Hydrogen for Automobiles

The key issues to an efficient H energy infrastructure

Why Hydrogen Storage?

What are the problems?

- Mediocre volumetric energy density
- Do we have a hydrogen mine?
- Gaseous under most circumstances

Typical H Storage Means

- High pressure
- Cryogenic
- Chemical Hydrides
- Metal Hydrides
- Physical Sorption

Basic H Storage Requirements

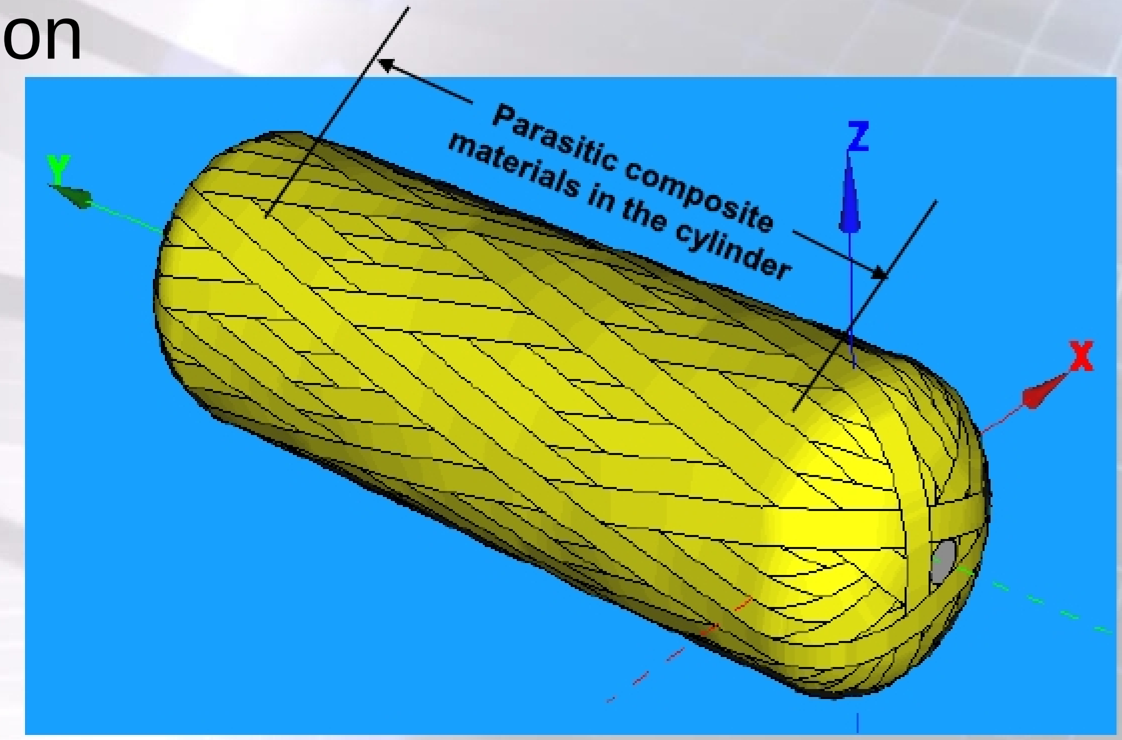
- H mass percentage (~ 6%-wt at least)
- Volumetric density (~0.15 kg/liter at least)
- Low cost
- Ease of recharge or regeneration
- Fast release, fast recharge
- Environmentally sound

High Pressure H Storage

- 3000, 5000, 7000 psi, maybe up to 10000
- Gravimetric density up to 3%-wt H
- Volumetric density ~ 0.06 kg/liter
- Cost high for bottles > 7000 psi
- Environmentally sound
- But how about safety? it’s like a bomb!
- Relative ease of refueling though taking time
- Composite construction with metal liner

High Pressure H Storage

Construction



➡ **64.9 kg composite usage in the 1st hybrid vessel vs. 76.0 kg in the baseline tank (FW alone)**

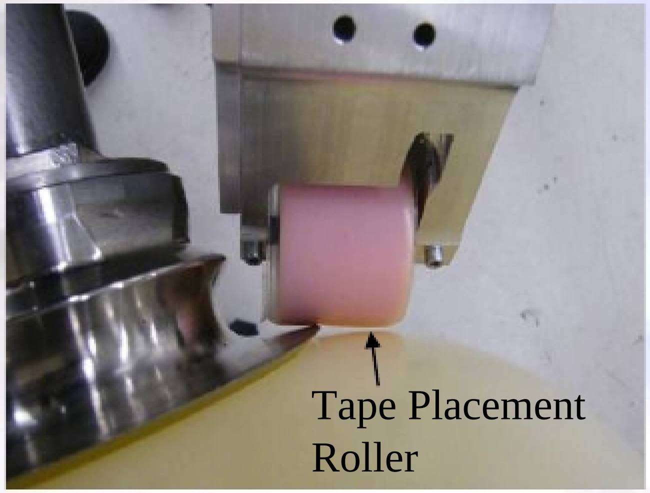
- The end-user H_2 storage system weight efficiency = 1.67 kWh/kg vs. 1.50 kWh/kg in the system with the baseline tank

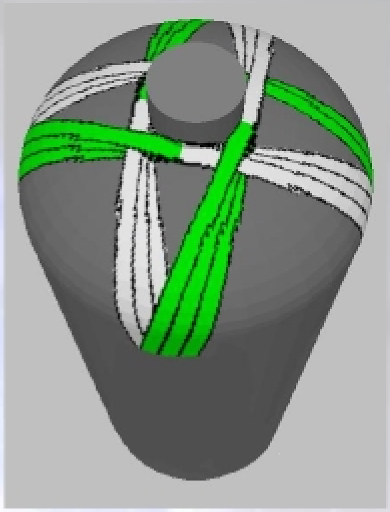
- The end-user H_2 storage system cost efficiency:

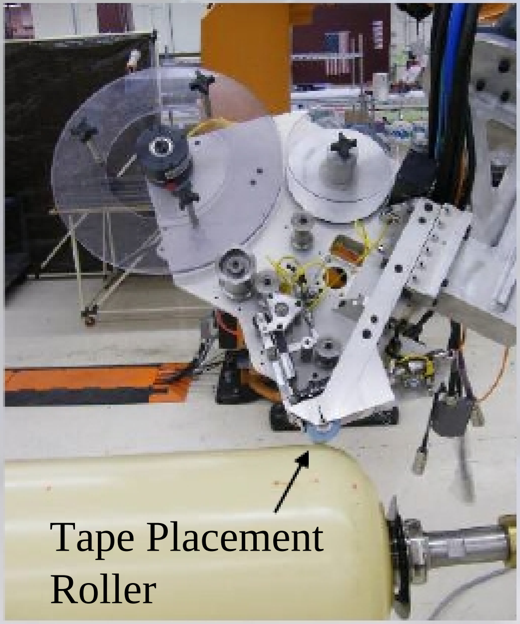
$11/lb CF	Baseline $23.45	Fully Integrated $21.91	Fully Separate $21.75
$6/lb CF	Baseline $18.74	Fully Integrated $17.79	Fully Separate $17.63

Approach: Advanced Fiber Placement- Boeing

- **Advanced Fiber Placement:** A CNC process that adds multiple strips of composite material on demand.
  - Maximum weight efficiency - places material where needed
  - Fiber steering allows greater design flexibility
  - Process is scalable to hydrogen storage tanks
  - Optimize plies on the dome sections with minimal limitation on fiber angle
  - Reinforce dome without adding weight to cylinder

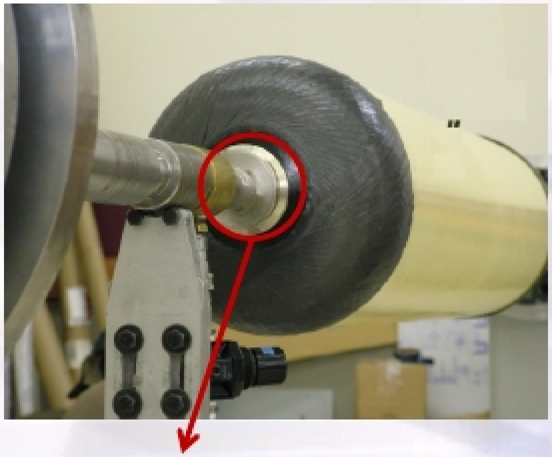






Strength

- Tank preparation and validation test



Representative smallest polar opening that the AFP process can currently make

The localized reinforcement protected the dome regions very well

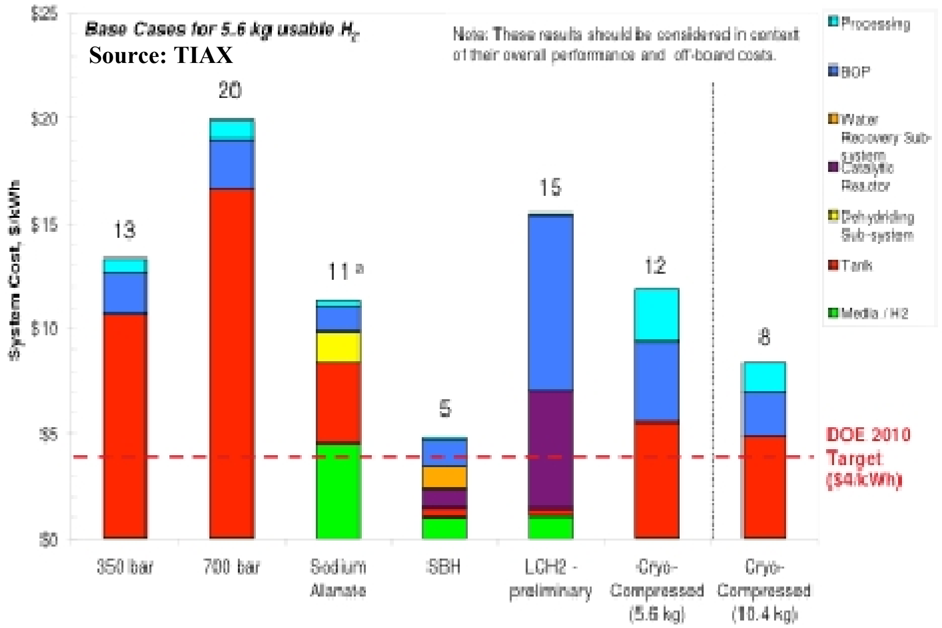
- Static Burst Result: 23420 PSI > 22804 PSI, EN standard (New European Standard superseding EIHP)
- 64.9 kg composite usage in the 1st hybrid vessel vs. 76 kg in the baseline tank (FW alone)

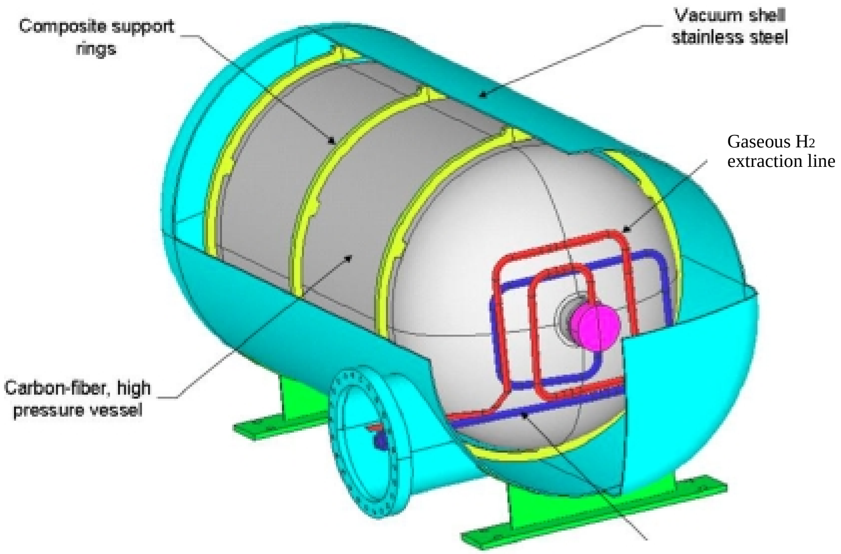
11.1 kg (14.6%) Savings!

Cryogenic H Storage

- **-252.87°C !**
- Very energy consuming to cool
- Energy consuming to maintain
- Gravimetric density up to 8~9%
- Volumetric density ~ 0.08 kg/liter
- Cost high
- Environmentally sound and safe
- Relative ease of refueling
- Vacuum Dewar

Relevance: High density cryogenic hydrogen enables compact, lightweight, and cost effective storage



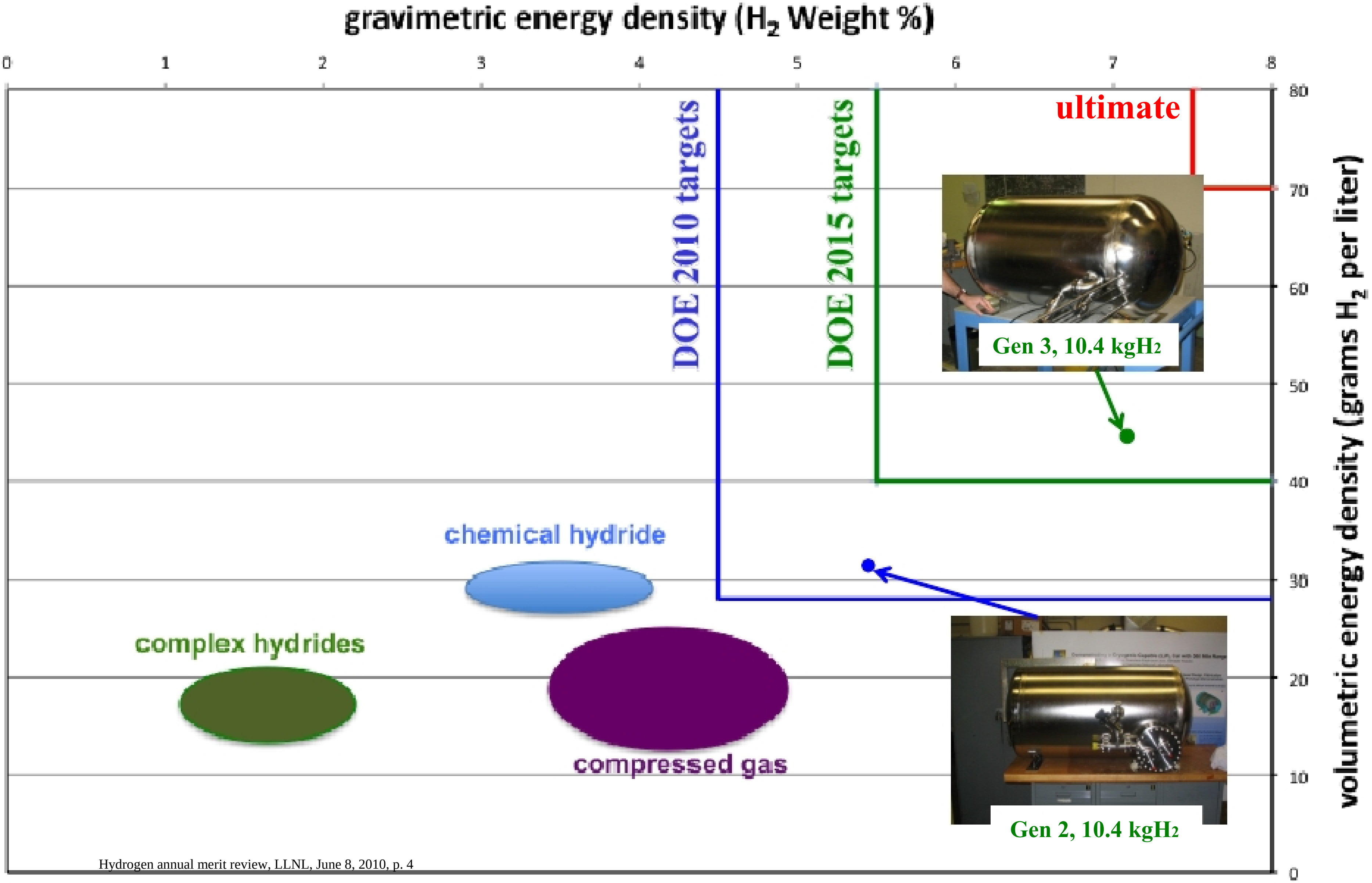


Hydrogen annual merit review, LLNL, June 8, 2010, p. 3

- ***Cost effective:*** **Cryogenic vessels use 2-4x less carbon fiber, reducing costs sharply at higher capacity**

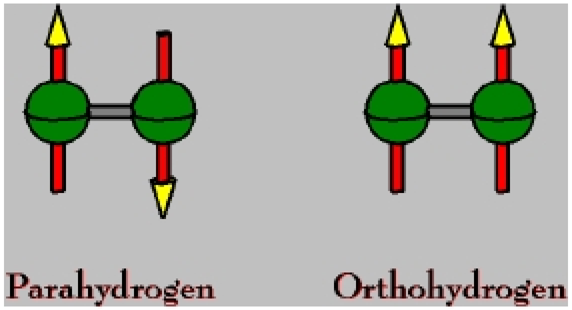
- ***Compact:*** **235 L system holds 151 L fuel (10.3-10.7 kg H_2)**

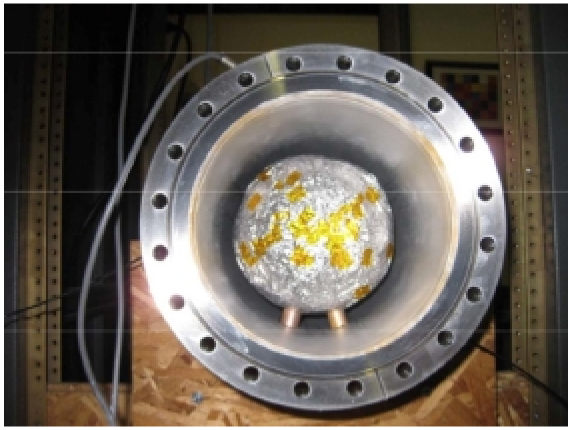
Relevance: Cryogenic pressure vessels can *exceed* 2015 H_2 storage targets and approach *ultimate*



Hydrogen annual merit review, LLNL, June 8, 2010, p. 4

Approach: reduce/eliminate H_2 venting losses by researching vacuum stability, insulation, and para-ortho conversion

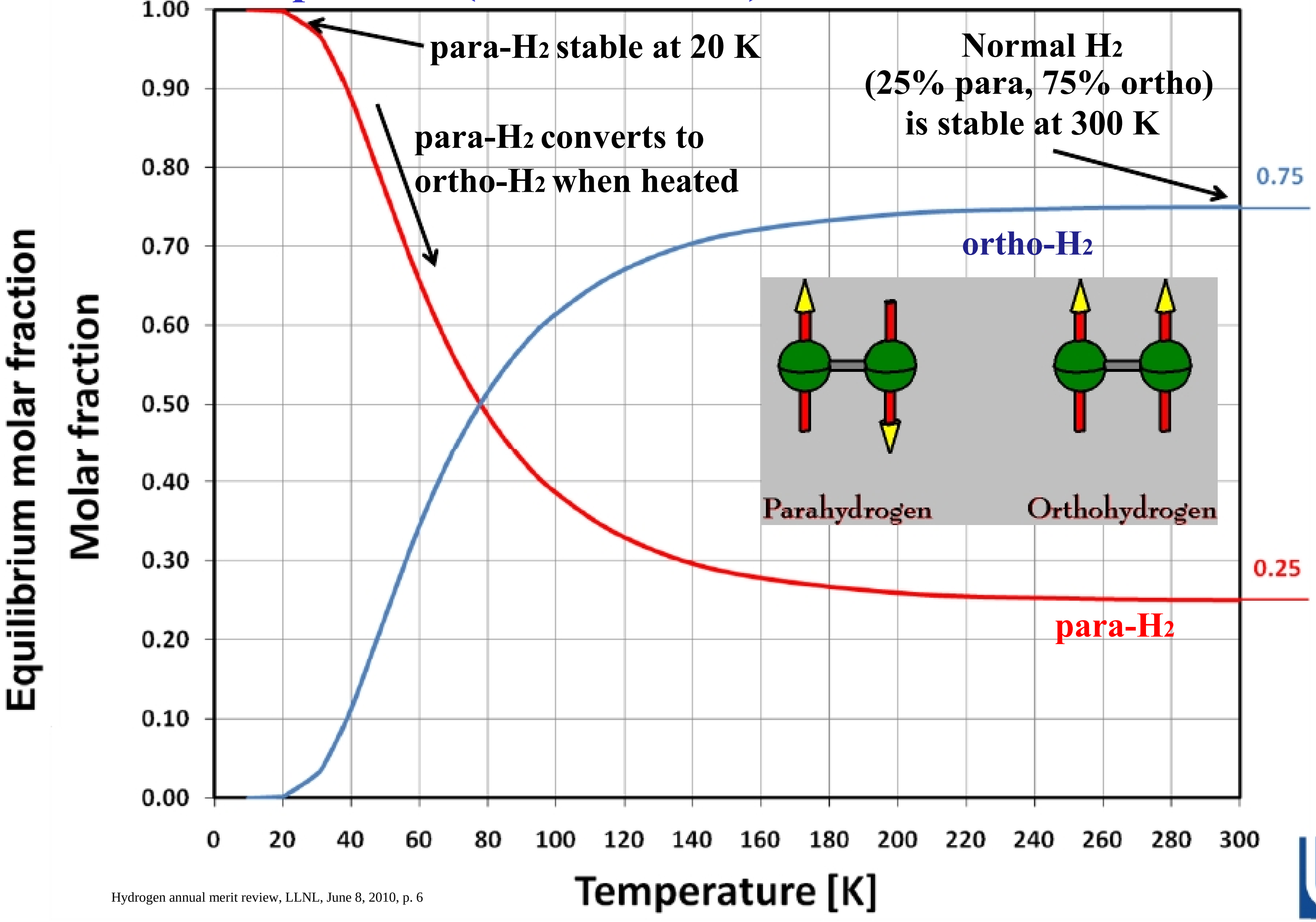




Hydrogen annual merit review, LLNL, June 8, 2010, p. 5

- *Determine para-ortho effect on pressurization and venting losses*
- *Directly measure para-ortho populations*
- *Determine vessel heat transfer mechanism (radiation vs. conduction)*
- *Evaluate vacuum stability by measuring pressure vessel outgassing*
- *Test ultra thin insulation for improved vessel volume performance*
- *Improve vessel design based on experimental results*

Hydrogen has two nuclear spin states: para-H_2 (stable at 20 K) and ortho-H_2



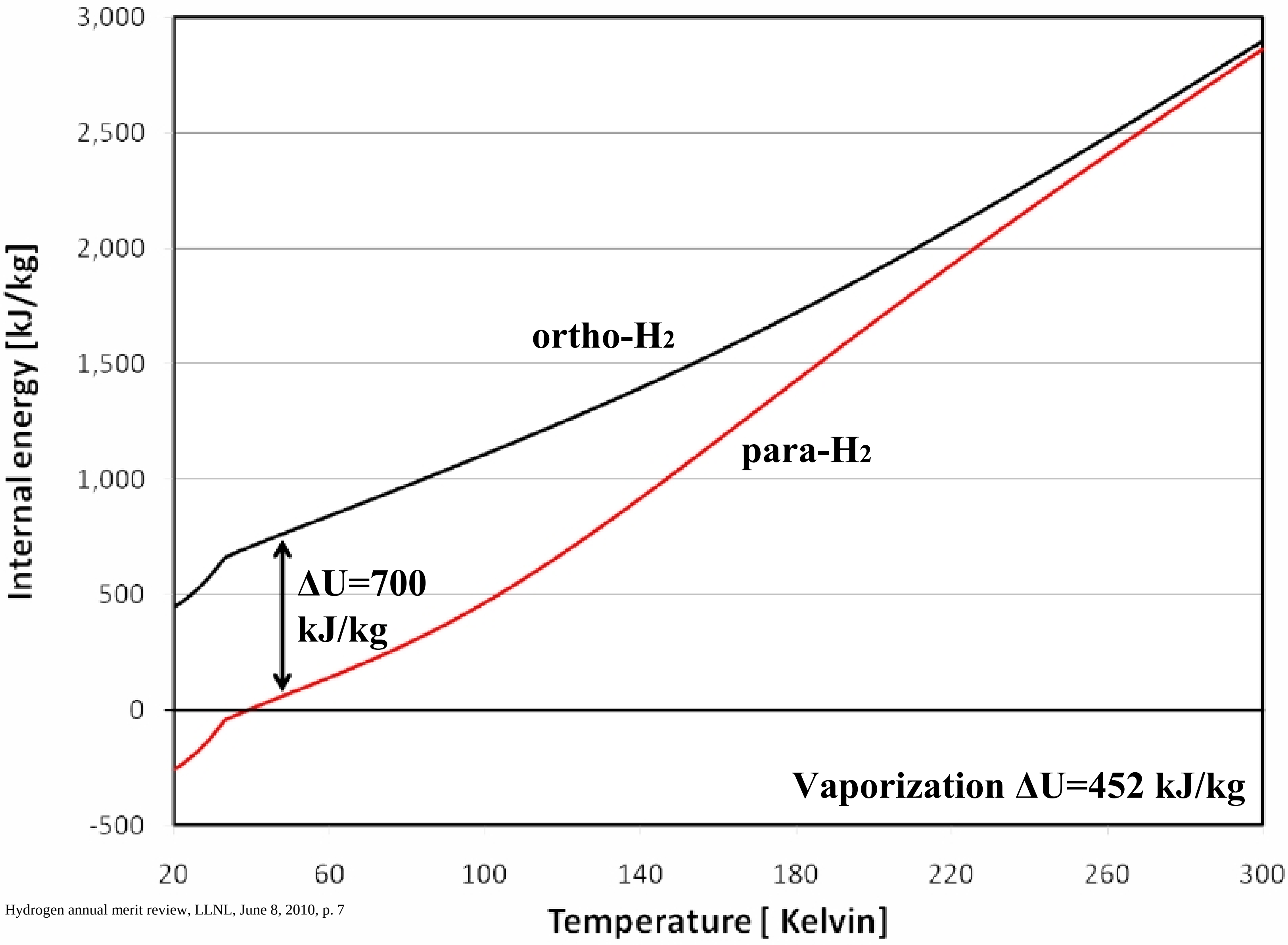
para-H_2 stable at 20 K

para-H_2 converts to ortho-H_2 when heated

Normal H_2
(25% para, 75% ortho)
is stable at 300 K

Hydrogen annual merit review, LLNL, June 8, 2010, p. 6

Para-ortho conversion absorbs energy & increases dormancy (equivalent to a second evaporation)



Hydrogen annual merit review, LLNL, June 8, 2010, p. 7

Chemical Hydrides

- Examples: NH3, N2H4, B2H6, NaBH4…
- Gravimetric density up to 20%-wt (LiBH4)
- Volumetric density up to 0.2 kg/liter
- Many are safe and sound, but not always
- Cost high except NH3 and hydrocarbons
- Regeneration has been problematic
- Utilization is less straight forwards than H2.

Chemical Hydrides: Examples

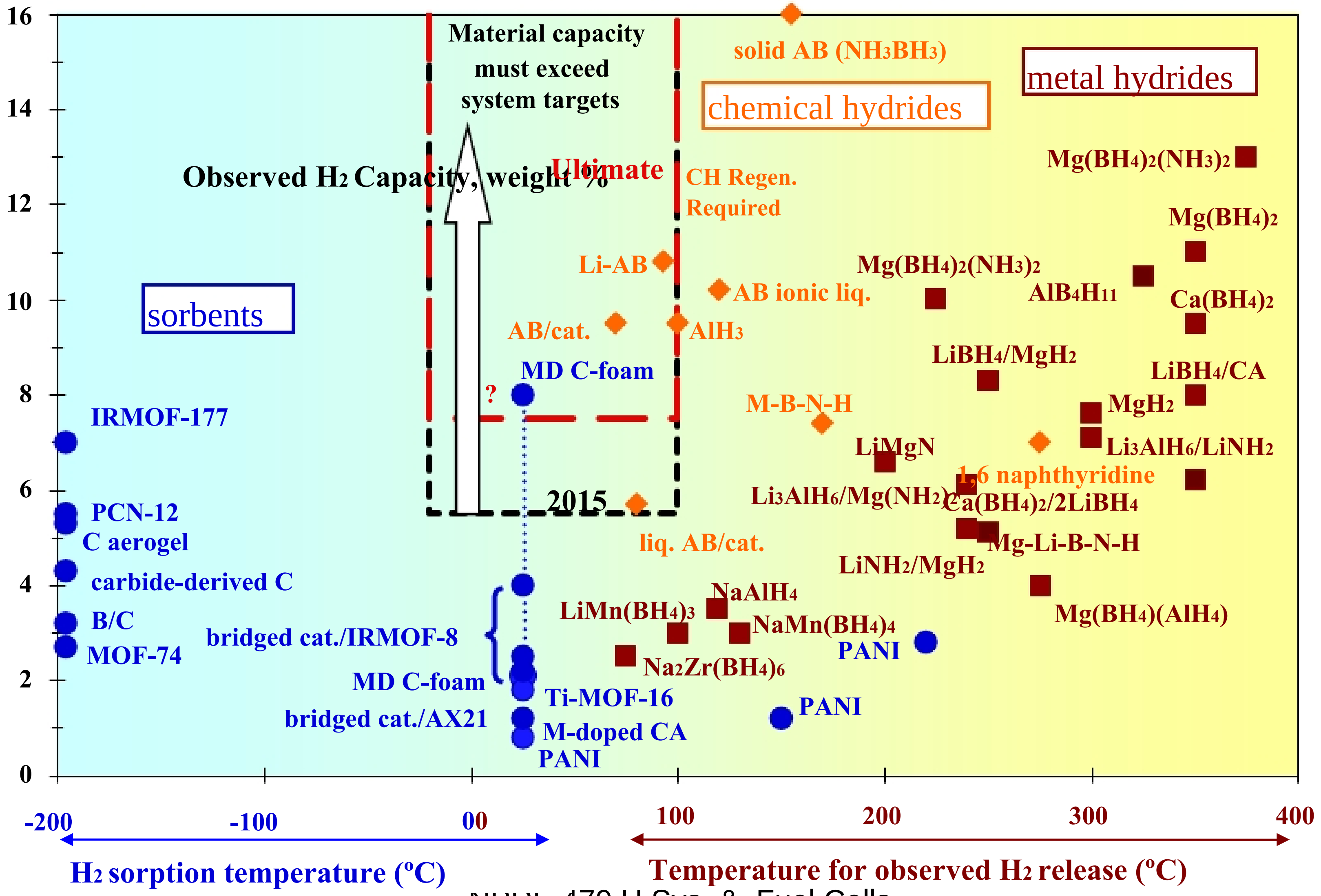
- Hydrocarbons: CH4, C2H6… (complicated reforming→ H2, dirty byproducts)
- NH3 (Ammonia) N2H4 (hydrazine) (toxic and … it stinks)
- B2H6 (diborane) (highly toxic)
- Borohydrides (LiBH4, NaBH4…) (relatively safe)
- Alanates (NaAlH4…) (highly reactive)

Chemical Hydrides: Borohydrides

- LiBH4, very high H content, but not soluble
- NaBH4, 12%-wt H dry
- NaBH4, can be made to 30% H2O solution
- NaBH4, 6%-wt H in 35% H2O stabilized with ammonium hydroxide
- Safe, low toxicity
- Still a challenge in regeneration

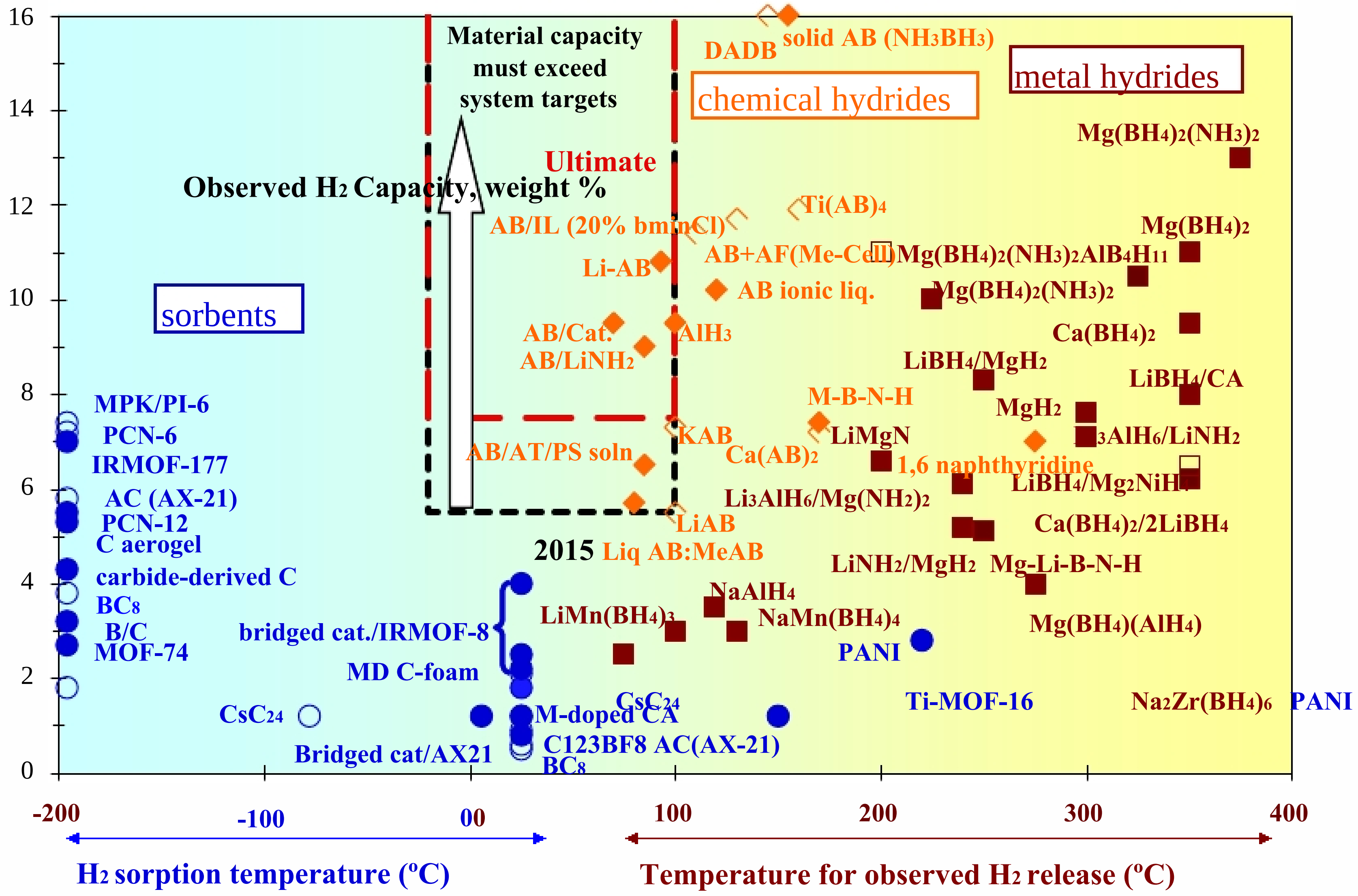
2009 Progress & Accomplishments

Status at 2009 AMR Review



2010 Progress & Accomplishments

Open symbols denote new materials since 2009 AMR



Metal Hydrides

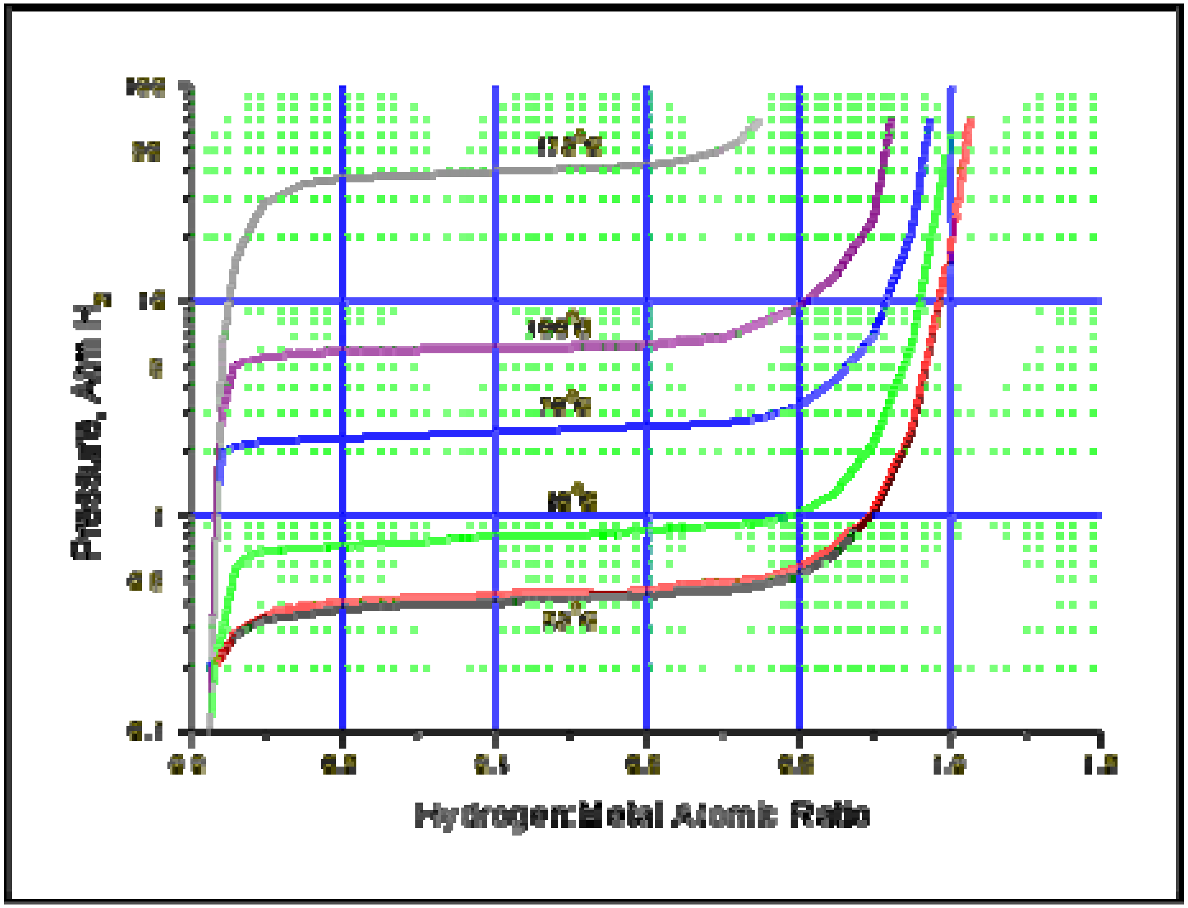
Simple metal hydrides

- Examples: NiH, PdH, $LaNi_5H_6$, MgH_2
- Metallic bond, H share mobile electrons with the metal atom
- Hydrogen mobility is generally high
- Gravimetric density from 1% ~ 8%
- Metal hydrides with lower H-content tend to have better reversibility

Simple Metal Hydrides: Classification

- AB_5 - $LaNi_5H_6$
- AB_2 - $ZnMn_2H_3$
- AB - $TiFeH_2$
- A_2B - Mg_2NiH_4
- Solid solution type -$V_{0.8}Ti_{0.2}$
- MgH_2 class (alkaline earth metal hydride)

Metal Hydrides: Isotherm

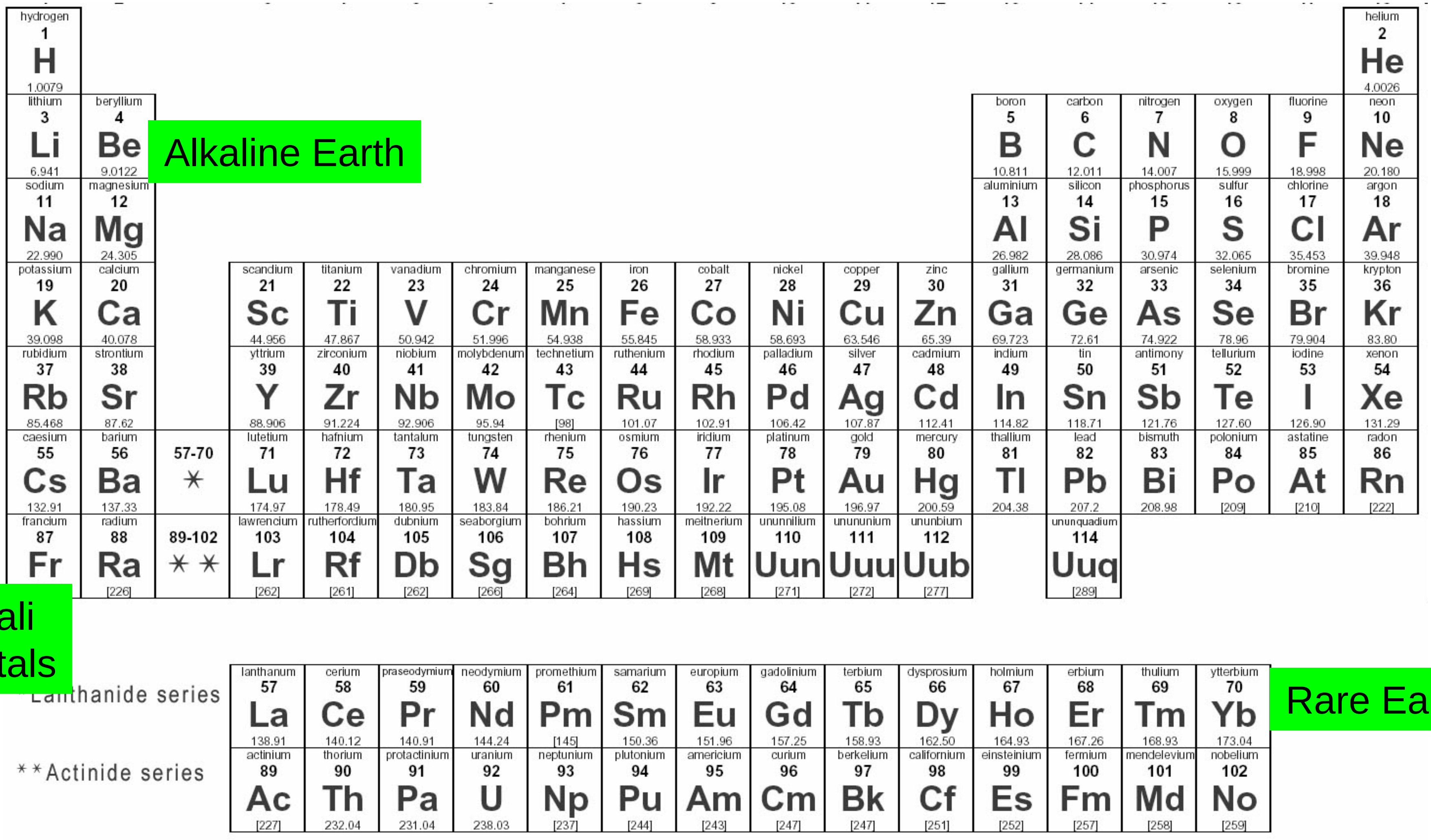


The isotherm tell us the working temperature and pressure of the hydride
And how much H it can store

Metal Hydrides: $LaNi_5H_6$

- Most widely utilized MH today
- Gravimetric density ~ 1.3%-wt H
- Volumetric density ~ 0.1 kg/liter
- Cost high due to nickel, lanthanum (rare earth)
- Relative ease of refueling (near ambient pressure)
- It’s the most representative AB_5 alloy
- Can be utilized in electrochemical cells (batteries and fuel cells) directly

The chemical elements



hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

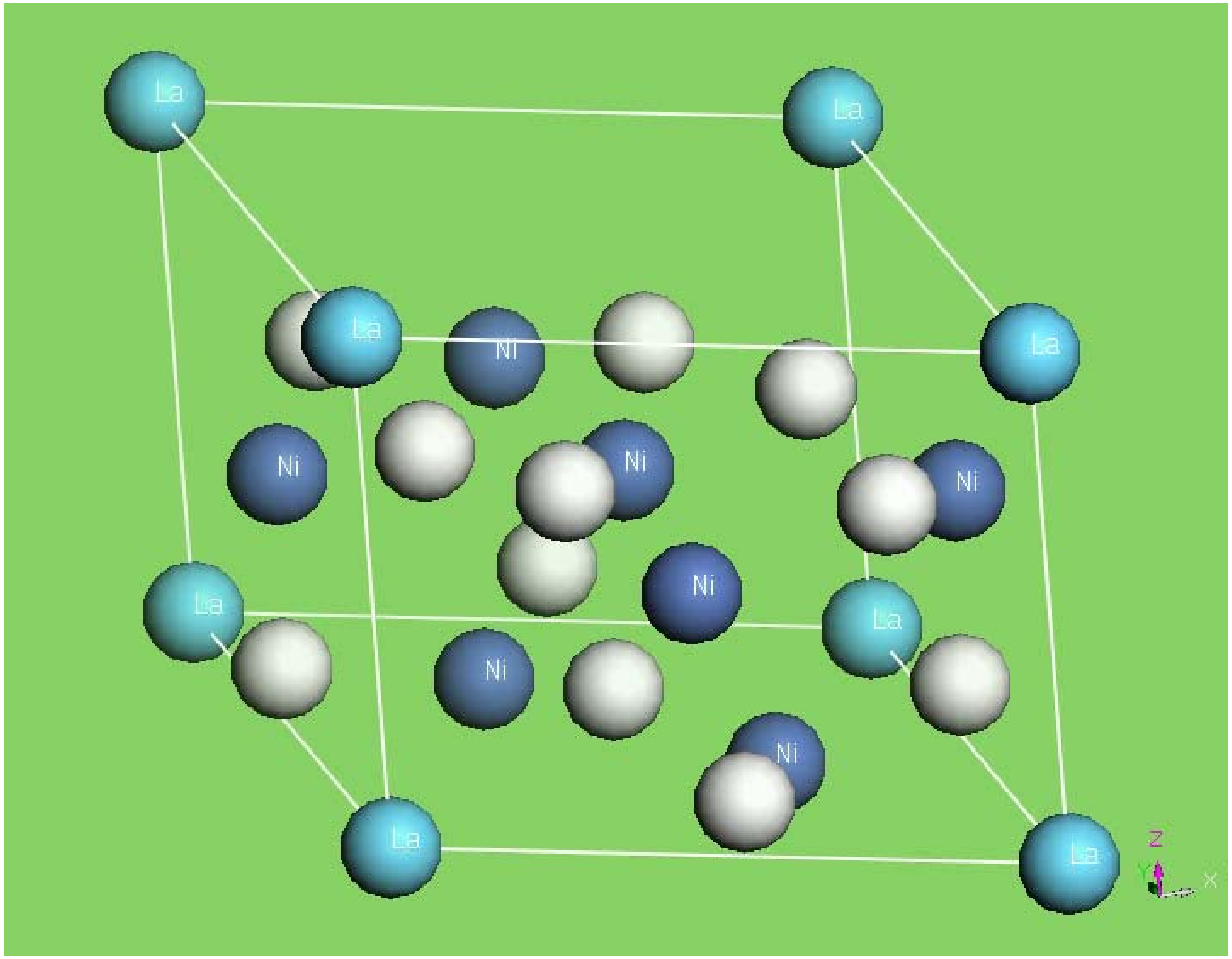
Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Alkaline Earth

Alkali metals

Rare Earth

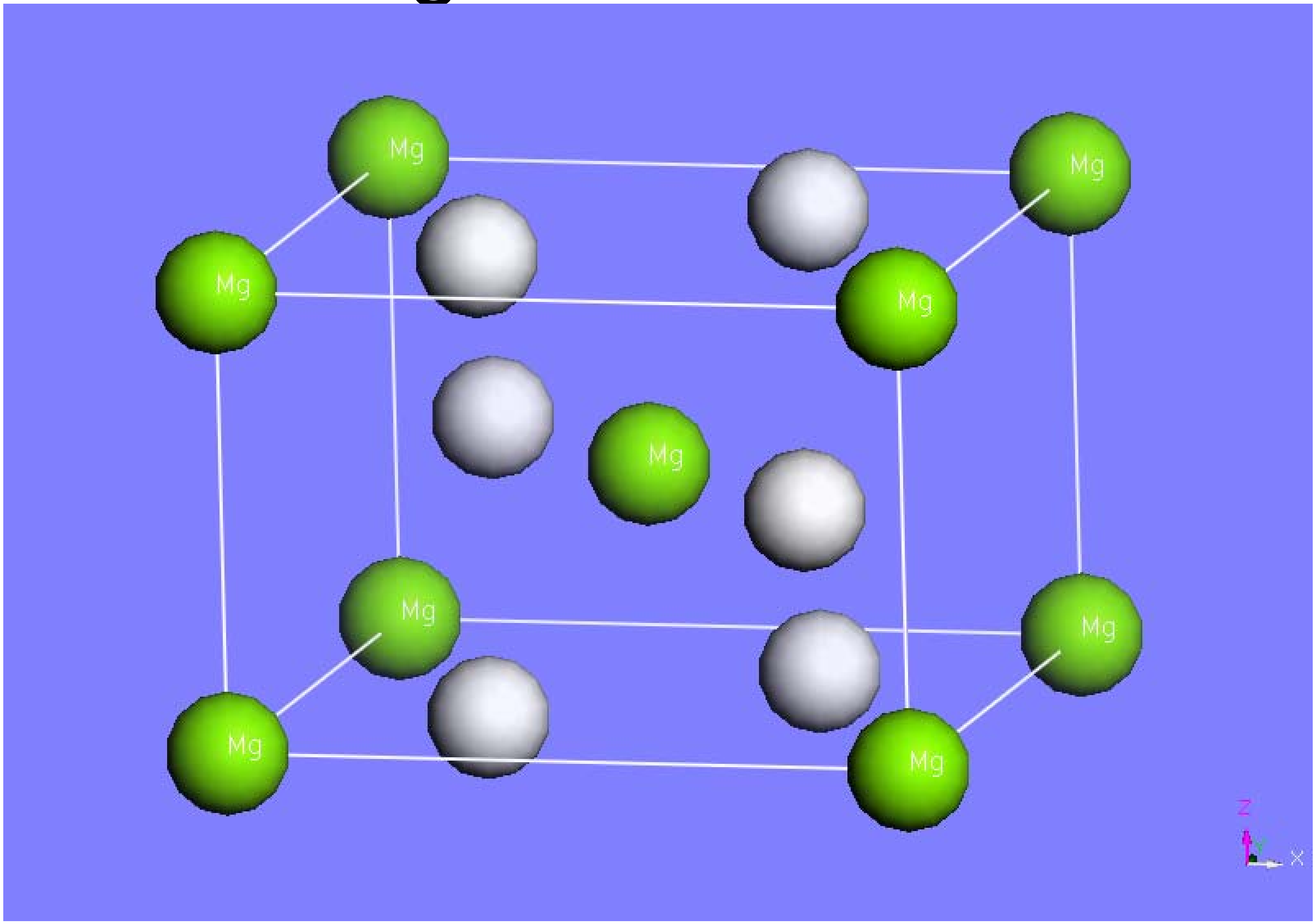
$LaNi_5H_6$: Structure



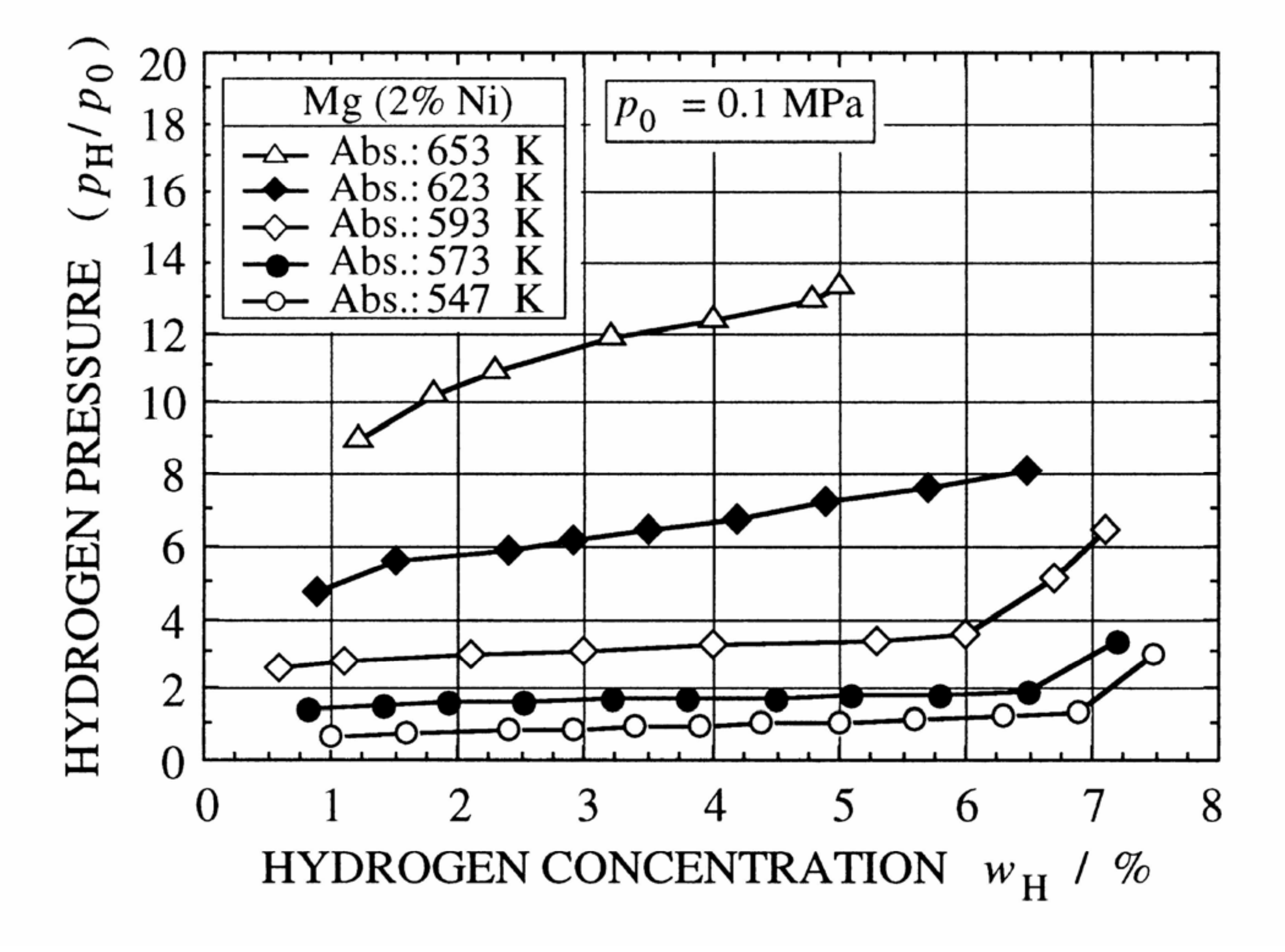
Metal Hydrides: MgH_2

- Gravimetric density ~ 8%-wt H
- Volumetric density >> 0.1 kg/liter
- Cost is low, very affordable
- Abundant element
- Clean
- Medium temperature absorption and de-sorption ~ 300 degrees C
- It’s the most representative alkaline earth metal hydride
- Not ideal for mobile H storage but ideal for stationary type applications

MgH_2: Structure



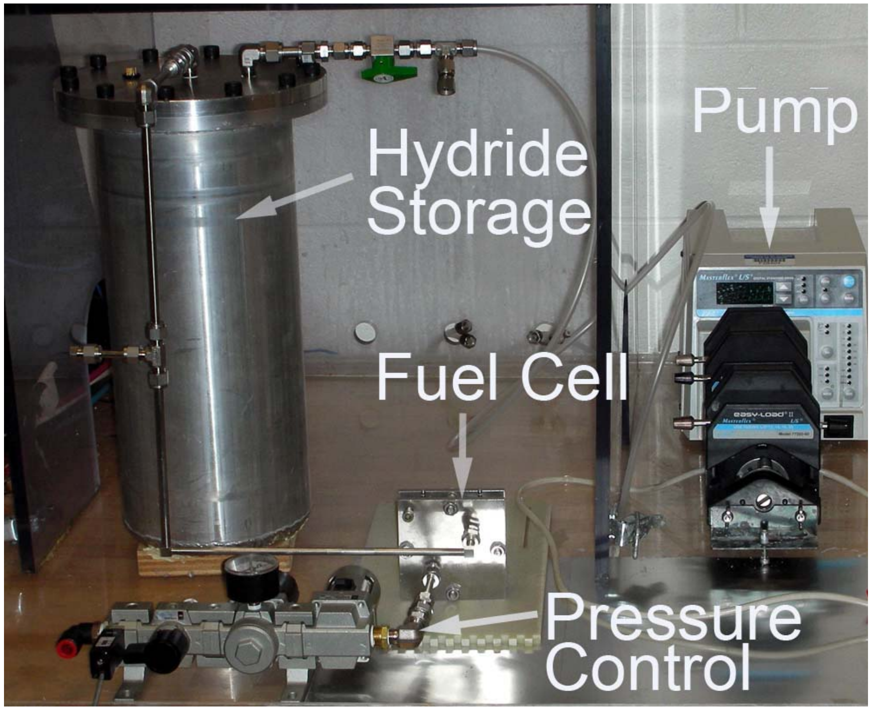
MgH_2: Isotherm

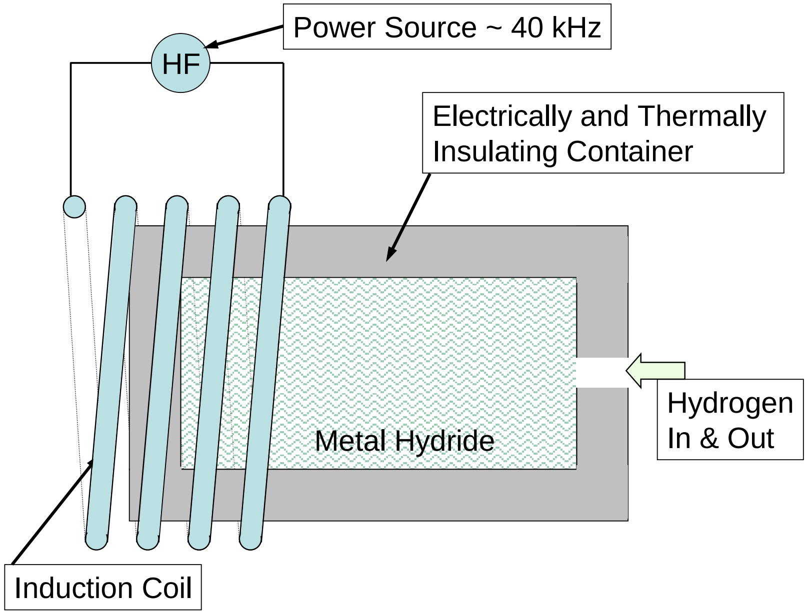


MgH_2: Kinetics

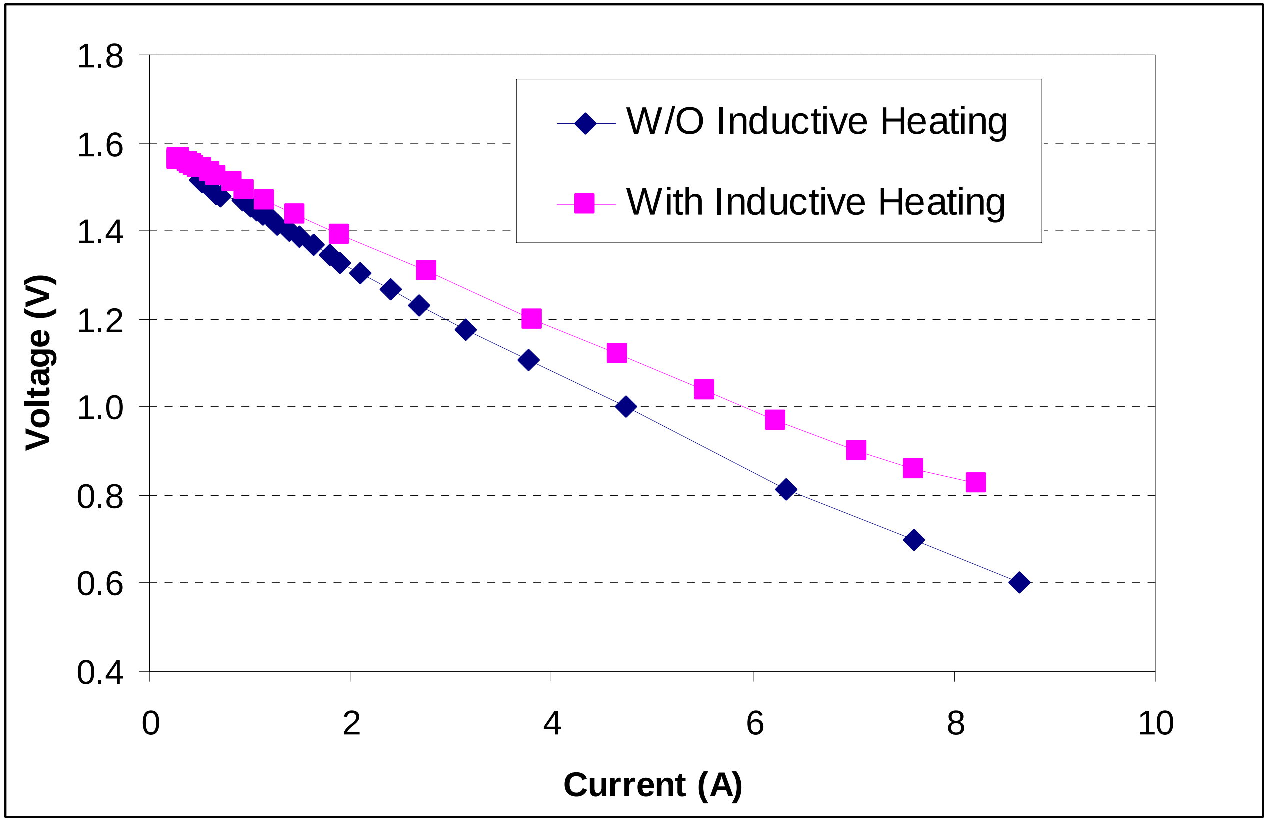
- Absorption and release is slow.
- ~ a few hours for a typical Ab/De-sorption cycle.
- Fast enough for stationary storage of renewable energy nevertheless.
- Can be expedited with innovative heating.
- For example inductive heating.

MgH_2: Fast release with induction Heating



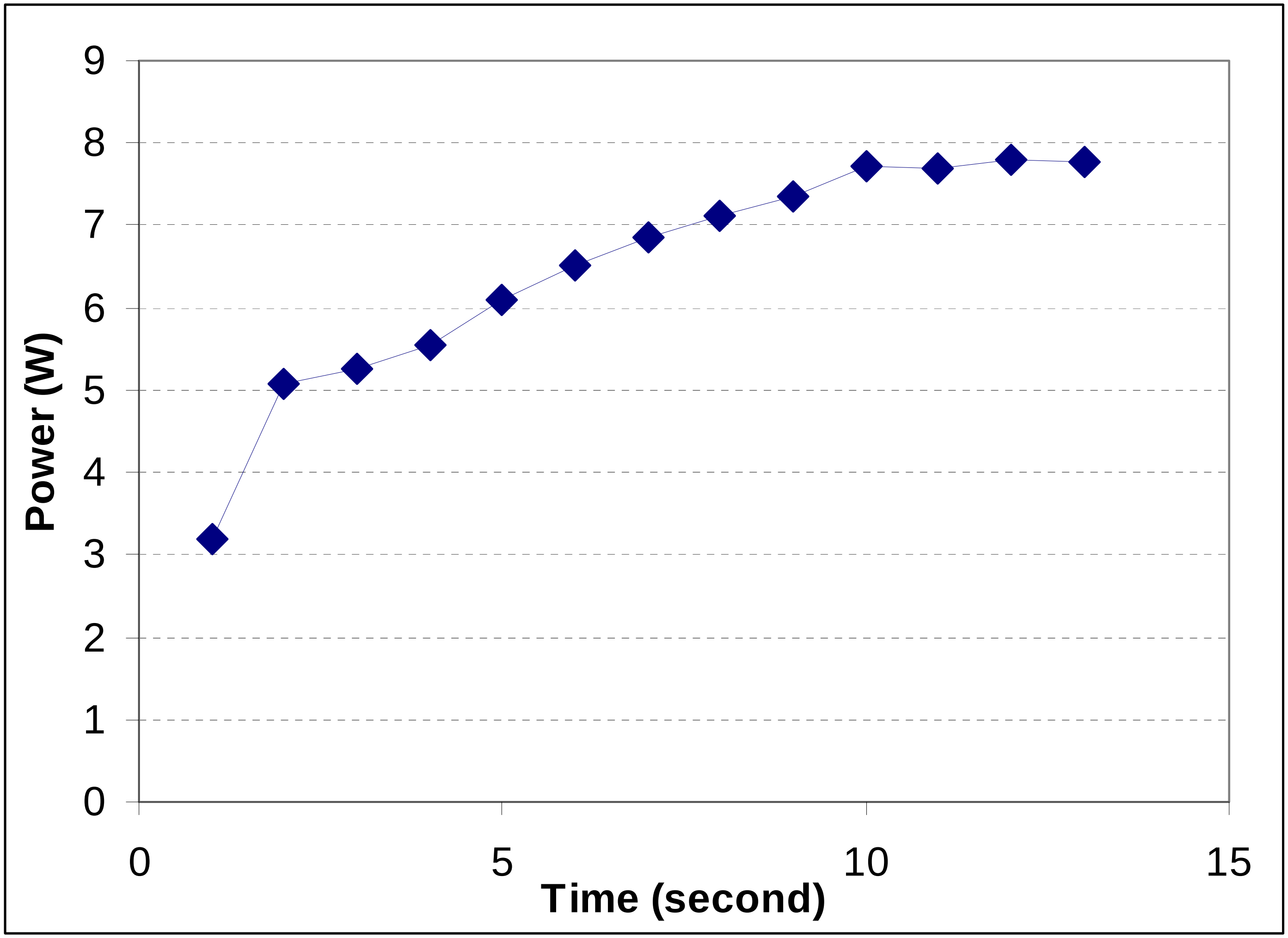


MgH_2: Fast release with induction heating



Fuel cell performance with and without induction heating

MgH_2: Fast release with induction heating



Fast fuel cell ramping with induction heating

Complex metal hydrides

The hydrogen bonding is more covalent or localized

- Examples: $Ca(BH_4)_2$, $Mg(BH_4)_2$, $LiNH_2$, $LiAlH_4$
- New development
- Many issues exist, like regeneration, volatiles, safeties

METAL HYDRIDE CENTER OF EXCELLENCE

Final Year Downselection Path

$Mg(NH_3)_xB_{10}H_{10}$

$NaSc(BH_4)_4$ $Mg(B_3H_8)_2$ $Li_3AlH_6/2LiBH_4$ MgH_2/TiH_2 $(NH_4)_2B_{12}H_{12}$

$Li_2B_{12}H_{12}/2CaH_2$ AlB_4H_{11}

$LiBH_4/MgH_2$@ aero. $LiNH_2$

$Mg(BH_4)_2$@ aero

$Al/LiBH_4$ $MgB_{12}H_{12}$

$2LiNH_2/MgH_2$ $ANH_2/B(BH_4)_x$

$NaPB_2H_8$ $4LiBH_4/Mg_2NiH_4$ $Ti(BH_4)_3$

Materials examined in final year of the MHCoE

11 More Downselects
(Removing from Study)

$4LiBH_4/Mg_2NiH_4$ (low wt. %)
$Mg(B_3H_8)_2$ (too unstable)
$Li_2B_{12}H_{12}/2CaH_2$ (too high T_{des})
$Mg(NH_3)_xB_{10}H_{10}$ (NH_3 release)
$Mg(NH_3)_6B_{12}H_{12}$ (NH_3 release)

$CaB_{12}H_{12}/CaH_2$ (not reversible)
$Li_2B_{12}H_{12}/6MgH_2$ (too high T_{des})
$Ti(BH_4)_3$ (not reversible)
$Li_3AlH_6/2LiBH_4$ (too high T_{des})
$Li(NH_3)_xB_{12}H_{12}$ (NH_3 release)
$NaBP_2H_8$ (not reversible)

Physical/Chemical Sorption

- Basically utilize the relatively weak forces: Van Der Waals force, hydrogen bonding…
- Sometimes the sorption could also have a chemical nature.
- Examples: activated carbon, zeolite, MOF (metal organic framework), COF (covalent organic framework), nanotubes…

MOF

- **One of best known MOF 177:**

  $Zn_4O(BTB)_2$, where BTB^{3-} = 1,3,5-benzenetribenzoate

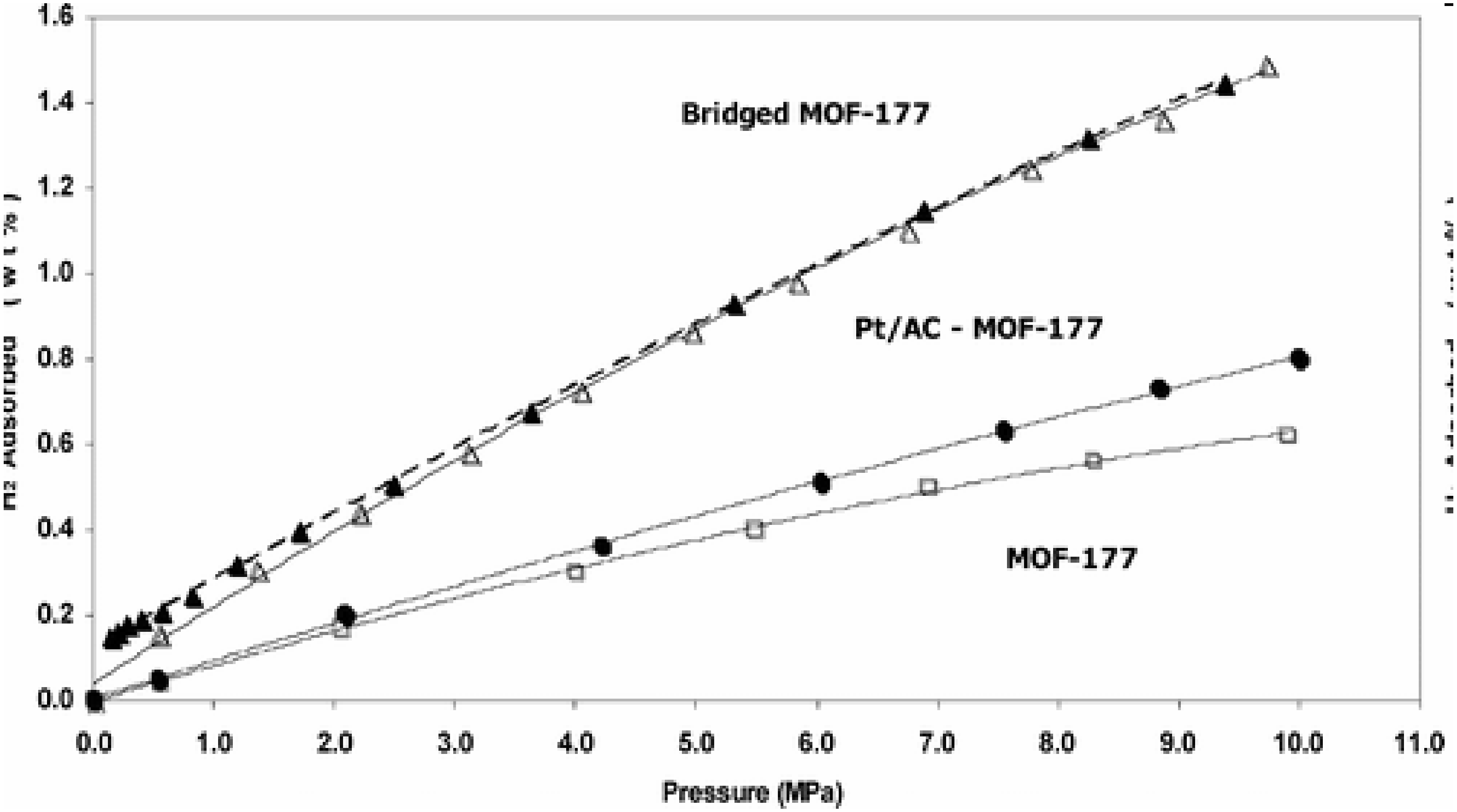
  Theoretical gravimetric density

  7.1 wt% at 77 K, 40 bar

  (not including dewar and pressure vessel)

  11.4 wt% at 77 K, 78 bar

MOF 177


1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
H2 Adsorbed (wt %)
Bridged MOF-177
Pt/AC - MOF-177
MOF-177
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
Pressure (MPa)

Physical/Chemical Sorption

Some remarks

- MOF still not matching the AB_5 metal hydride in gravimetric density
- Generally poor volumetric density (puffy material)
- Cycling and cycle life?
- Good with cryogenic means

New energy cars

- Electric (hybrid) cars (80Wh/kg)
- Natural gas cars (>800Wh/kg)
- Fuel cell cars with H (stored in various forms)

  (compressed H > 500Wh/kg)
- Others…

The problem?

1. Energy density
2. Cost

Battery cars

Part of complete coverage on

On the Move

The new fear: Electric car 'range anxiety'

By **Steve Almasy**, CNN

October 20, 2010 9:24 a.m. EDT

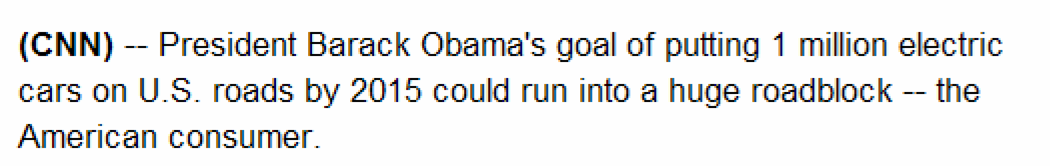
Nissan Leaf has a 24-*kWh*

EPA range of 73 miles

Study: Obama's electric car goal hits roadblock

By **Erika Dimmler**, CNN

February 3, 2011 9:02 a.m. EST

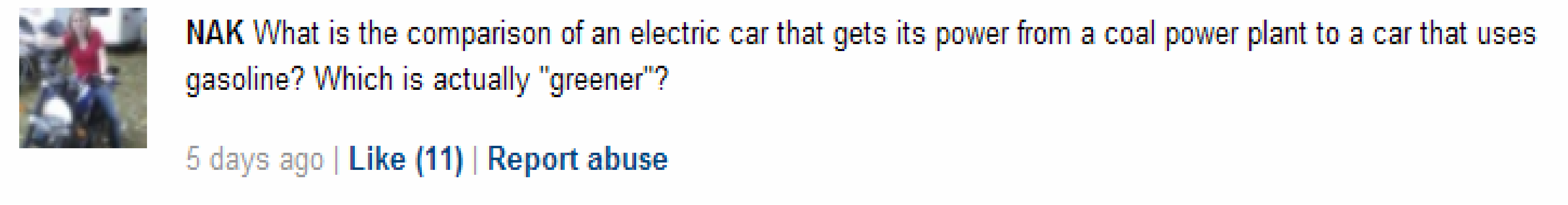


(CNN) -- President Barack Obama's goal of putting 1 million electric cars on U.S. roads by 2015 could run into a huge roadblock -- the American consumer.

Battery cars

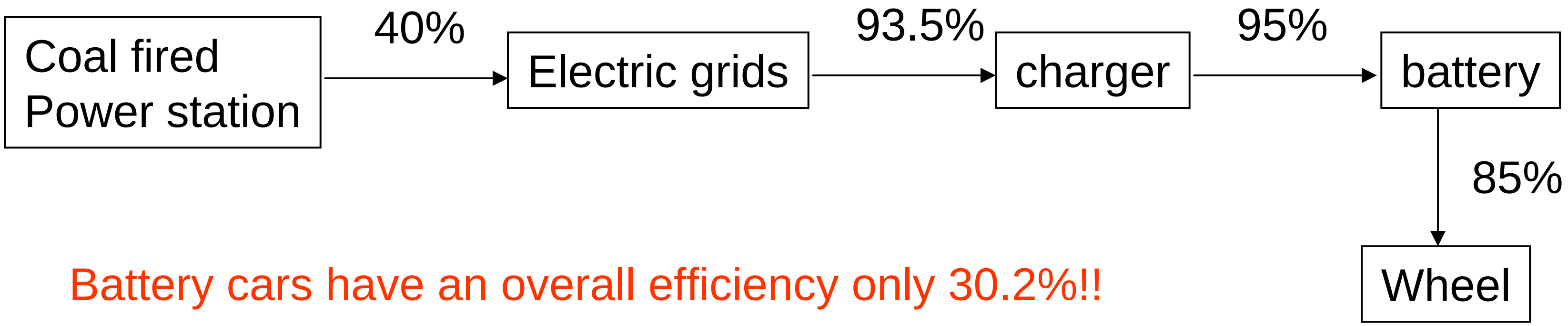
Are they really clean or green?

A bit of inconvenient truth?



NAK What is the comparison of an electric car that gets its power from a coal power plant to a car that uses gasoline? Which is actually "greener"?

5 days ago | **Like (11)** | **Report abuse**



Coal fired Power station

40%

Electric grids

93.5%

charger

95%

battery

85%

Wheel

Battery cars have an overall efficiency only 30.2%!!

Compared to the gasoline engine cars of ~30%

<u>And what is cleaner? Coal vs Oil</u>

Battery cars

Some remarks

- Unless there is a major breakthrough in batteries, say doubling the current energy density, battery cars will be a niche.
- Put in perspective, battery chemistry improves from the 1859 Plante lead acid cell (40Whr/kg) to todays lithium ion (80Whr/kg). It doubled in 150 years!

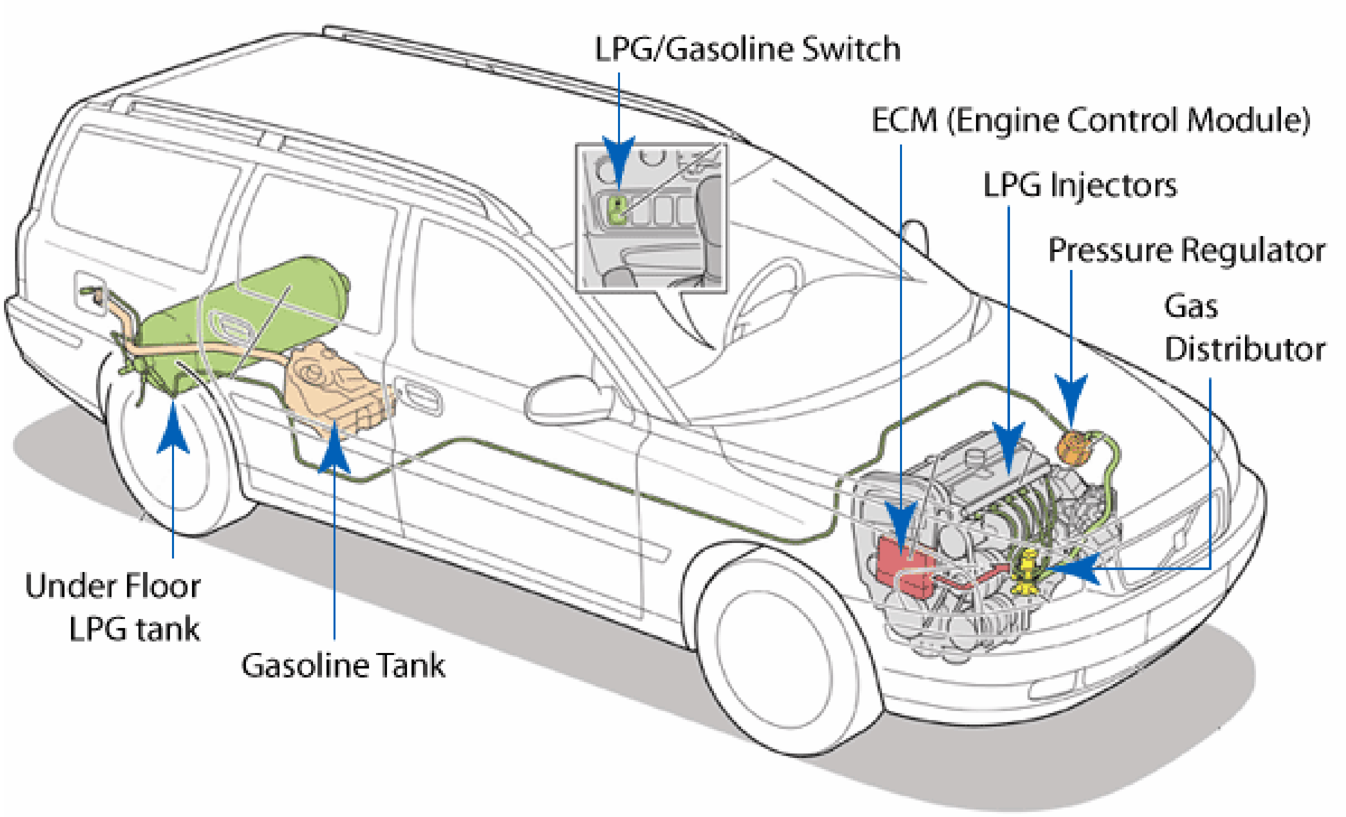
Natural gas cars

The rationale

- NG is 1/3 the price of gasoline equivalent
- It at least triples the range of a battery for less than ½ of the added weight compared to a Li-ion battery car
- For 2 thousand dollars you can modify your car to burn NG, with a range of 70+ miles, bettering that of Chevy Volt!

Natural gas cars

- Most cars can be converted to burn NG + gasoline
- The NG is good enough to daily commute



Natural gas cars

- Then you can charge it overnight at your home
- $2000 conversion vs plug-in hybrids (PHEV) of $12000 battery
- 1/3 of gasoline operation cost, on par with PHEV or cheaper
- More NG reserve than oil. And NG is going up with shale NG and methane hydrates
- NG twice clean as gasoline, four times as coal

Natural gas cars

- The technology is mature
- Only problem existing is political