

# Hydrogen Storage (II)

The key to an efficient energy storage

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

# Metal Hydrides

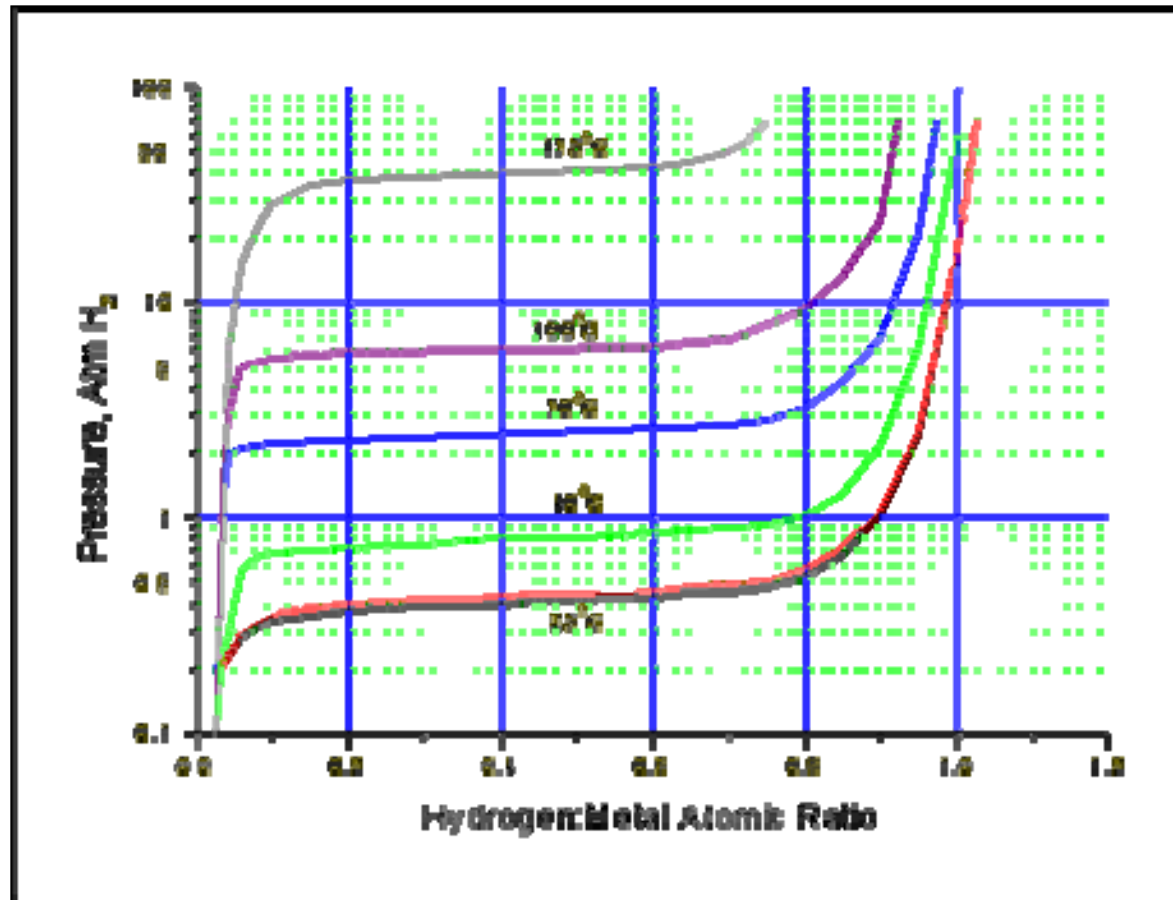
## Simple metal hydrides

- Examples: NiH, PdH, LaNi<sub>5</sub>H<sub>6</sub>, MgH<sub>2</sub>
- 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: $\text{LaNi}_5\text{H}_6$

- Most widely utilized MH today
- Gravimetric density  $\sim 1.3\%$ -wt H
- Volumetric density  $\sim 0.1$  kg/liter
- Cost high due to nickel, lanthanum (rare earth)
- Relative ease of refueling (near ambient pressure)
- It's the most representative  $\text{AB}_5$  alloy
- Can be utilized in electrochemical cells (batteries and fuel cells) directly

# The chemical elements

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

Alkaline Earth

Alkali metals

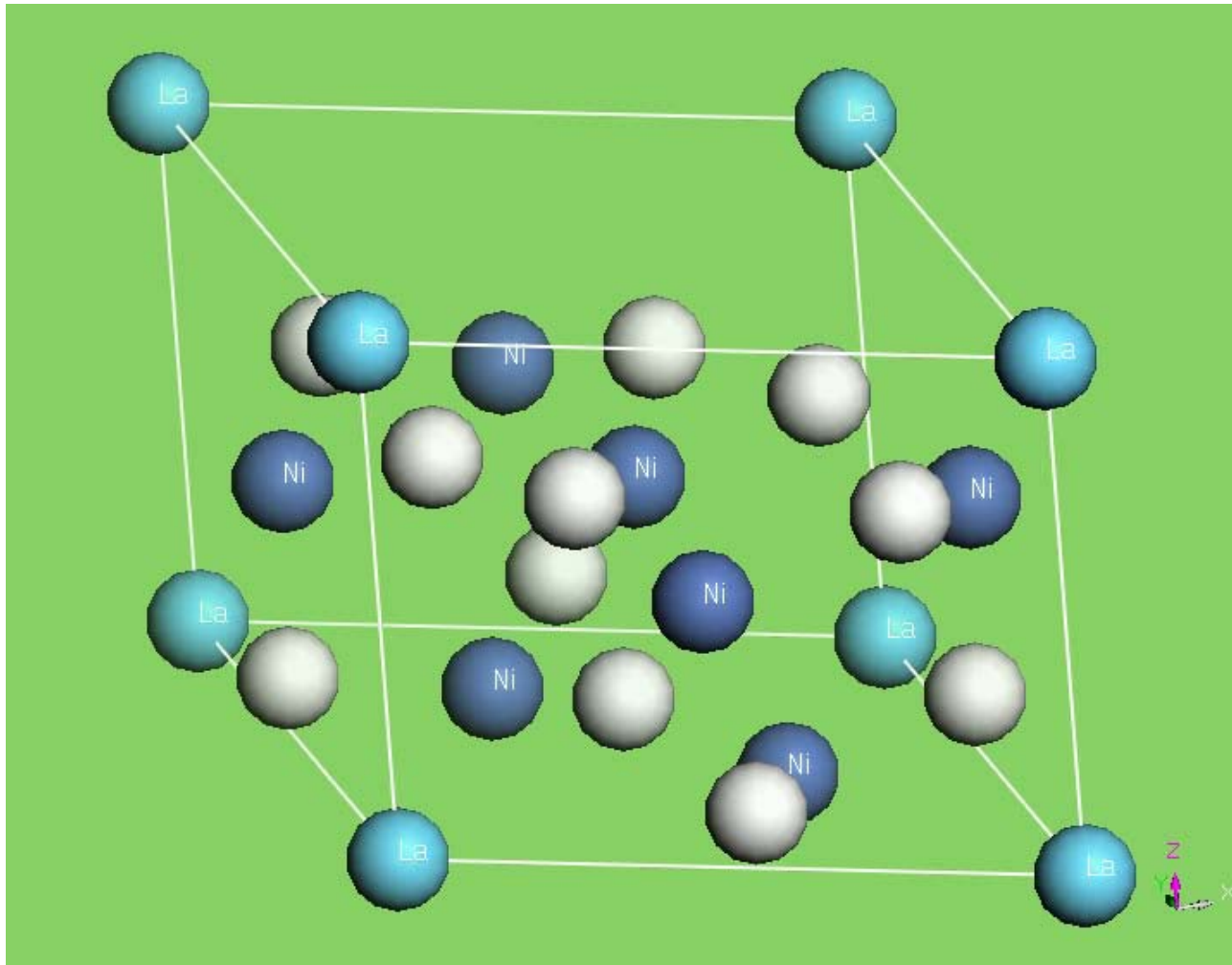
Lanthanide series

\*\* Actinide series

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

Rare Earth

# LaNi<sub>5</sub>H<sub>6</sub>: Structure



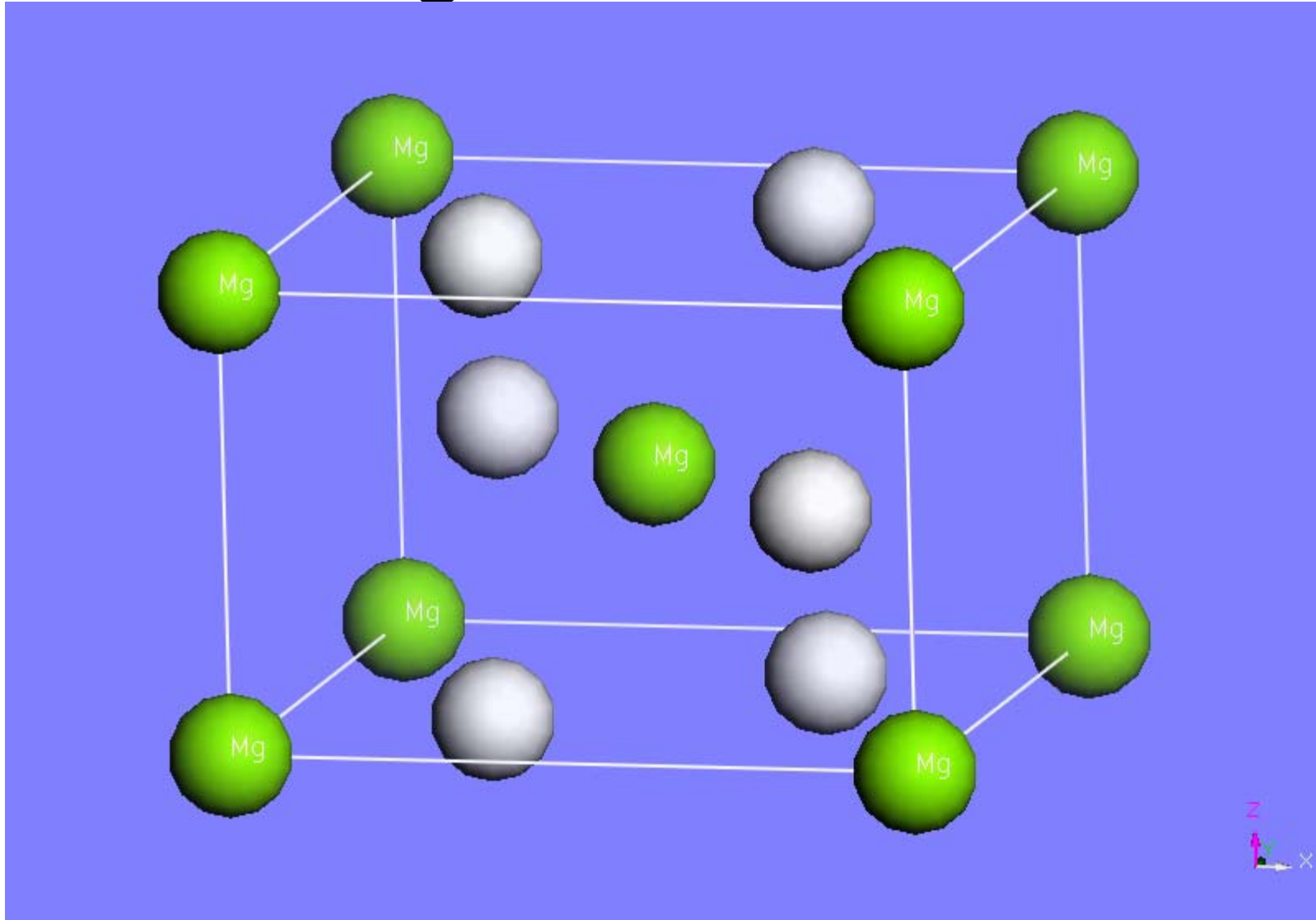
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# Metal Hydrides: $\text{MgH}_2$

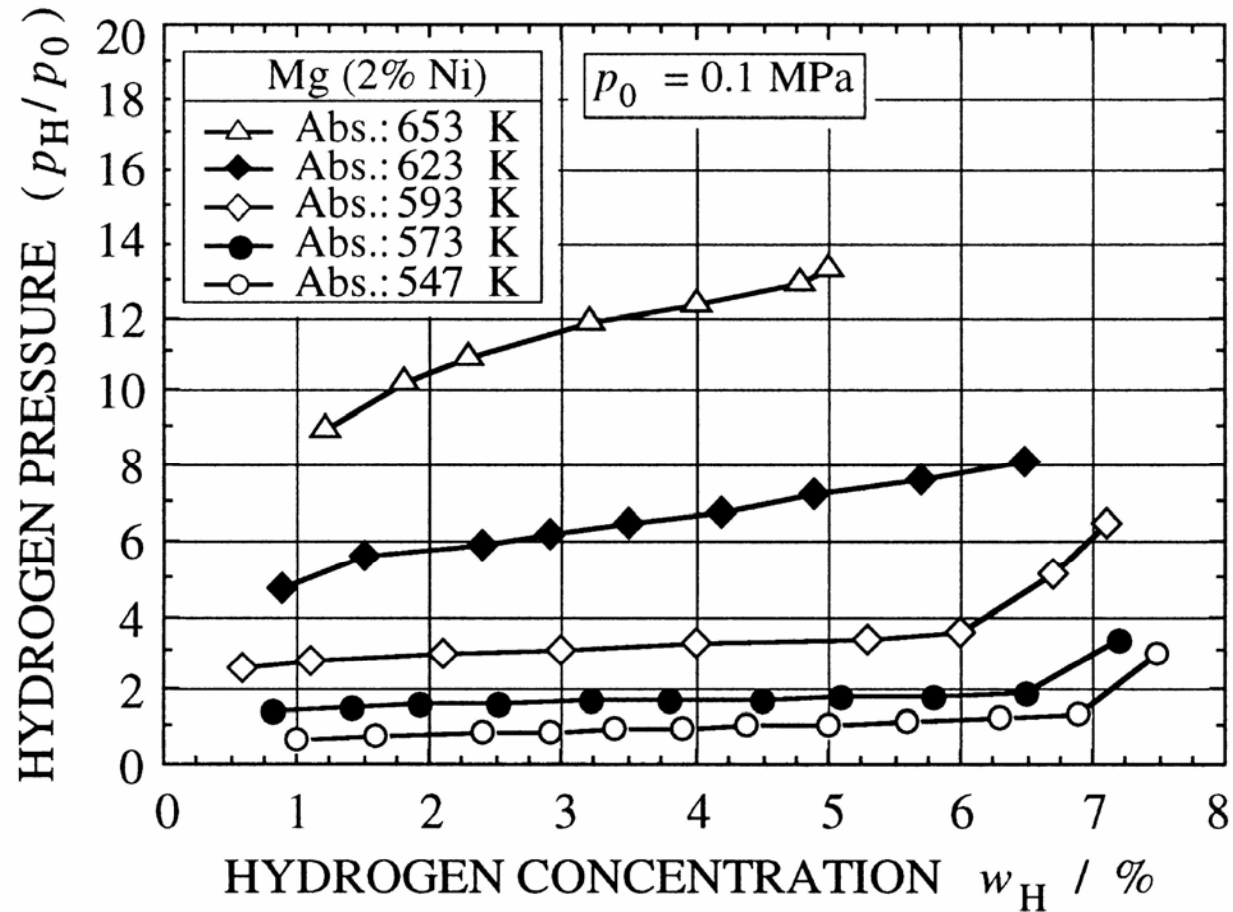
- Gravimetric density ~ 8%-wt H
- Volumetric density  $\gg$  0.1 kg/liter
- Cost is low, very affordable
- Abundant element
- Clean
- Medium temperature absorption and desorption ~ 300 degrees C
- It's the most representative alkaline earth metal hydride
- Not ideal for mobile H storage but ideal for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



# MgH<sub>2</sub>: Structure



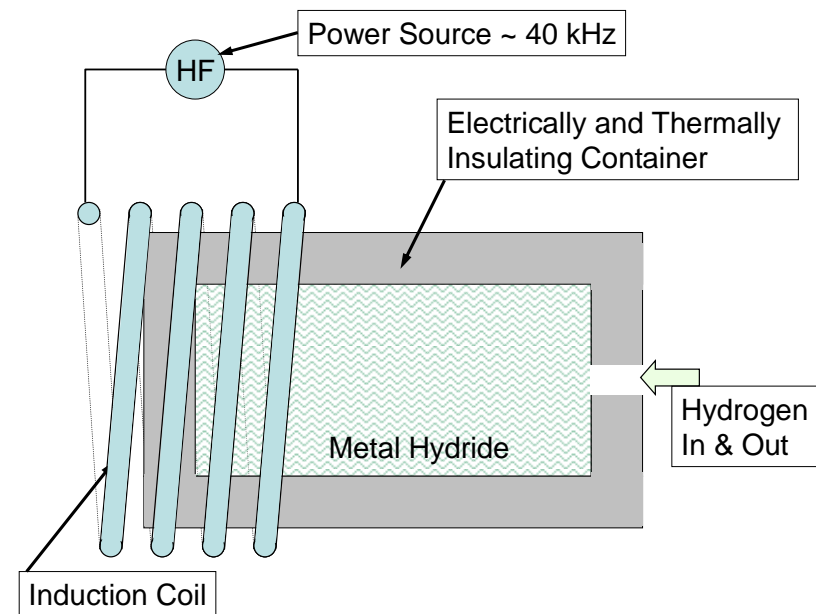
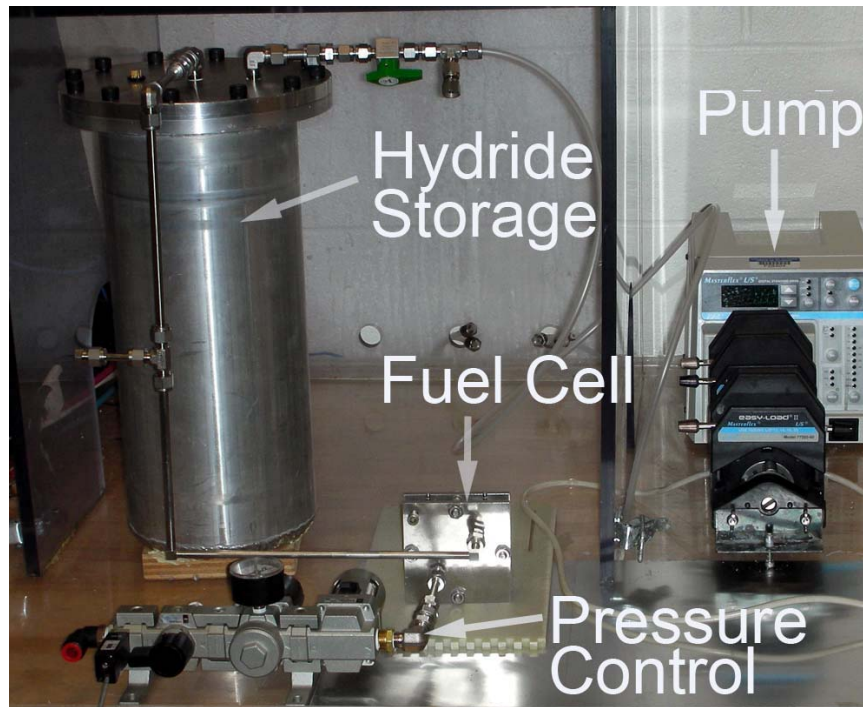
# MgH<sub>2</sub>: Isotherm



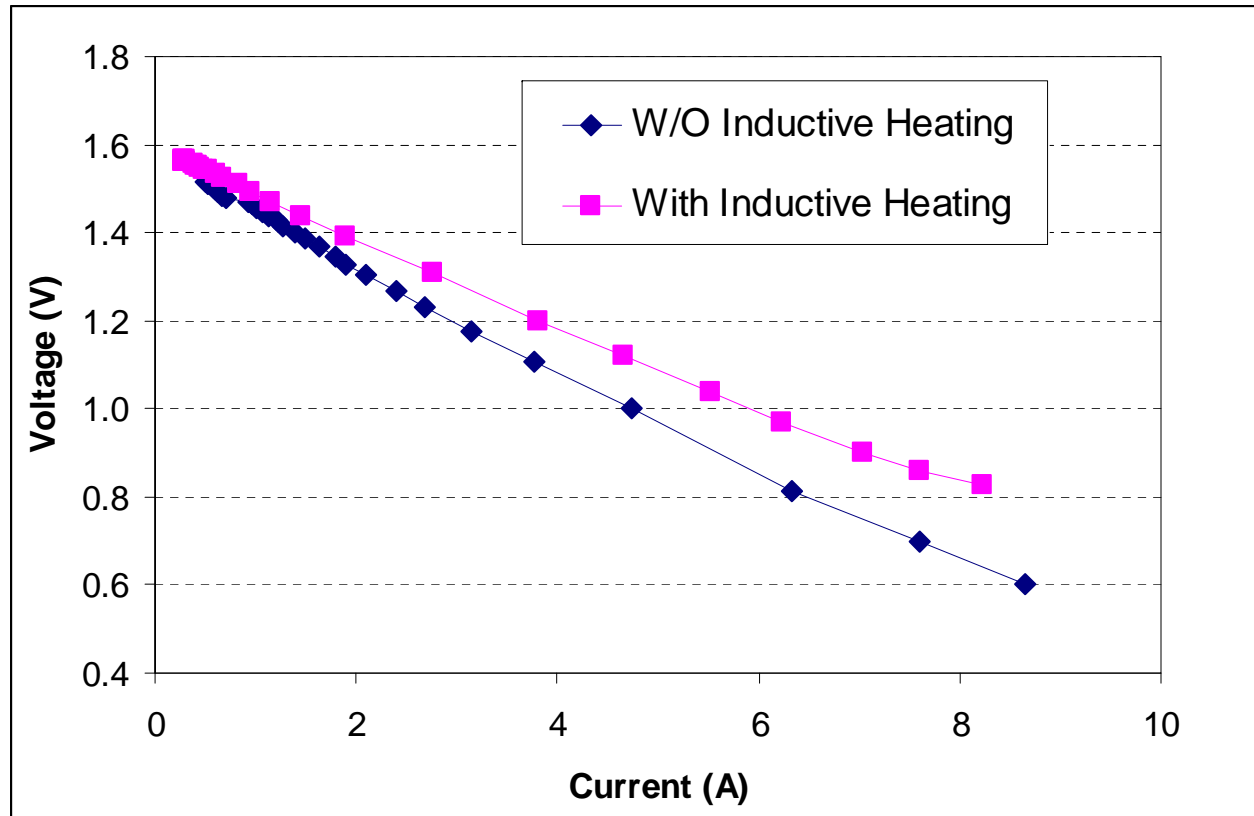
# MgH<sub>2</sub>: Kinetics

- 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<sub>2</sub>: Fast release with induction Heating

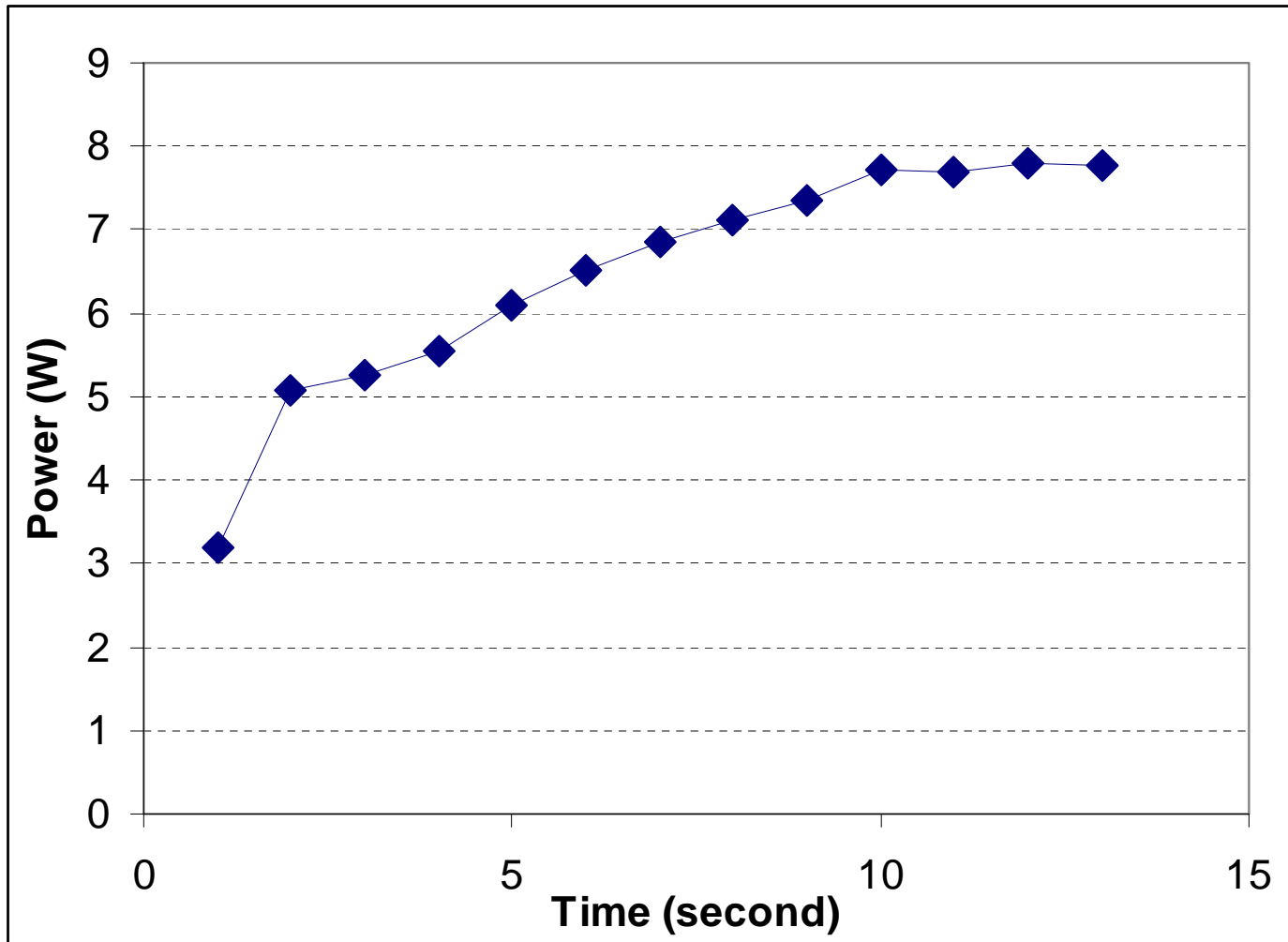


# MgH<sub>2</sub>: Fast release with induction heating



Fuel cell performance with and without induction heating

# MgH<sub>2</sub>: Fast release with induction heating



Fast fuel cell ramping with induction heating

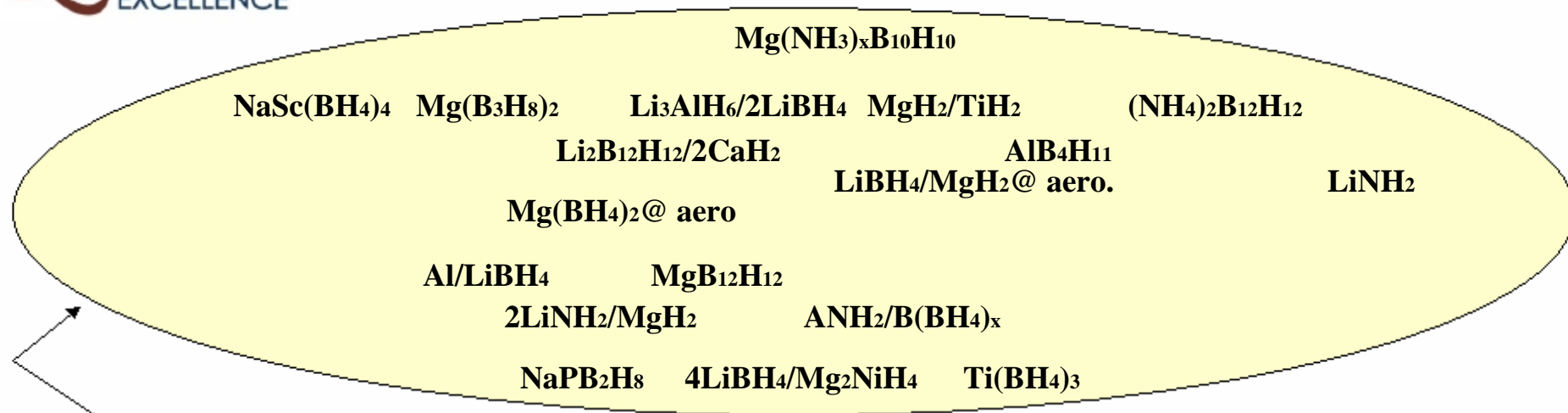
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# Complex metal hydrides

The hydrogen bonding is more covalent or localized

- Examples:  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{LiNH}_2$ ,  $\text{LiAlH}_4$
- New development
- Many issues exist, like regeneration, volatiles, safeties

# Final Year Downselection Path



*Materials examined in  
final year of the MHCoe*

11 More Downselects  
(Removing from Study)

$4\text{LiBH}_4/\text{Mg}_2\text{NiH}_4$  (low wt. %)  
 $\text{Mg}(\text{B}_3\text{H}_8)_2$  (too unstable)  
 $\text{Li}_2\text{B}_{12}\text{H}_{12}/2\text{CaH}_2$  (too high  $T_{\text{des}}$ )  
 $\text{Mg}(\text{NH}_3)_x\text{B}_{10}\text{H}_{10}$  ( $\text{NH}_3$  release)  
 $\text{Mg}(\text{NH}_3)_6\text{B}_{12}\text{H}_{12}$  ( $\text{NH}_3$  release)

$\text{CaB}_{12}\text{H}_{12}/\text{CaH}_2$  (not reversible)  
 $\text{Li}_2\text{B}_{12}\text{H}_{12}/6\text{MgH}_2$  (too high  $T_{\text{des}}$ )  
 $\text{Ti}(\text{BH}_4)_3$  (not reversible)  
 $\text{Li}_3\text{AlH}_6/2\text{LiBH}_4$  (too high  $T_{\text{des}}$ )  
 $\text{Li}(\text{NH}_3)_x\text{B}_{12}\text{H}_{12}$  ( $\text{NH}_3$  release)  
 $\text{NaBP}_2\text{H}_8$  (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:**

$\text{Zn}_4\text{O}(\text{BTB})_2$ , where  $\text{BTB}^{3-} = 1,3,5$ -  
benzenetribenzoate

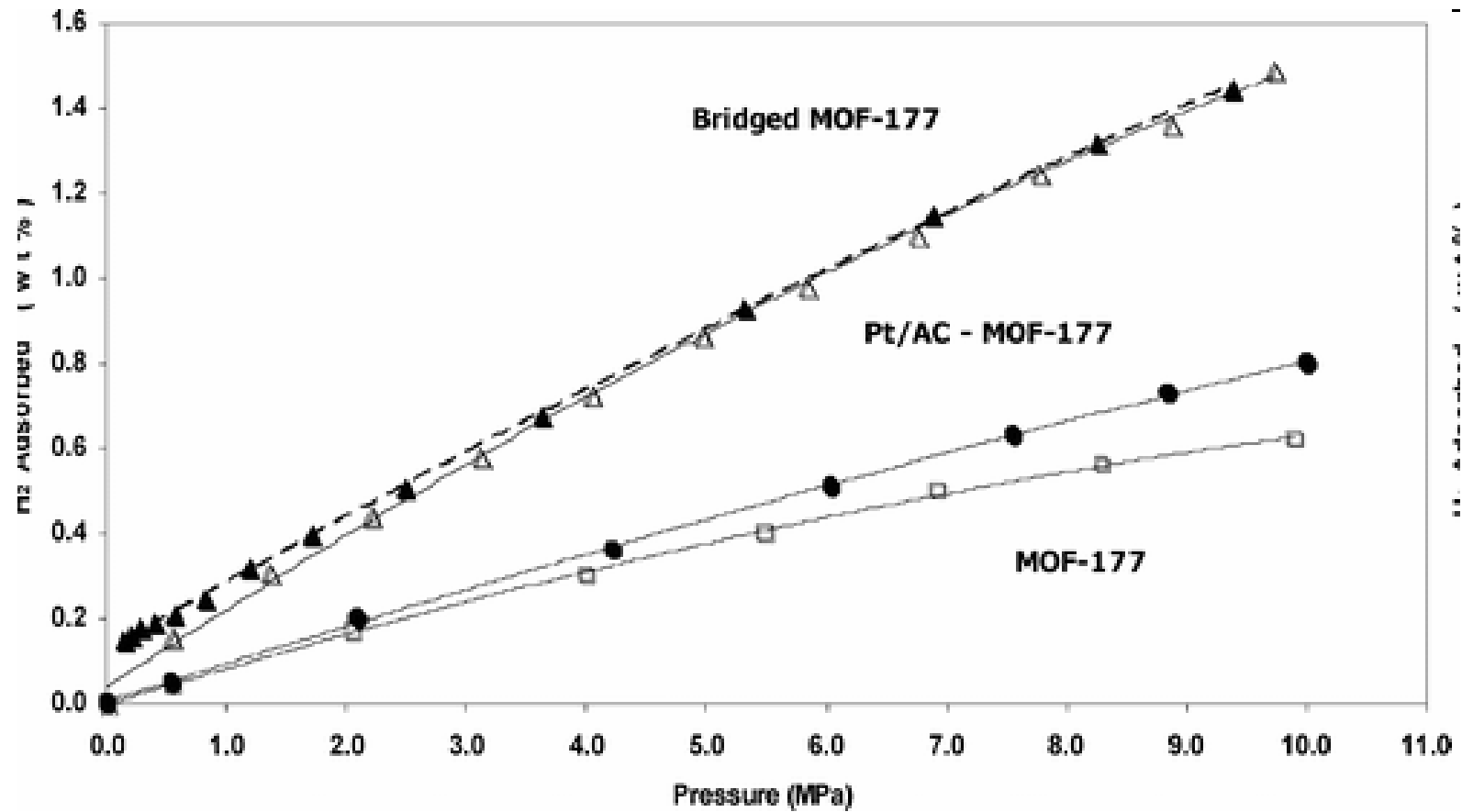
Theoretical gravimetric density

7.1 wt% at 77 K, 40 bar

(not including dewar and pressure vessel)

11.4 wt% at 77 K, 78 bar

# MOF 177



# 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