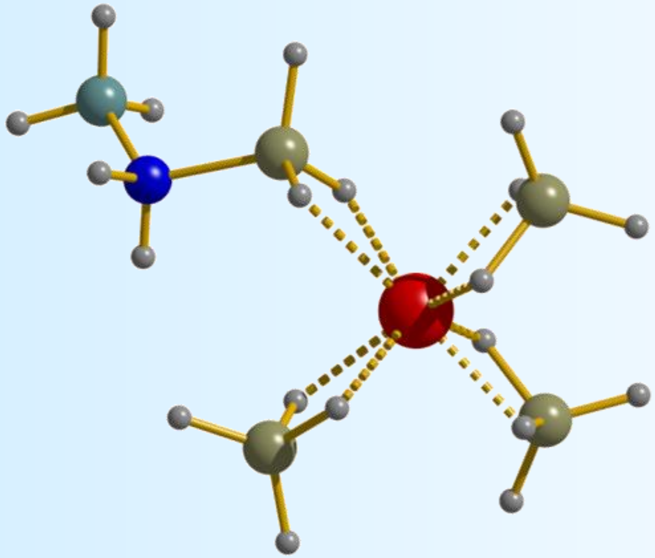
✓ $Al(BH_4)_3 \cdot NH_3BH_3$ is the promising system for the reversible dehydrogenation of AB: endothermic + pure hydrogen desorbed.
The second decomposition step is the problem.

To get around:
- replace BH_4 by other ligands L, like Cl
- use BH_3NH_2R to stabilize $Al(BH_4)_3 \cdot NHBH$ and to test the reversibility

Al-H(B)

Tuning the $AlL_3 \cdot R\text{-}NH_2BH_3$ system

I – Change of NH_3BH_3 to other ligands ($CH_3NH_3BH_3$, $(CH_2NH_2BH_3)_2$ etc.)

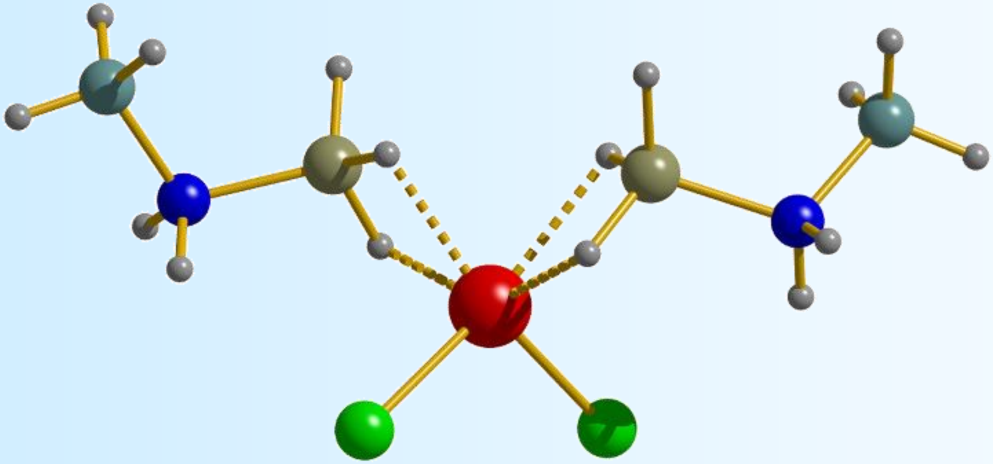


Works well

Al-H(B)

Tuning the $AlL_3 \cdot R\text{-}NH_2BH_3$ system

II – Change of $Al(BH_4)_3$ to AlL_3 ($L = F^–, Cl^–, H^–$)



Works well

$2\ CH_3\text{-}NH_2BH_3 + 2\ AlCl_3 \rightarrow [Al(CH_3\text{-}NH_2BH_3)_2Cl_2][AlCl_4]$

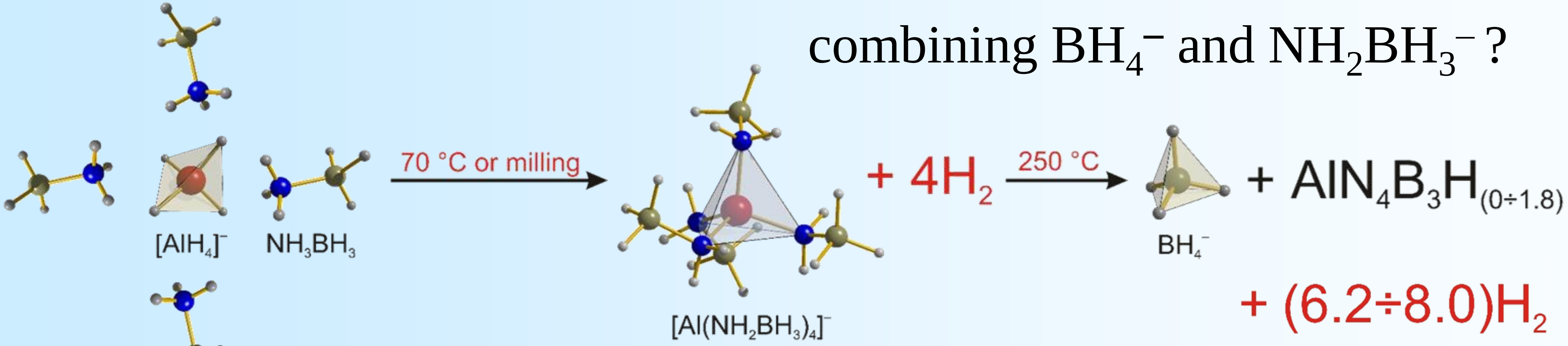
Twice more AB per Al

Al-H(N)

Al-based amidoborane

$NaAlH_4 + 4\ NH_3BH_3 \rightarrow Na[Al(NH_2BH_3)_4] + 4\ H_2$

combining BH_4^- and $NH_2BH_3^-$?



Partial reversibility is achieved

Dovgaliuk et al., *Chem. Eur. J.* 21 (2015) 14562