Hydrogen Storage

Main Energy Storage Market Segments

1. Utility/industrial applications including: grid reinforcement, renewables integration and uninterruptible power supply (UPS) Applications

2. Transport / mobile applications including: on-board power for vehicles, new drive trains (electric and hybrid electric vehicles) and leisure applications (caravanning)

3. Portable applications including**:** computing, cell-phones and cameras (the 3 ‘C’s’).

Source: Ian Edwards, ITI Energy, May 24th, 2005

Generic Storage Systems

Electrochemical systems
batteries and flow cells

Mechanical systems
fly-wheels and compressed air energy storage (CAES)

Electrical systems
super-capacitors and superconducting magnetic energy storage (SMES)

Chemical systems
hydrogen cycle (electrolysis -> storage -> power conversion)

Thermal systems
sensible heat (storage heaters) and phase change

Source: Ian Edwards, ITI Energy, May 24th, 2005

Potential Fuel

Energy Sources	Typical Chemical Energy Density
Hydrogen	**142.0 MJ/kg**
Ethanol	**29.7 MJ/kg**
Ammonia	**17.0 MJ/kg**
Automotive Gasoline	**45.8 MJ/kg**
Methane	**55.5 MJ/kg**
Methanol	**22.7 MJ/kg**

(Source: Chemical Energy, The Physics Hyper text Book)

Energy Density

Fuel	Typical Stored Chemical Energy Density	
Hydrogen	**7.1 MJ/kg**	**@ 5wt%**
Ethanol	**26.7 MJ/kg**	**@ 90wt%**
Ammonia	**13.6 MJ/kg**	**@ 80wt%**
Automotive Gasoline	**41.2 MJ/kg**	**@ 90wt%**
Methane	**44.5 MJ/kg**	**@ 80wt%**
Methanol	**20.4 MJ/kg**	**@ 90wt%**

Source: Ian Edwards, ITI Energy, May 24th, 2005

Energy Densities

Fuel	Hydrogen weight fraction	Ambient state	Liquid volumetric energy density(MJ/L)	Mass energy density (MJ/kg)
Hydrogen	1	Gas	8.4-10.4[3]	120
Methane	0.25	Gas	21(17.8)[2]	50 (43)[2]
Ethane	0.2	Gas	23.7	47.5
Propane	0.18	Gas (liquid)[1]	22.8	46.4
Ammonia	0.18	Gas (liquid)[1]	13.1	17.0
Gasoline	0.16	Liquid	31.1	44.4
Ethanol	0.13	Liquid	21.2	26.8
Methanol	0.12	Liquid	15.8	19.9

[1] A gas at room temperature, but normally stored as a liquid at moderate pressure.

[2] The larger values are for pure methane. The values in parentheses are for a “typical” Natural Gas.

[3] The higher value refers to hydrogen density at the triple point

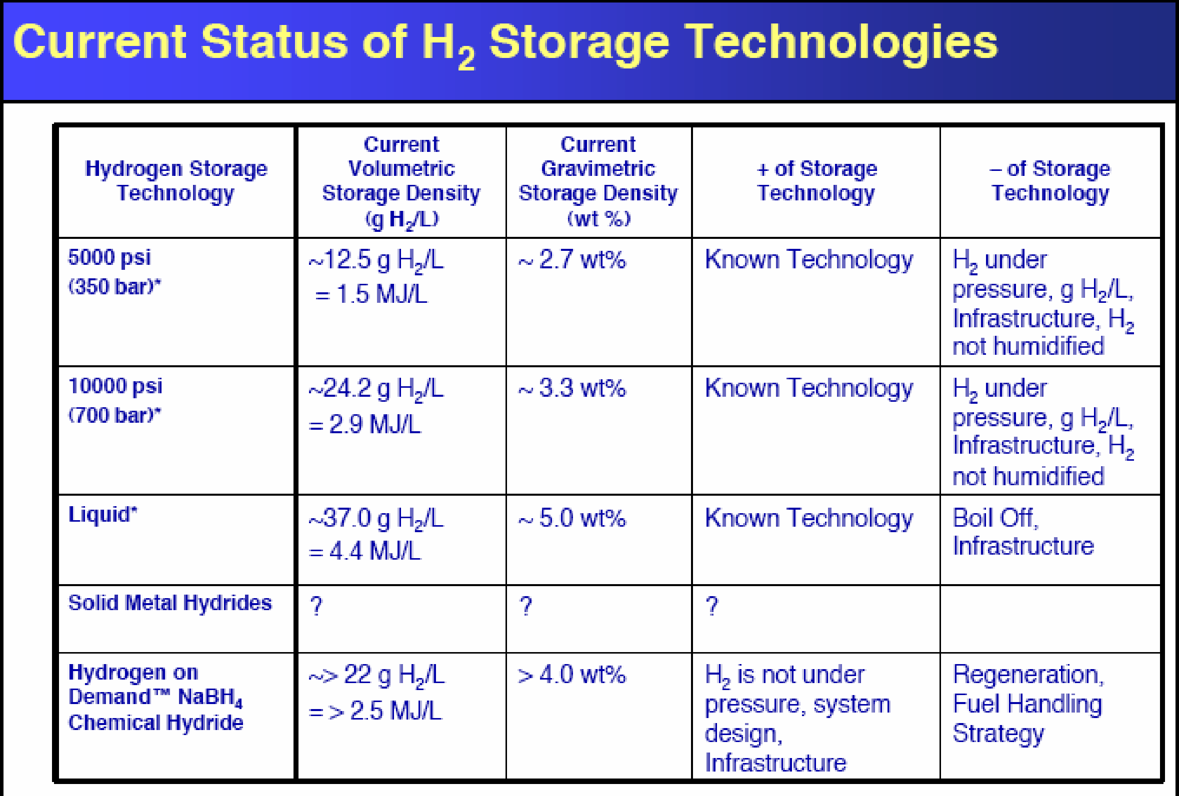
Source: Ian Edwards, ITI Energy, May 24th, 2005

Energy Density in wh/liter

Material	Volumetric	Gravimetric
Diesel	10942 Wh/l	13762Wh/kg
Gasoline	9,700 Wh/l	12,200 Wh/kg
LNG	7,216 Wh/l	12,100 Wh/kg
Propane	6,600 Wh/l	13,900 Wh/kg
Ethanol	6,100 Wh/l	7,850 Wh/kg
Methanol	4,600 Wh/l	6,400 Wh/kg
Liquid H2	2600 Wh/l	39,000 Wh/kg
150 Bar H2	405 Wh/l	39,000 Wh/kg
Lithium	250 Wh/l	350 Wh/kg
Nickel Metal Hydride	100 W·h/L	60Wh/kg
Lead Acid Battery	40 Wh/l	25 Wh/kg
Compressed Air	17 Wh/l	34 Wh/kg

Objective

To achieve adequate stored energy in an efficient, safe and cost effective system.



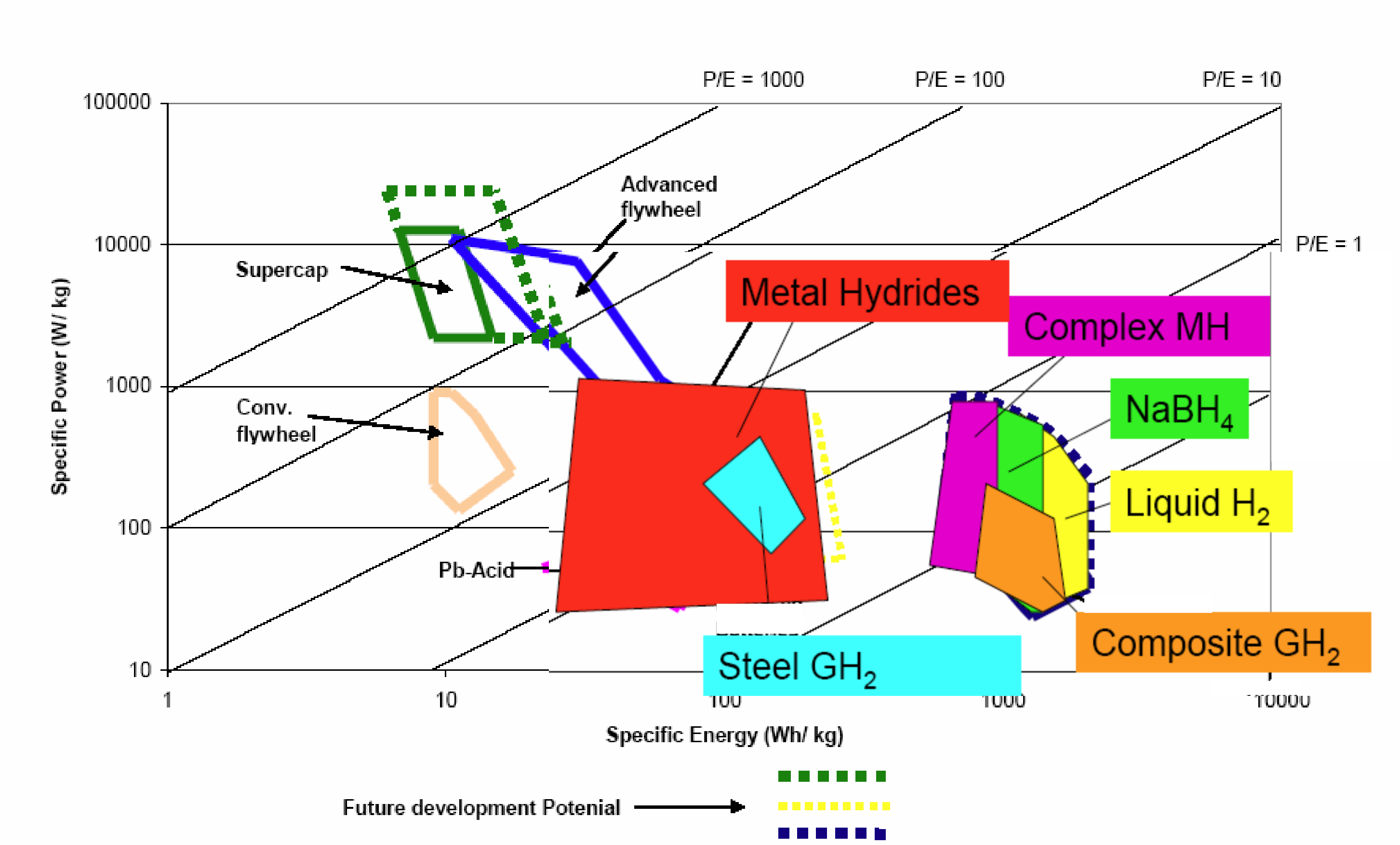
Current Status of H_2 Storage Technologies

Hydrogen Storage Technology	Current Volumetric Storage Density ($g H_2/L$)	Current Gravimetric Storage Density (wt %)	+ of Storage Technology	– of Storage Technology
5000 psi (350 bar)*	~12.5 g H_2/L = 1.5 MJ/L	~ 2.7 wt%	Known Technology	H_2 under pressure, g H_2/L, Infrastructure, H_2 not humidified
10000 psi (700 bar)*	~24.2 g H_2/L = 2.9 MJ/L	~ 3.3 wt%	Known Technology	H_2 under pressure, g H_2/L, Infrastructure, H_2 not humidified
Liquid*	~37.0 g H_2/L = 4.4 MJ/L	~ 5.0 wt%	Known Technology	Boil Off, Infrastructure
Solid Metal Hydrides	?	?	?	
Hydrogen on Demand™ $NaBH_4$ Chemical Hydride	~> 22 g H_2/L = > 2.5 MJ/L	> 4.0 wt%	H_2 is not under pressure, system design, Infrastructure	Regeneration, Fuel Handling Strategy

Gravimetric storage density: the gravimetric storage density is the weight of the hydrogen being stored divided by the weight of the storage and delivery system proposed

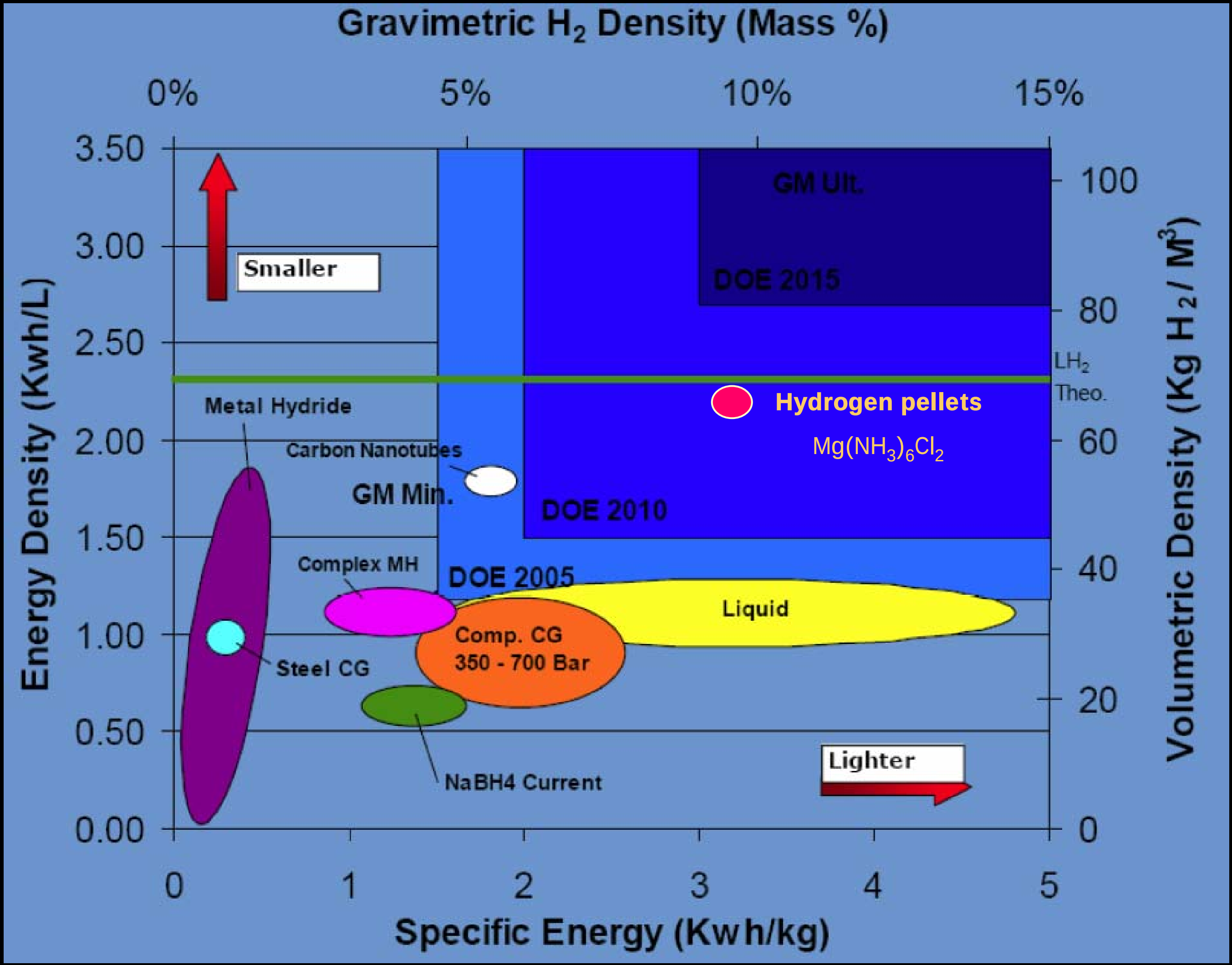
Source: Oak Ridge National Laboratory Hydrogen Storage Work Shop, May 2003

Energy Storage



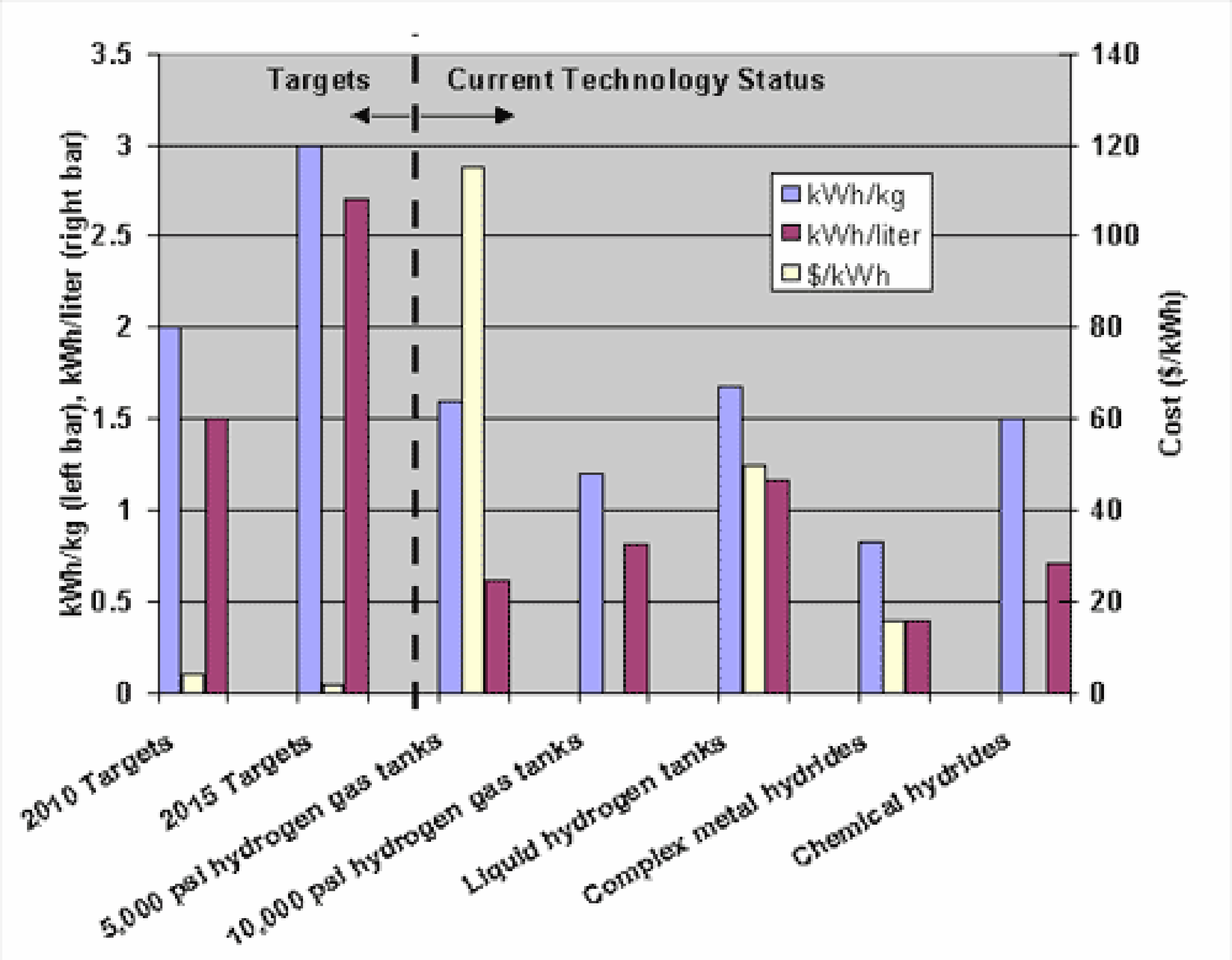
Source: Ian Edwards, ITI Energy, May 24th, 2005

Hydrogen Storage

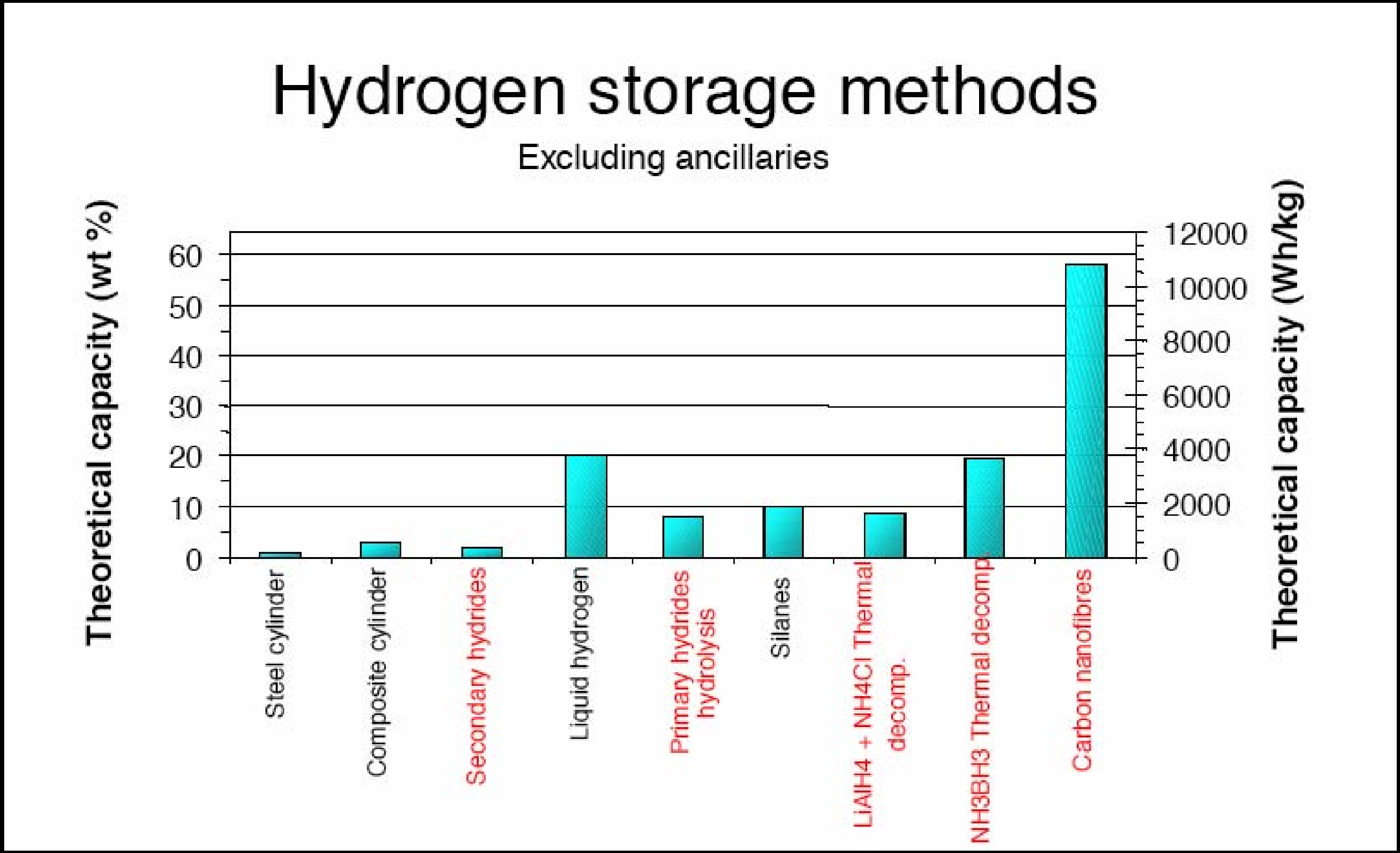


Source: Ian Edwards, ITI Energy, May 24th, 2005

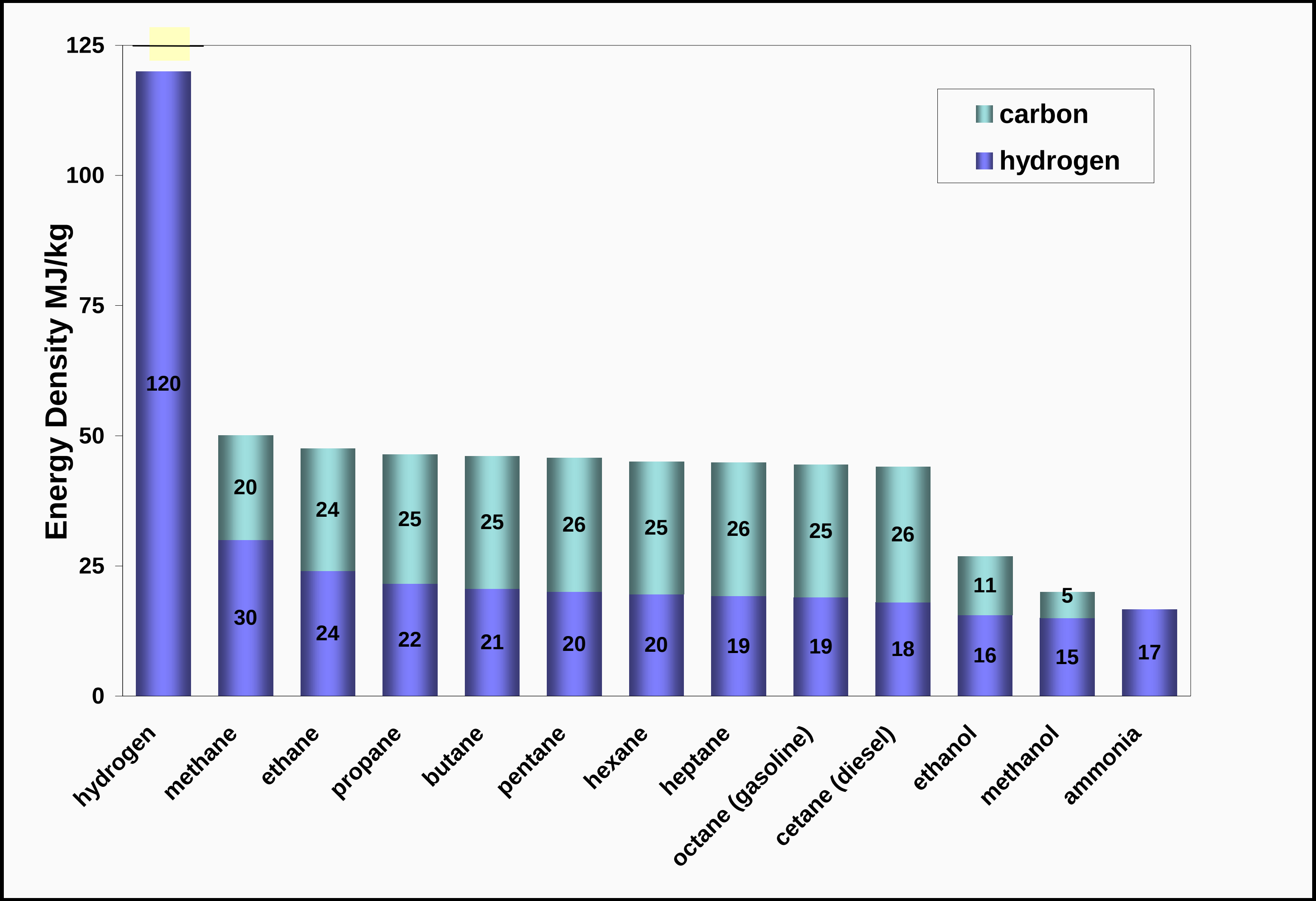
Technology Status



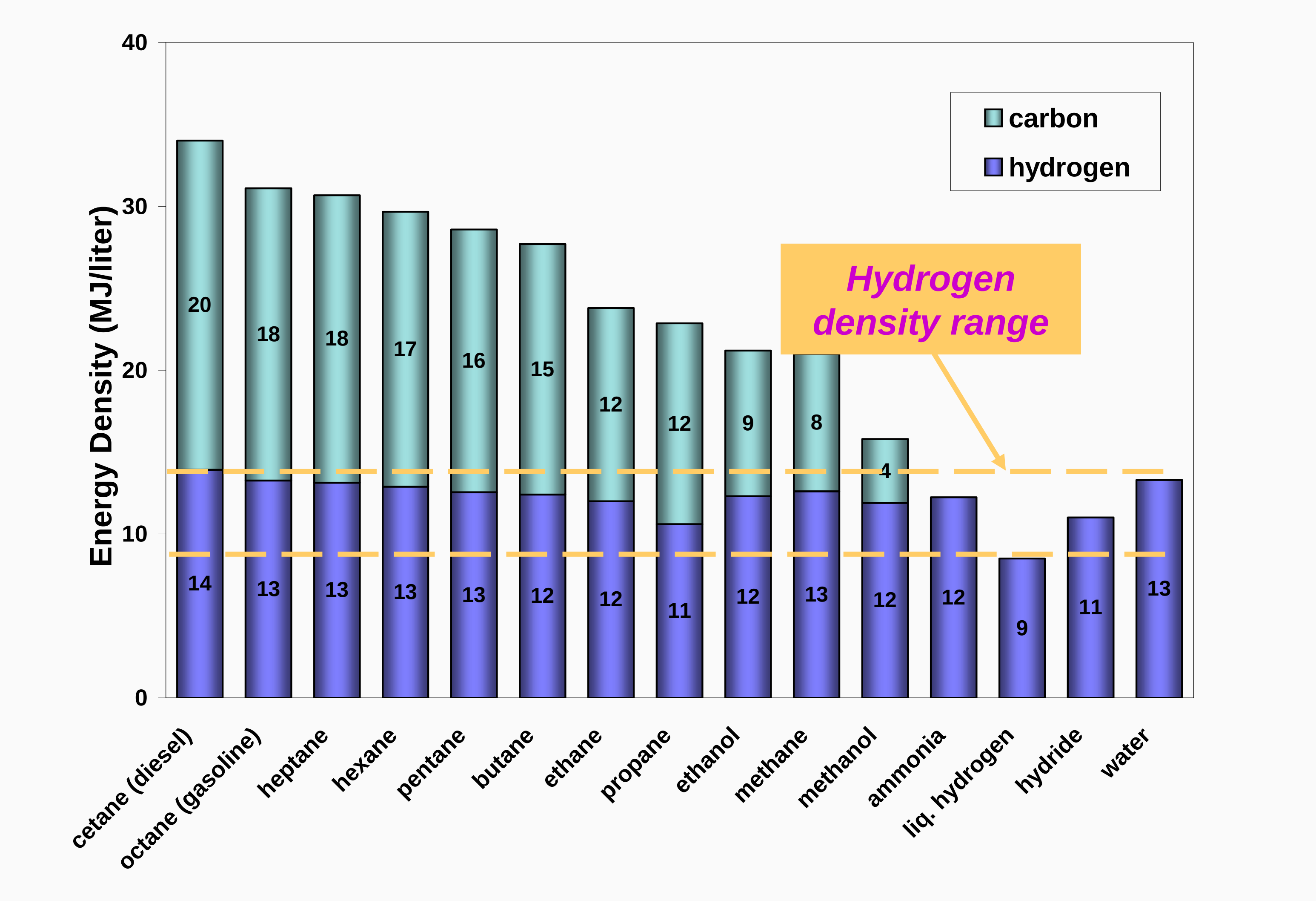
Storage Methods



Specific energy of fuels (LHV)

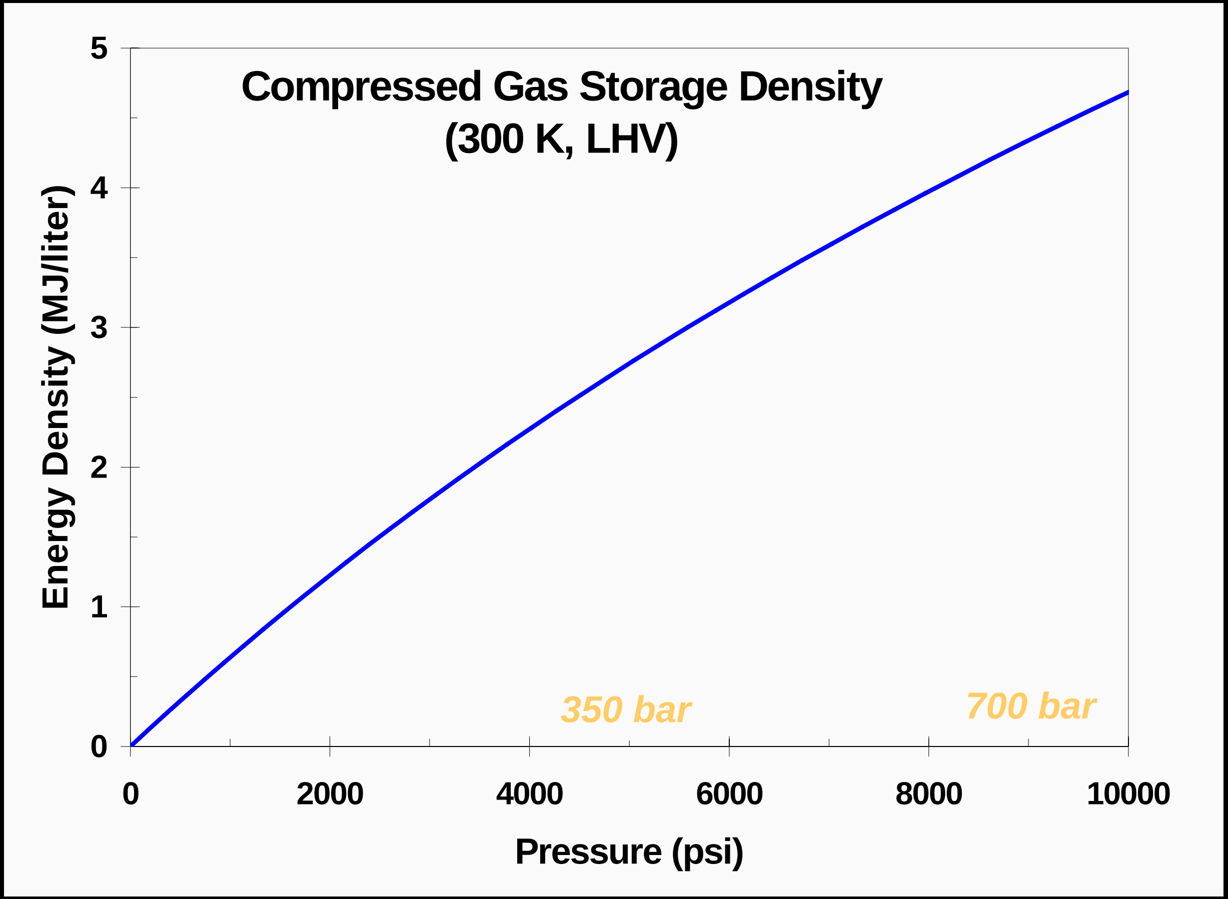


Energy Densities (LHV) in Liquid state



Hydrogen density range

Compressed Gas



Gasoline: 13 MJ/L

Compressed Gas

- increased pressure (>700 bar)
  - stronger, lighter composite tanks (cost)
  - hydrogen permeation
  - non-ideal gas behavior
- conformable tanks
  - maximum volume gain ~20% (cylind./rect. volumes)
  - some increase in weight
- microspheres
  - multiple shell volumes
  - close-packed packing density ~60% of volume
  - hydrogen release/reload mechanism

Compressed Gas Cylinders

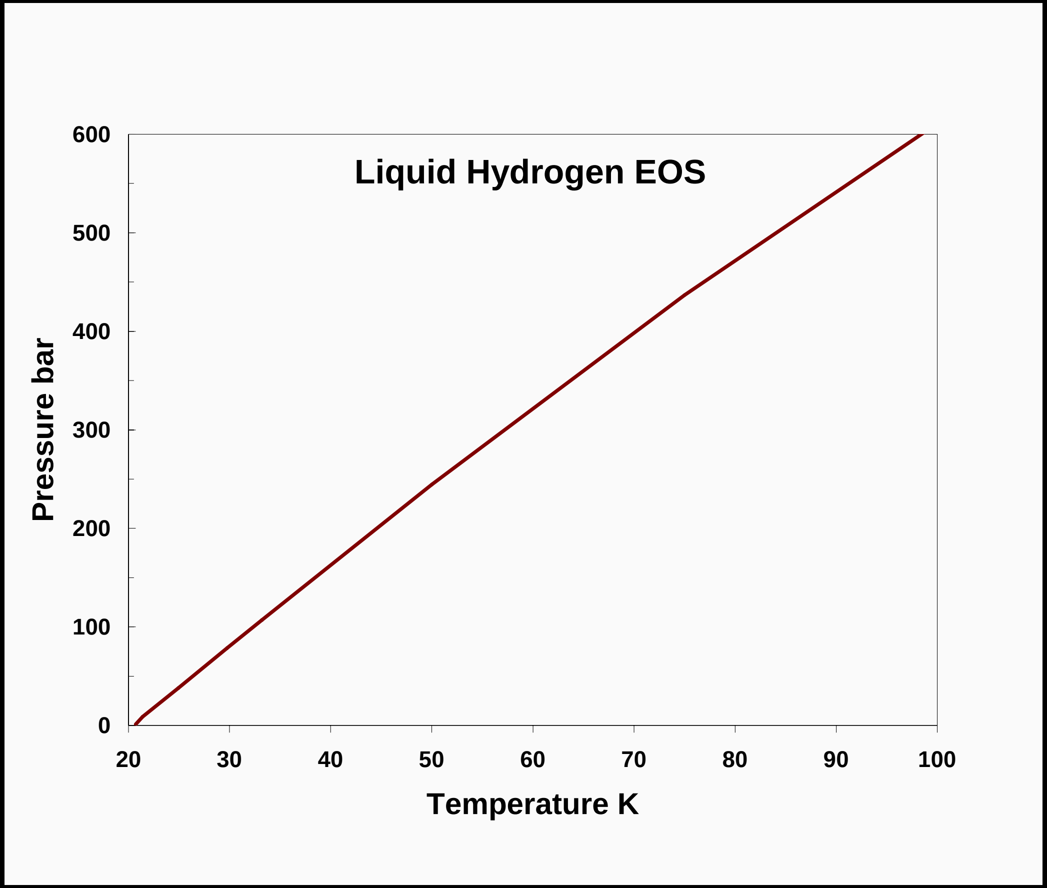
Carbon fiber wrap/polymer liner tanks are lightweight and commercially available.

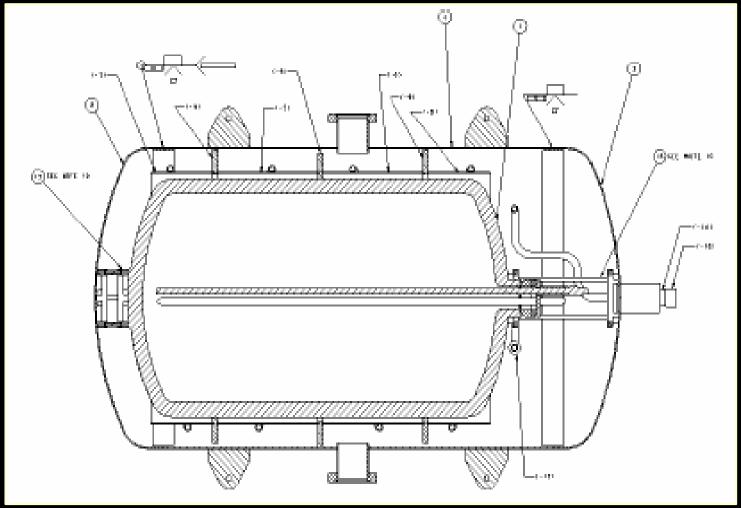
weight	specific energy
6 wt.%	7.2 MJ/kg
7.5 wt.%	9.0 MJ/kg
10 wt.%	12 MJ/kg

Energy density is the issue:

Pressure	Gas density	System density
350 bar	2.7 MJ/L	1.95 MJ/L
700 bar	4.7 MJ/L	3.4 MJ/L

High Pressure Cryogenic Tank





S. Aceves, et al 2002

Estimated energy density:
4.9 MJ/L (Berry 1998)

- *reduces temperature requirements*
- *eliminates liquifaction requirement*
- *essentially eliminates latency issue*

Liquid Storage

Requires cryogenic systems

- Equilibrium temperature at 1 bar for liquid hydrogen is ~20 K.
- Estimated storage densities[1]

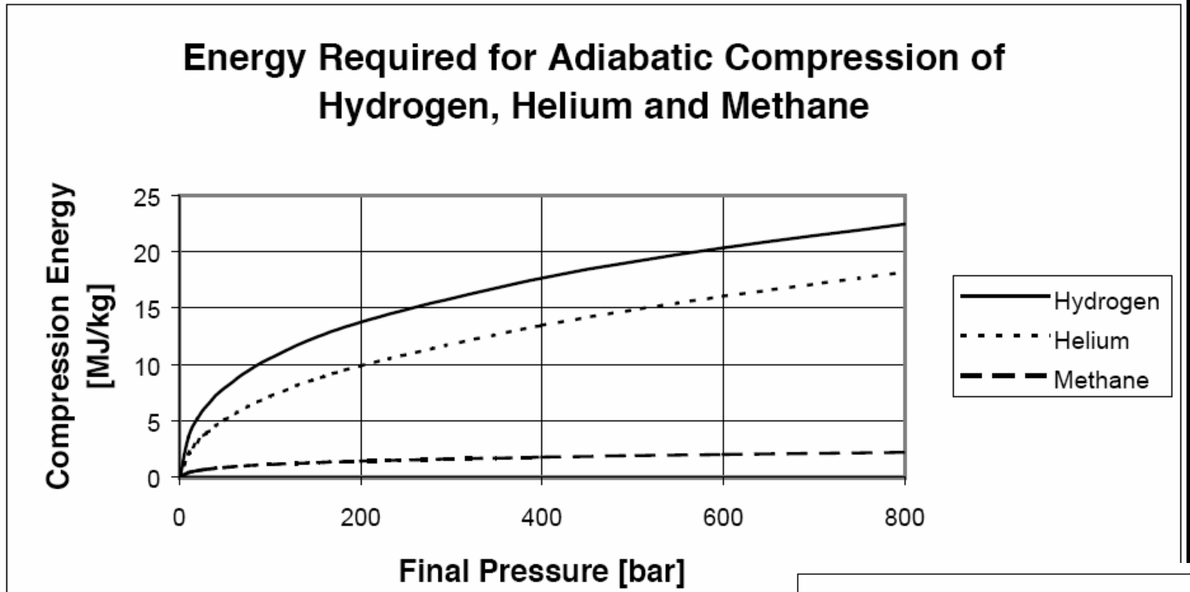
Berry (1998)	4.4 MJ/liter
Dillon (1997)	4.2 MJ/liter
Klos (1998)	5.6 MJ/liter

- Issues with this approach are:
  - dormancy.
  - energy cost of liquifaction.

---

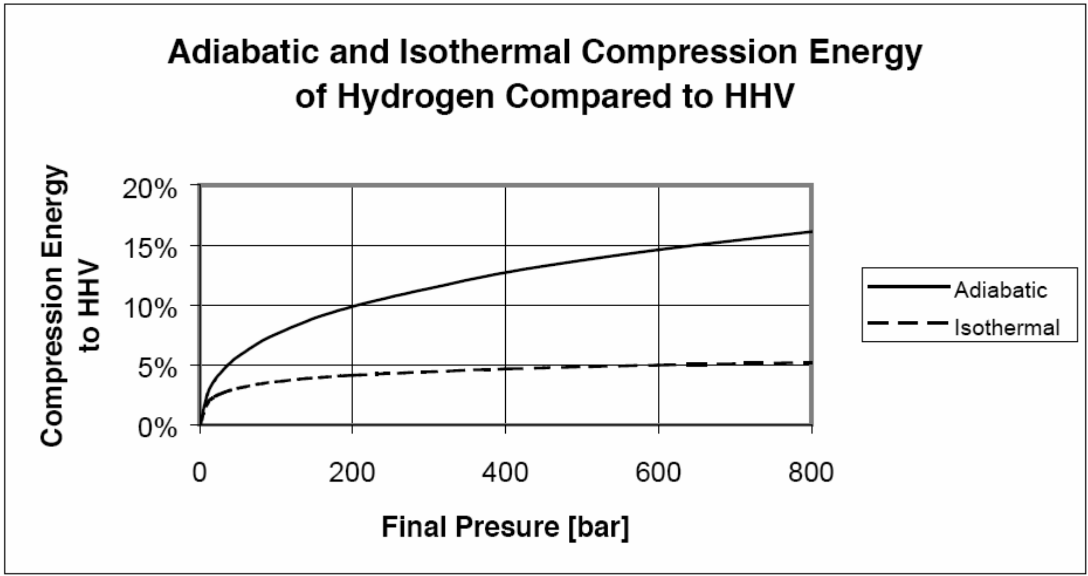
[1] **J. Pettersson and O Hjortsberg, KFB-Meddelande 1999:27**

Gaseous Hydrogen Storage



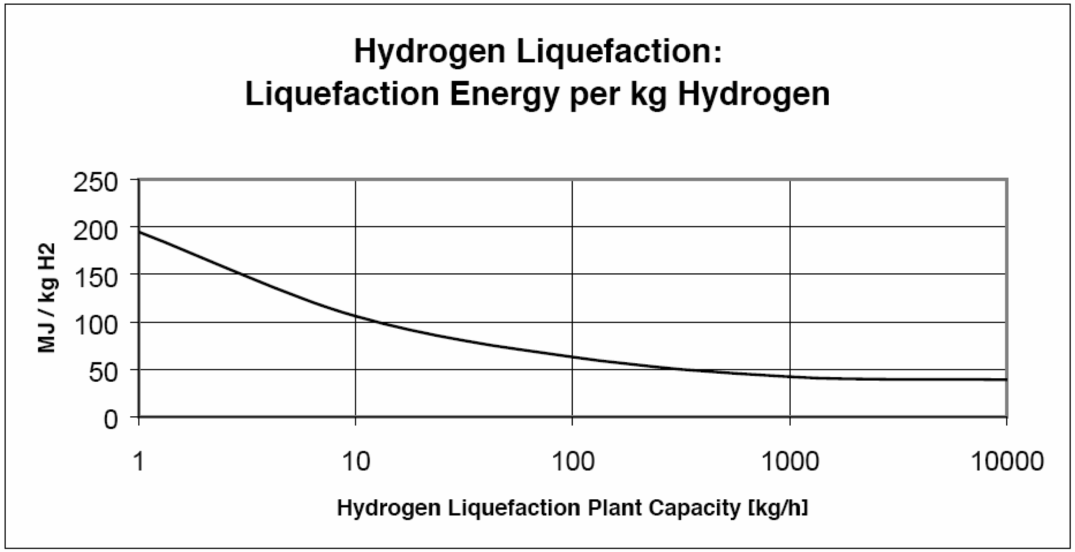
Hydride storage of hydrogen may be compared to the compression of hydrogen

Higher Heating value of Hydrogen: 142 MJ/kg

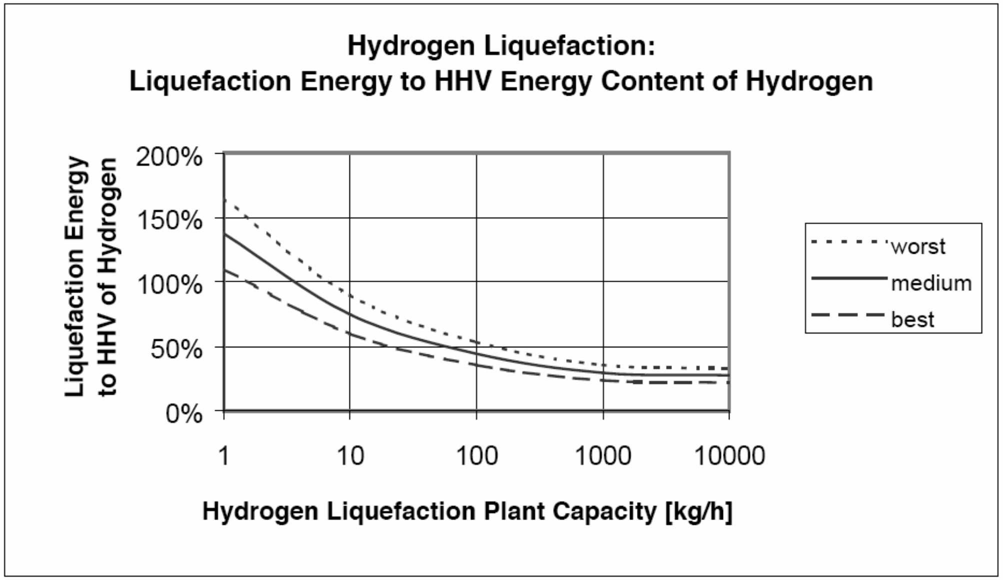


Source: The Future of Hydrogen Economy: Bright or Bleak?
Baldur Eliasson and Ulf Bossel, ABB Switzerland Ltd.

Hydrogen Storage - Liquefaction

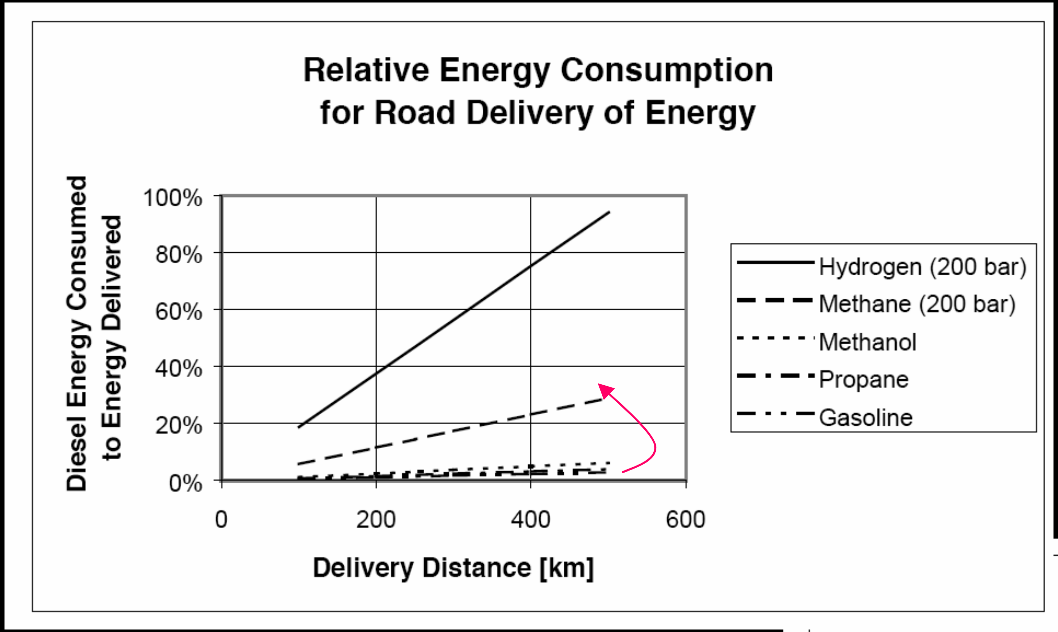


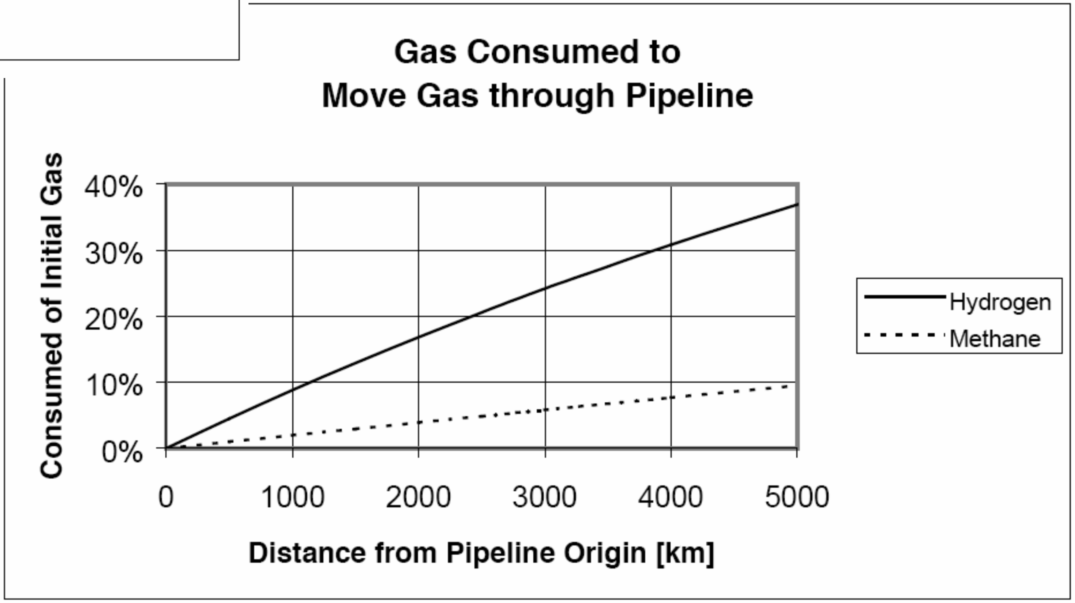
Total energy requirement for liquefaction of 1 kg of H_2



Source: The Future of Hydrogen Economy: Bright or Bleak?
Baldur Eliasson and Ulf Bossel, ABB Switzerland Ltd.

Hydrogen Delivery - Pipelines





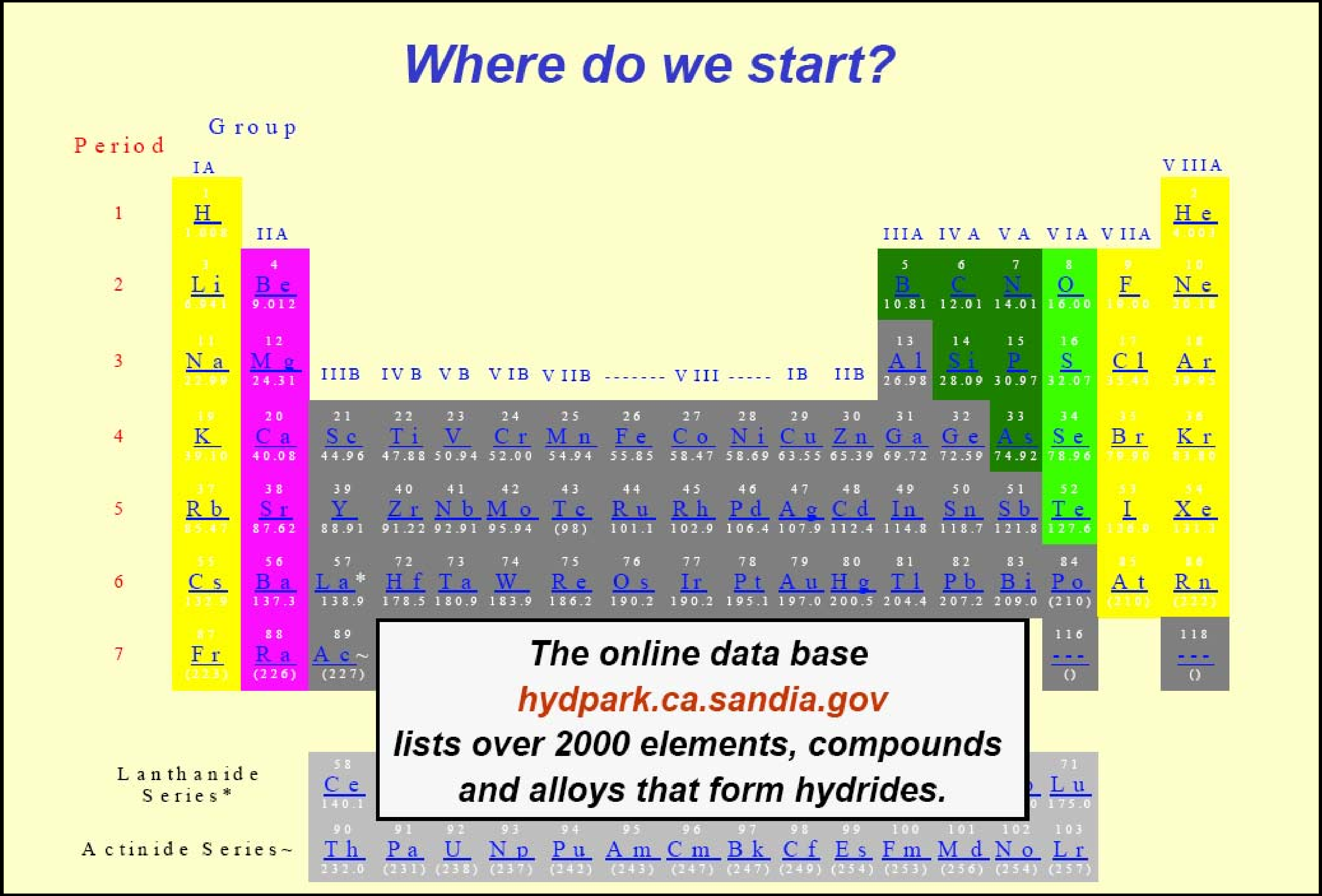
Source: The Future of Hydrogen Economy: Bright or Bleak?
Baldur Eliasson and Ulf Bossel, ABB Switzerland Ltd.

Hydrides

Chemically bond hydrogen in a solid material

- This storage approach should have the highest hydrogen packing density.
- However, the storage media must meet certain requirements:
  - reversible hydrogen uptake/release
  - lightweight with high capacity for hydrogen
  - rapid kinetic properties
  - equilibrium properties (P,T) consistent with near ambient conditions.
- Two solid state approaches
  - hydrogen absorption (bulk hydrogen)
  - hydrogen adsorption (surface hydrogen)
    including cage structures

Hydrides



Where do we start?

Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	------- VIII		-----	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac~ (227)													116 --- ()		118 --- ()

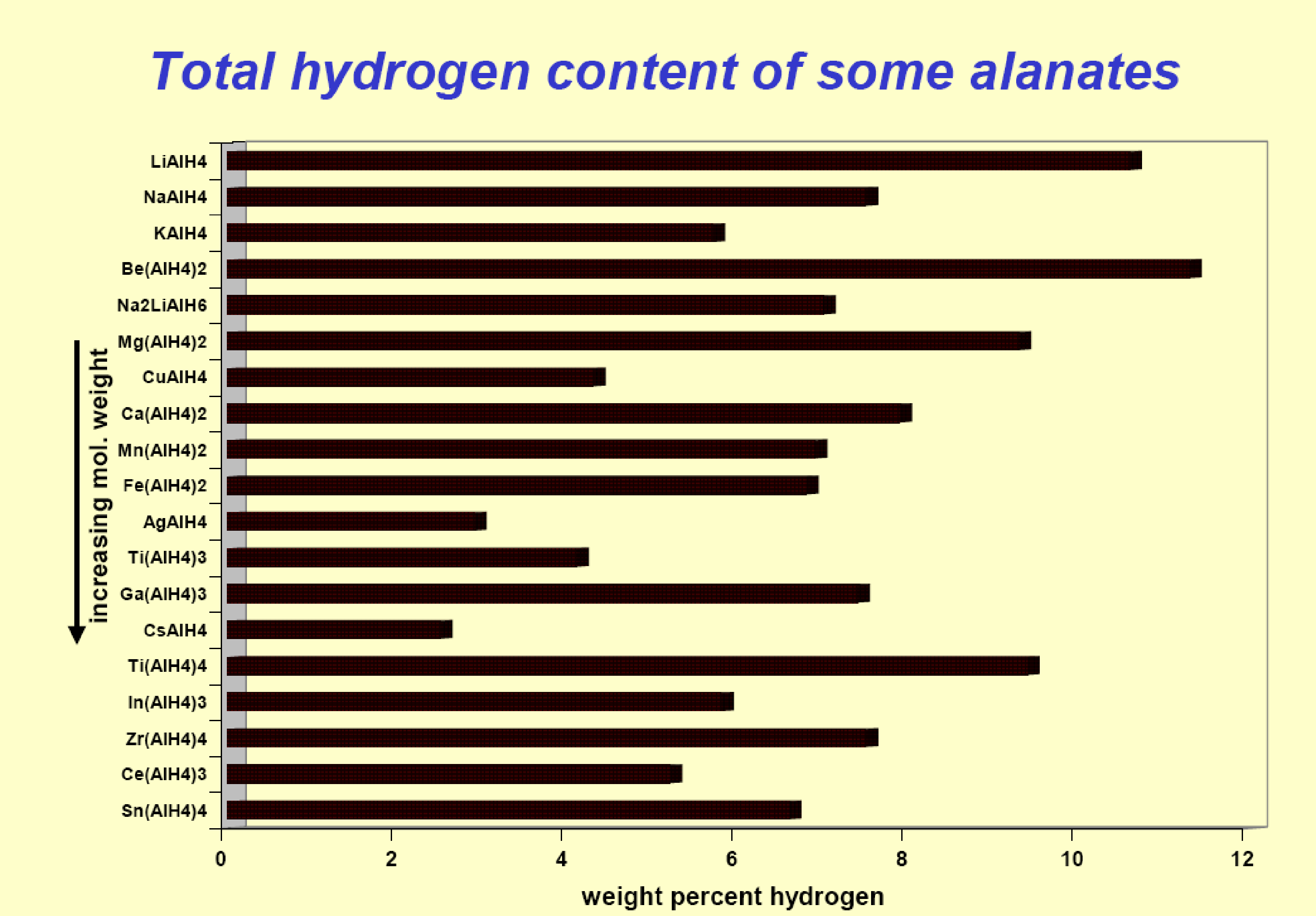
Lanthanide Series*	58 Ce 140.1													71 Lu 175.0
Actinide Series~	90 Th 232.0	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

The online data base

hydpark.ca.sandia.gov

lists over 2000 elements, compounds and alloys that form hydrides.

Alanates


Total hydrogen content of some alanates
LiAlH4
NaAlH4
KAlH4
Be(AlH4)2
Na2LiAlH6
Mg(AlH4)2
CuAlH4
Ca(AlH4)2
Mn(AlH4)2
Fe(AlH4)2
AgAlH4
Ti(AlH4)3
Ga(AlH4)3
CsAlH4
Ti(AlH4)4
In(AlH4)3
Zr(AlH4)4
Ce(AlH4)3
Sn(AlH4)4
increasing mol. weight
0
2
4
6
8
10
12
weight percent hydrogen

Complex Hydrides

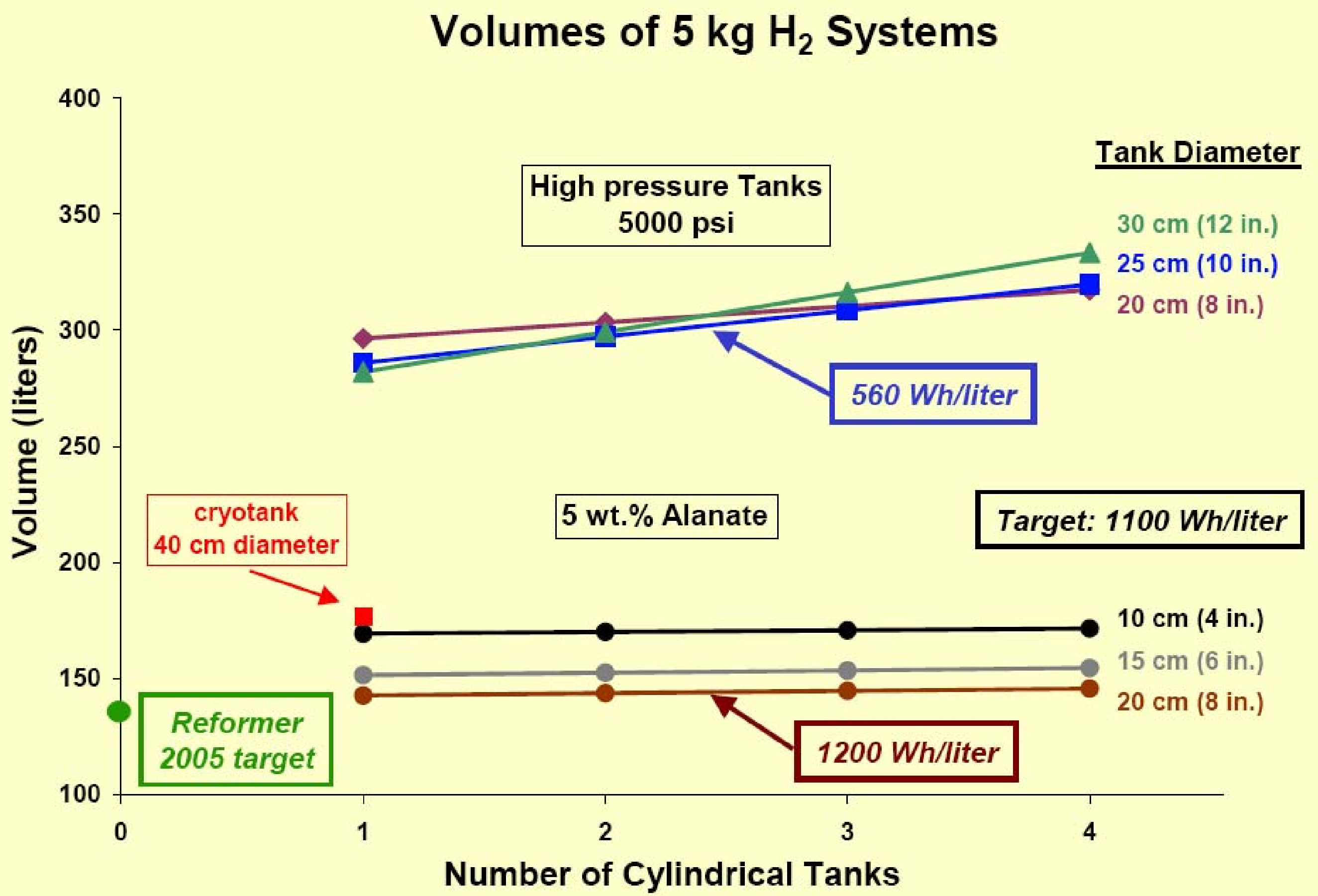
Issues with complex hydrides

- Reversibility
  - role of catalyst or dopant
- Thermodynamics
  - pressure, temperature
- Kinetics
  - long-range transport of heavy species
- Cyclic stability
- Synthesis
- Compatibility/safety

only $NaAlH_4$ has been studied in detail to date this material serves as a model system to better understand other complex hydrides

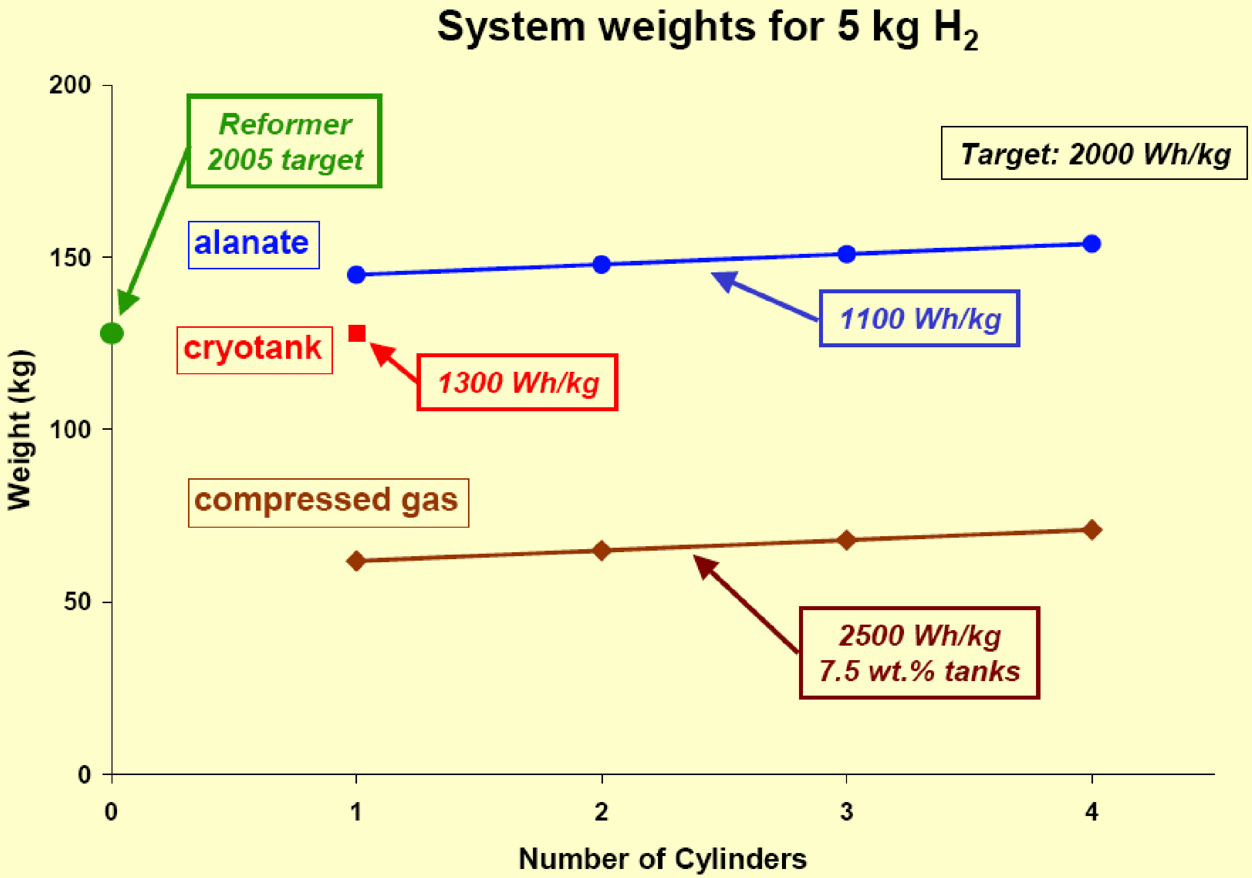
Hydrogen Storage Volume

5 kg H_2 system volumes



Hydrogen System Weight

5 kg H_2 system weights


System weights for 5 kg H_2

Future

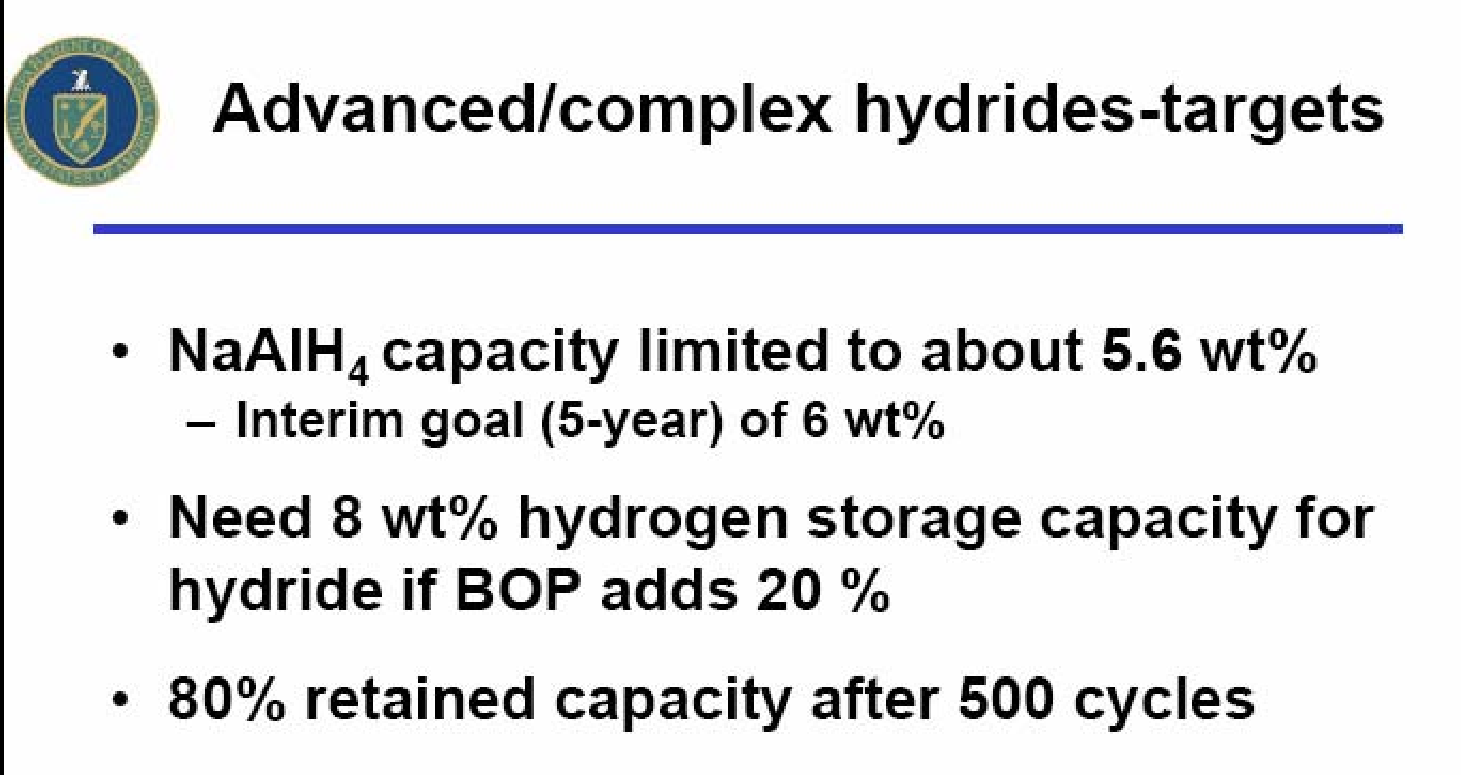
Where do we go from here?

- What’s beyond $NaAlH_4$?
  - Capacity appears limited to ~5 wt.%
  - modifications or new complexes needed.
- Some improvements in weight, volume and cost can be realized by better container engineering.

Intermetallic hydrides were studied for thirty years before doped alanates provided a significant improvement in capacity.

We need to be a little faster!

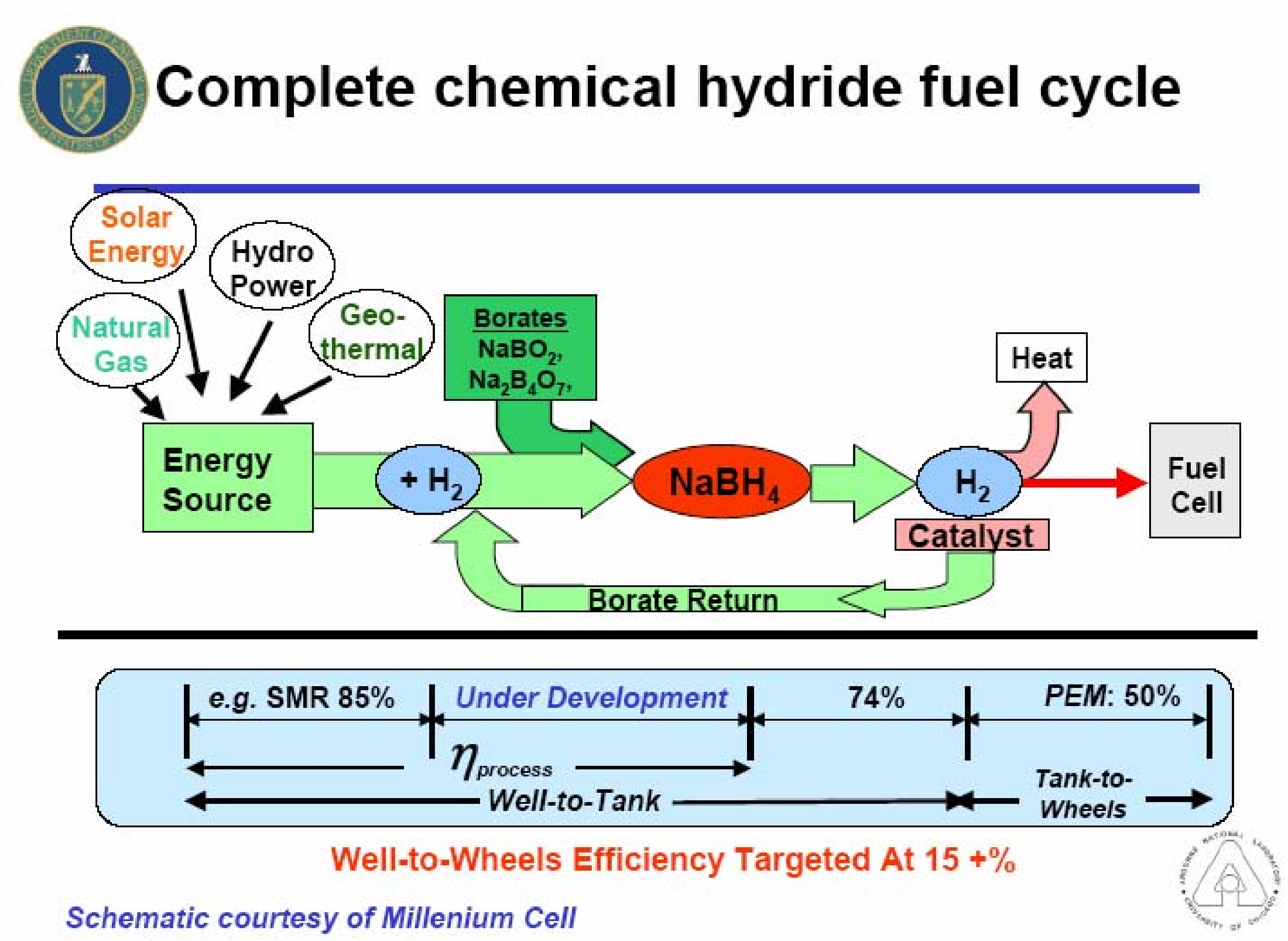
US DOE Strategy



Advanced/complex hydrides-targets

- $NaAlH_4$ capacity limited to about 5.6 wt%
  - Interim goal (5-year) of 6 wt%
- Need 8 wt% hydrogen storage capacity for hydride if BOP adds 20 %
- 80% retained capacity after 500 cycles

US DOE Strategy

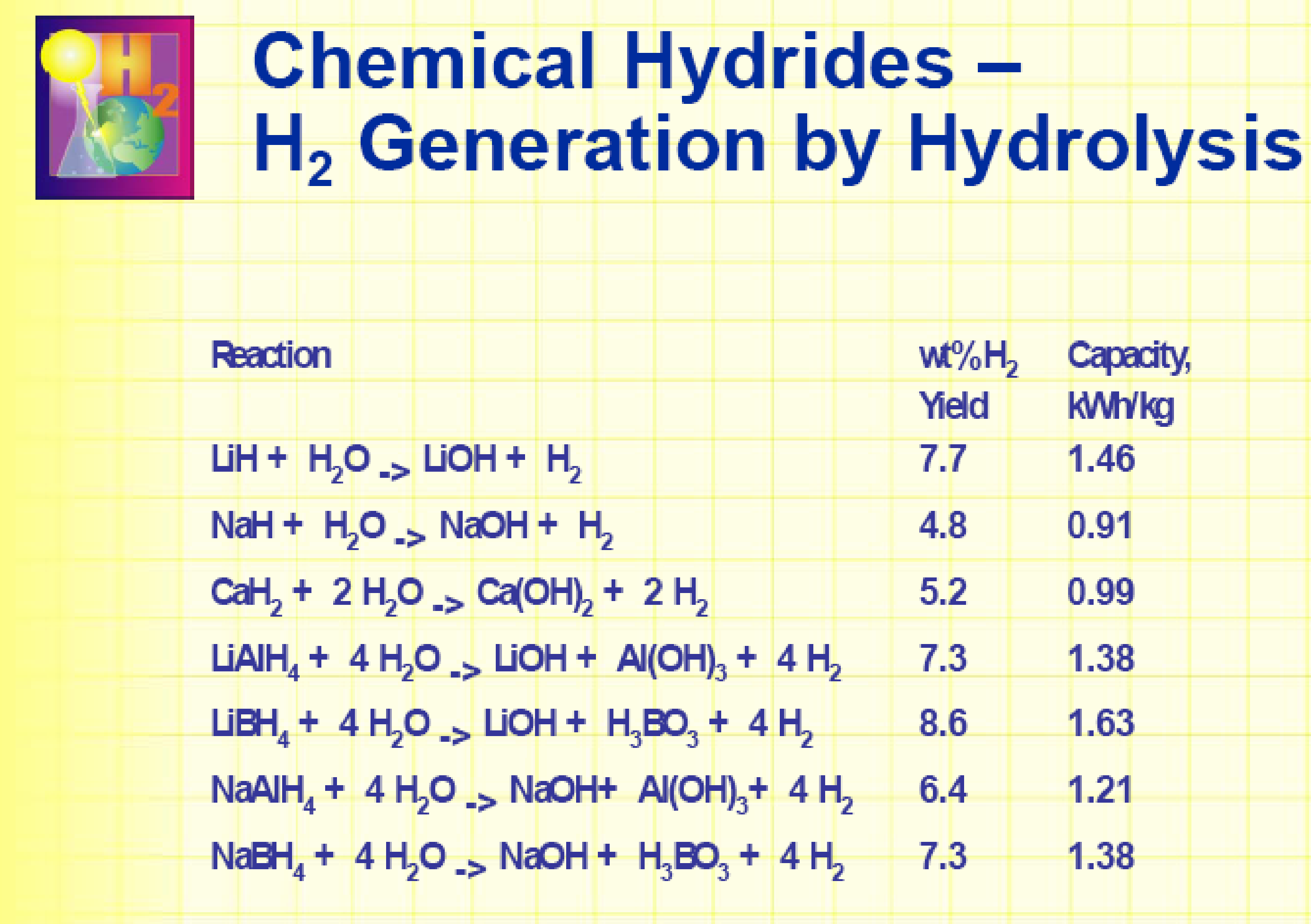


Complete chemical hydride fuel cycle

Well-to-Wheels Efficiency Targeted At 15 +%

Schematic courtesy of Millenium Cell

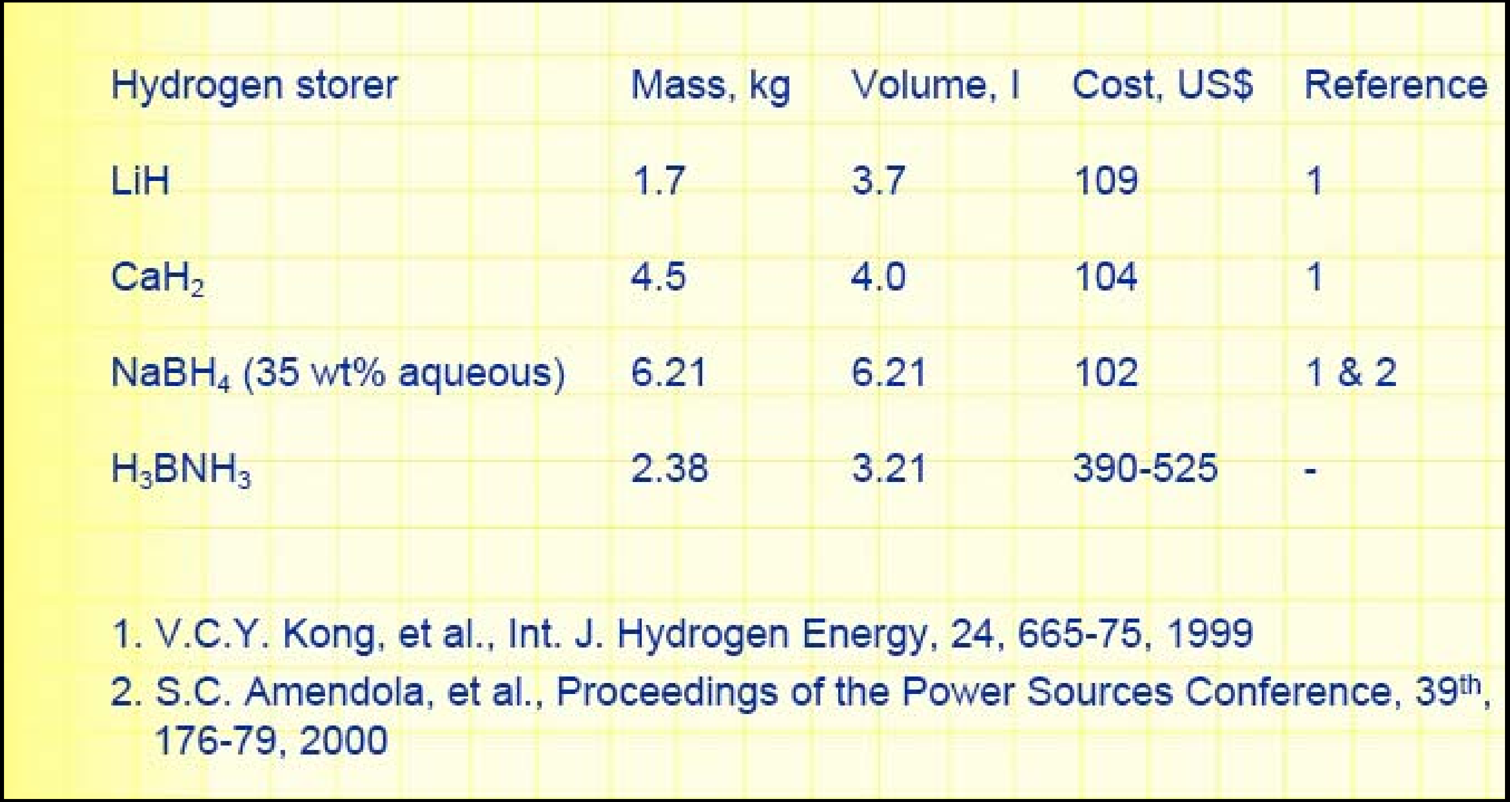
Complex Hydrides



Chemical Hydrides – H_2 Generation by Hydrolysis

Reaction	wt% H_2 Yield	Capacity, kWh/kg
$LiH + H_2O \rightarrow LiOH + H_2$	7.7	1.46
$NaH + H_2O \rightarrow NaOH + H_2$	4.8	0.91
$CaH_2 + 2\,H_2O \rightarrow Ca(OH)_2 + 2\,H_2$	5.2	0.99
$LiAlH_4 + 4\,H_2O \rightarrow LiOH + Al(OH)_3 + 4\,H_2$	7.3	1.38
$LiBH_4 + 4\,H_2O \rightarrow LiOH + H_3BO_3 + 4\,H_2$	8.6	1.63
$NaAlH_4 + 4\,H_2O \rightarrow NaOH + Al(OH)_3 + 4\,H_2$	6.4	1.21
$NaBH_4 + 4\,H_2O \rightarrow NaOH + H_3BO_3 + 4\,H_2$	7.3	1.38

Complex Hydrides

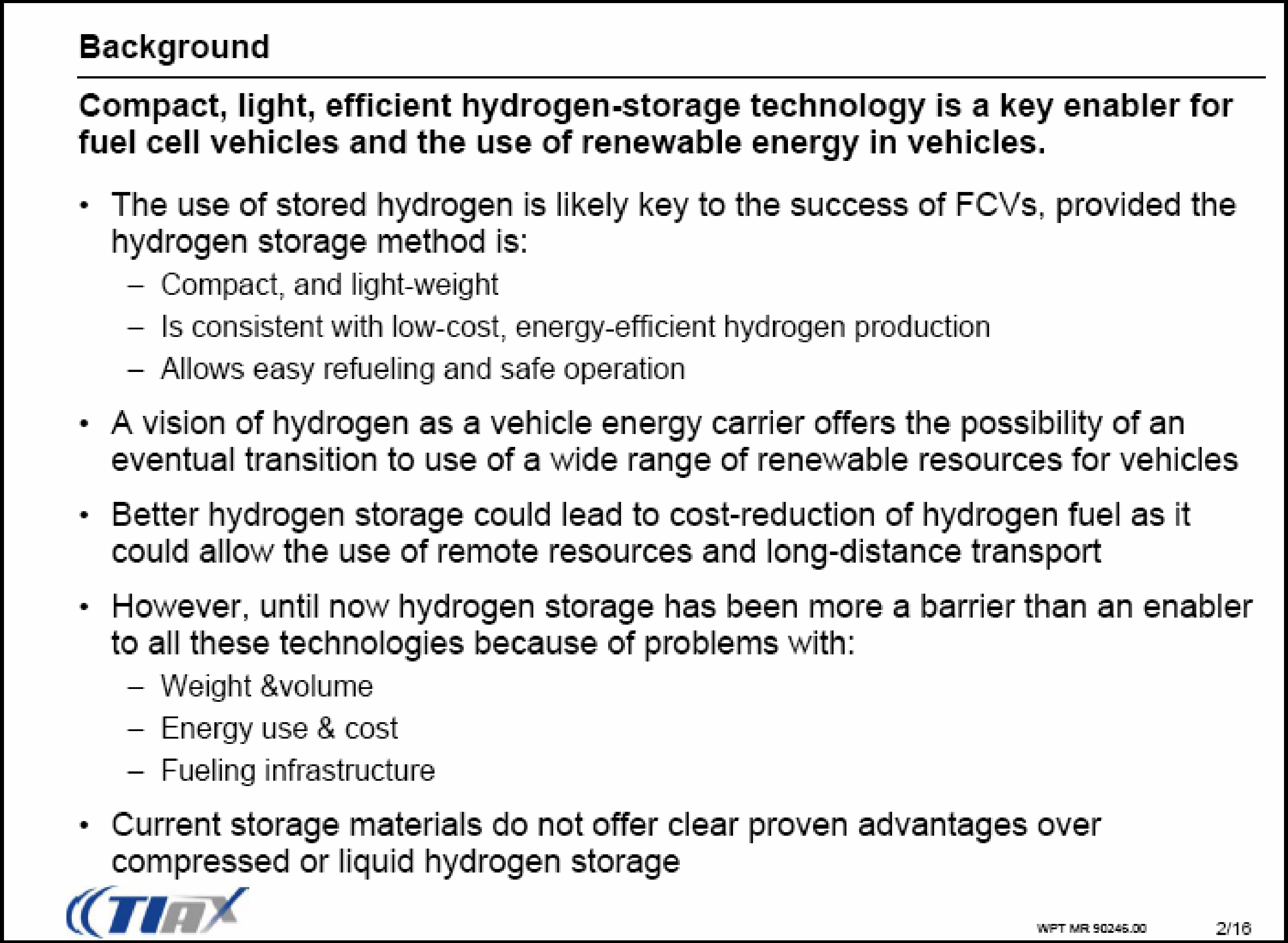


Hydrogen storer	Mass, kg	Volume, l	Cost, US$	Reference
LiH	1.7	3.7	109	1
CaH_2	4.5	4.0	104	1
$NaBH_4$ (35 wt% aqueous)	6.21	6.21	102	1 & 2
H_3BNH_3	2.38	3.21	390-525	-

1. V.C.Y. Kong, et al., Int. J. Hydrogen Energy, 24, 665-75, 1999
2. S.C. Amendola, et al., Proceedings of the Power Sources Conference, 39th, 176-79, 2000

Source: Ali T. Raissi, FSEC

Fuel Tank Problem

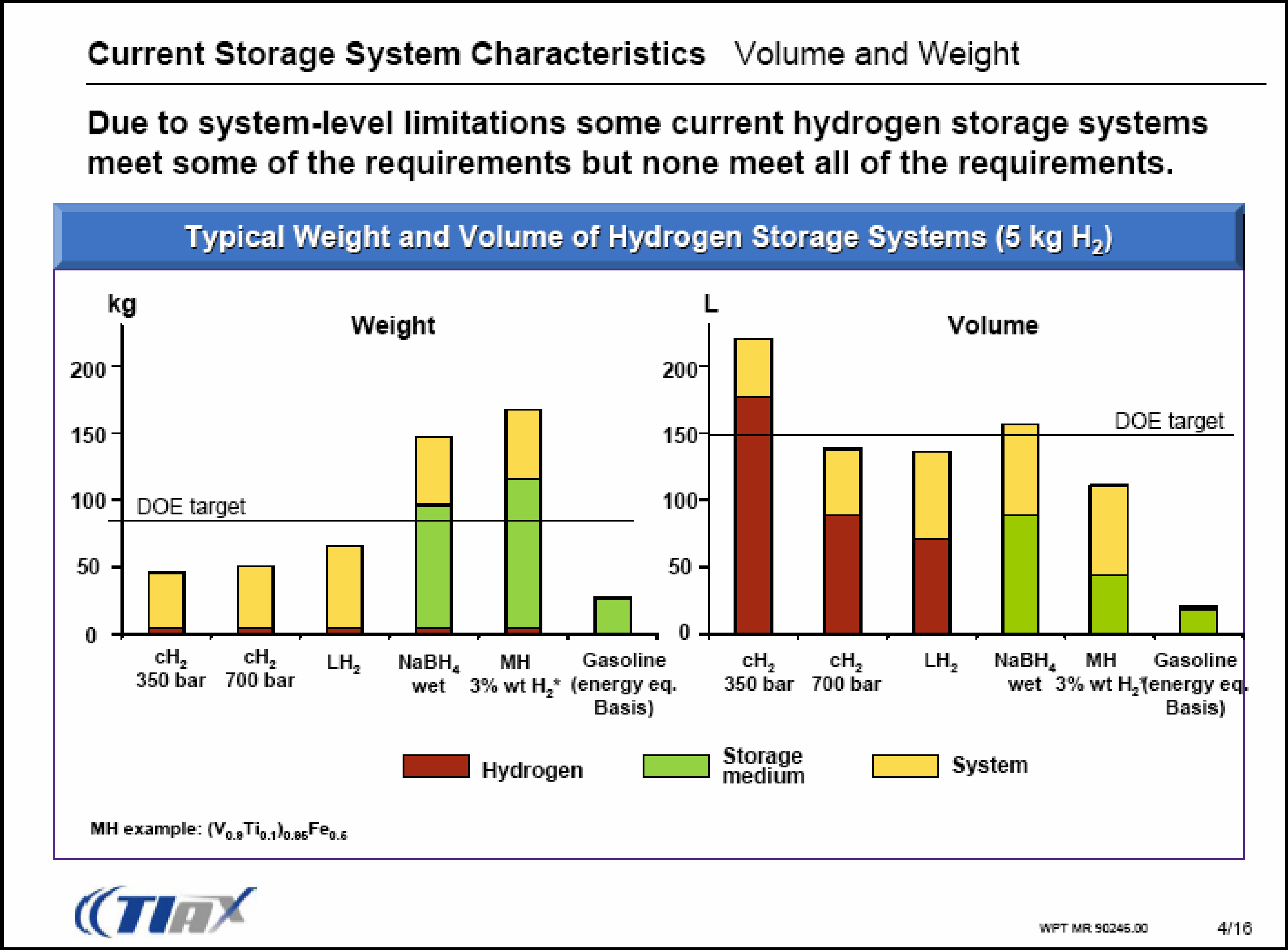


Background

Compact, light, efficient hydrogen-storage technology is a key enabler for fuel cell vehicles and the use of renewable energy in vehicles.

- The use of stored hydrogen is likely key to the success of FCVs, provided the hydrogen storage method is:
  - Compact, and light-weight
  - Is consistent with low-cost, energy-efficient hydrogen production
  - Allows easy refueling and safe operation
- A vision of hydrogen as a vehicle energy carrier offers the possibility of an eventual transition to use of a wide range of renewable resources for vehicles
- Better hydrogen storage could lead to cost-reduction of hydrogen fuel as it could allow the use of remote resources and long-distance transport
- However, until now hydrogen storage has been more a barrier than an enabler to all these technologies because of problems with:
  - Weight &volume
  - Energy use & cost
  - Fueling infrastructure
- Current storage materials do not offer clear proven advantages over compressed or liquid hydrogen storage

Current Status



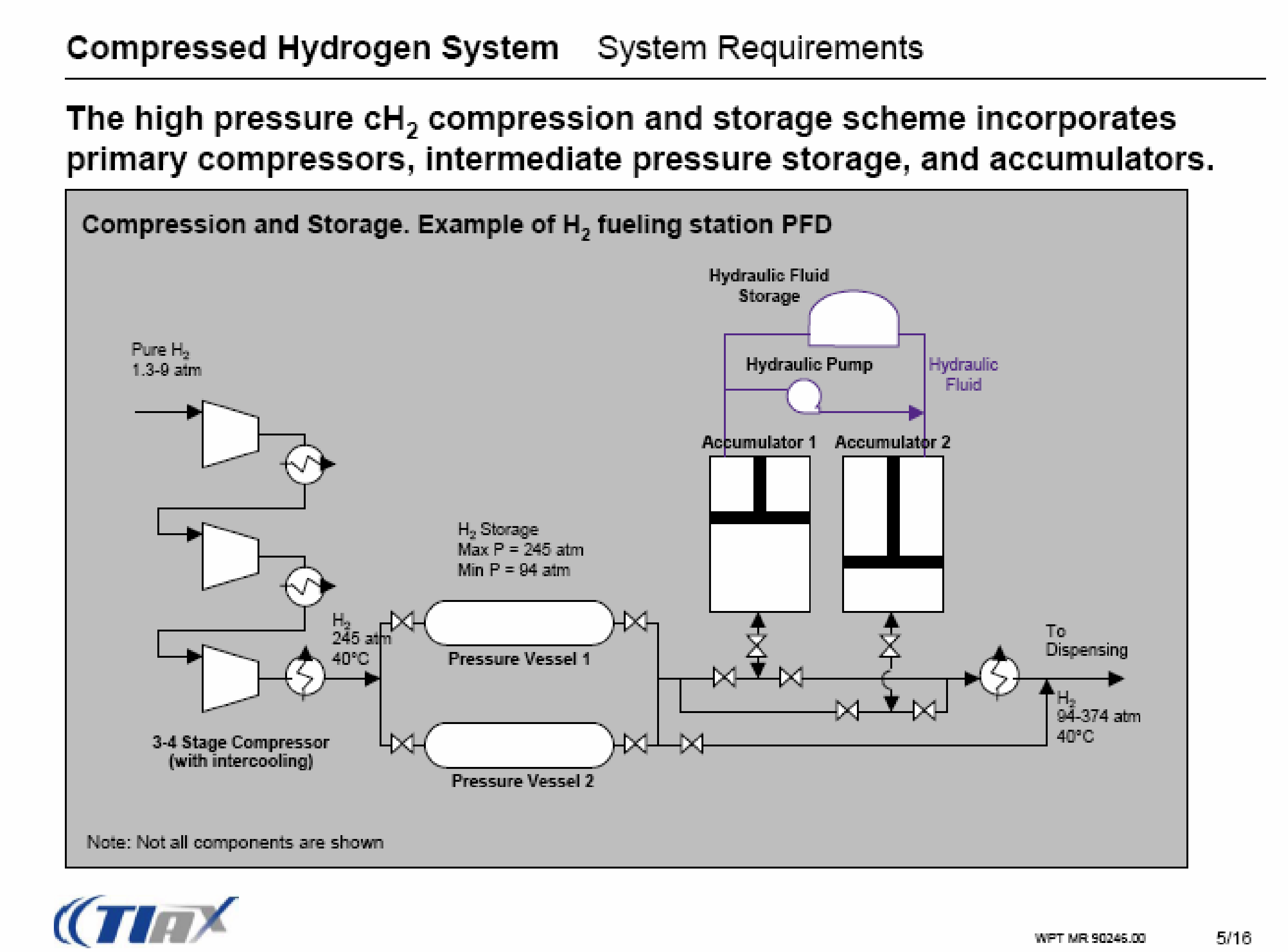
Current Storage System Characteristics Volume and Weight

Due to system-level limitations some current hydrogen storage systems meet some of the requirements but none meet all of the requirements.

Typical Weight and Volume of Hydrogen Storage Systems (5 kg H_2)

MH example: $(V_{0.9}Ti_{0.1})_{0.95}Fe_{0.5}$

Compressed Gas System Requirements



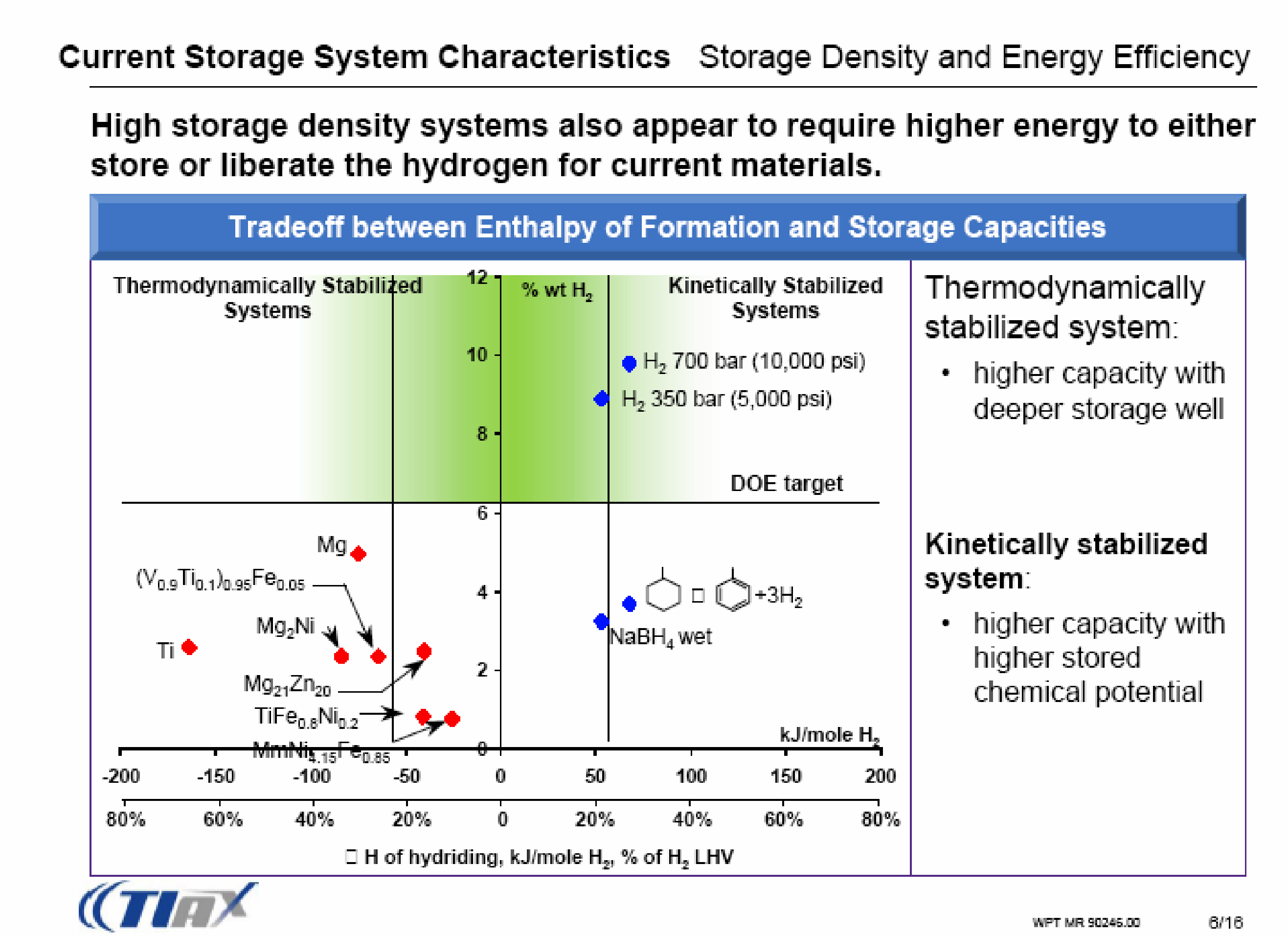
Compressed Hydrogen System System Requirements

The high pressure cH_2 compression and storage scheme incorporates primary compressors, intermediate pressure storage, and accumulators.

Compression and Storage. Example of H_2 fueling station PFD

Note: Not all components are shown

Storage System Requirements



Current Storage System Characteristics Storage Density and Energy Efficiency

High storage density systems also appear to require higher energy to either store or liberate the hydrogen for current materials.

Tradeoff between Enthalpy of Formation and Storage Capacities

Thermodynamically stabilized system:

- higher capacity with deeper storage well

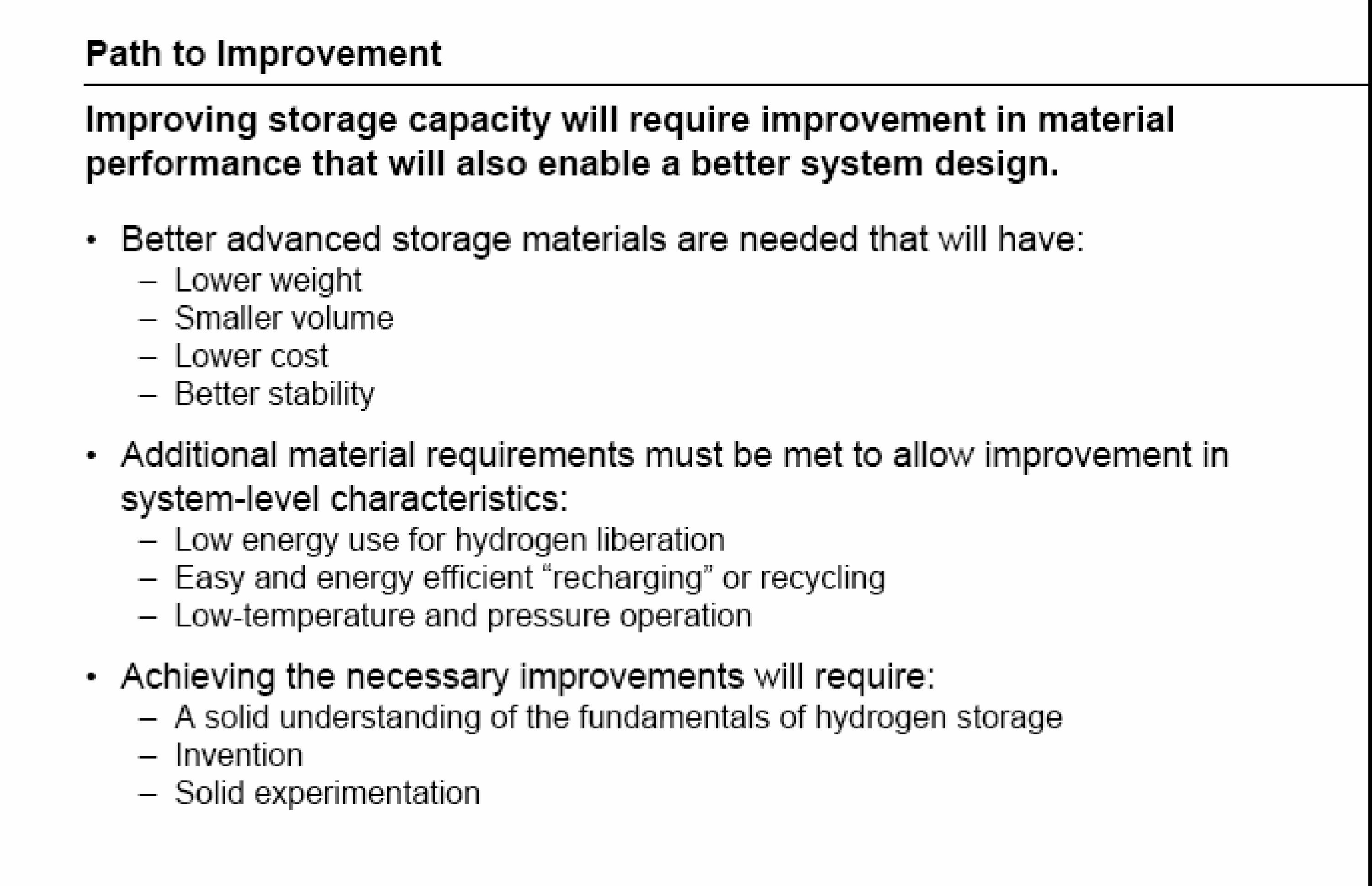
Kinetically stabilized system:

- higher capacity with higher stored chemical potential

TIAX

WPT MR 90245.00 6/16

Improvements

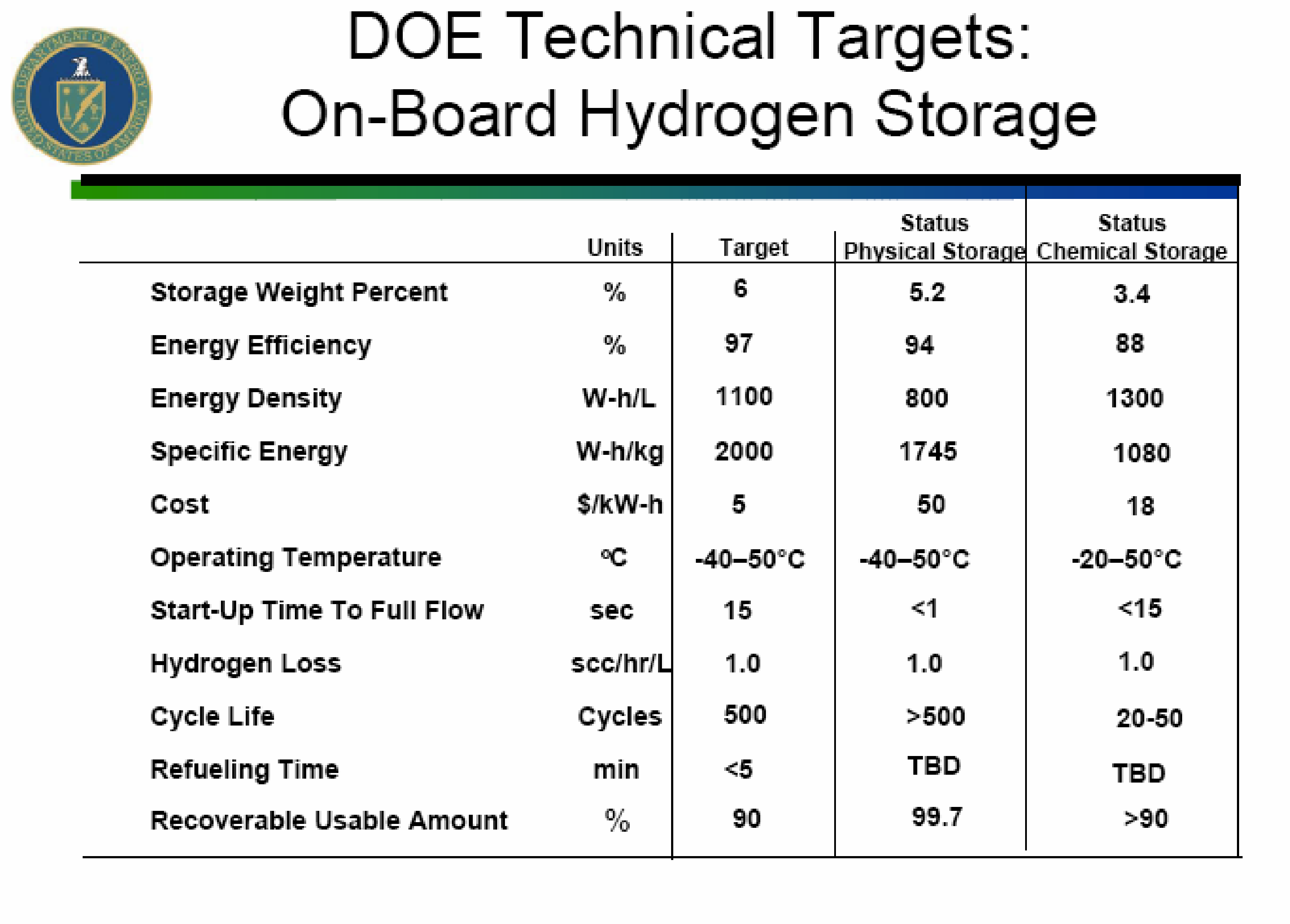


Path to Improvement

Improving storage capacity will require improvement in material performance that will also enable a better system design.

- Better advanced storage materials are needed that will have:
  - Lower weight
  - Smaller volume
  - Lower cost
  - Better stability
- Additional material requirements must be met to allow improvement in system-level characteristics:
  - Low energy use for hydrogen liberation
  - Easy and energy efficient “recharging” or recycling
  - Low-temperature and pressure operation
- Achieving the necessary improvements will require:
  - A solid understanding of the fundamentals of hydrogen storage
  - Invention
  - Solid experimentation

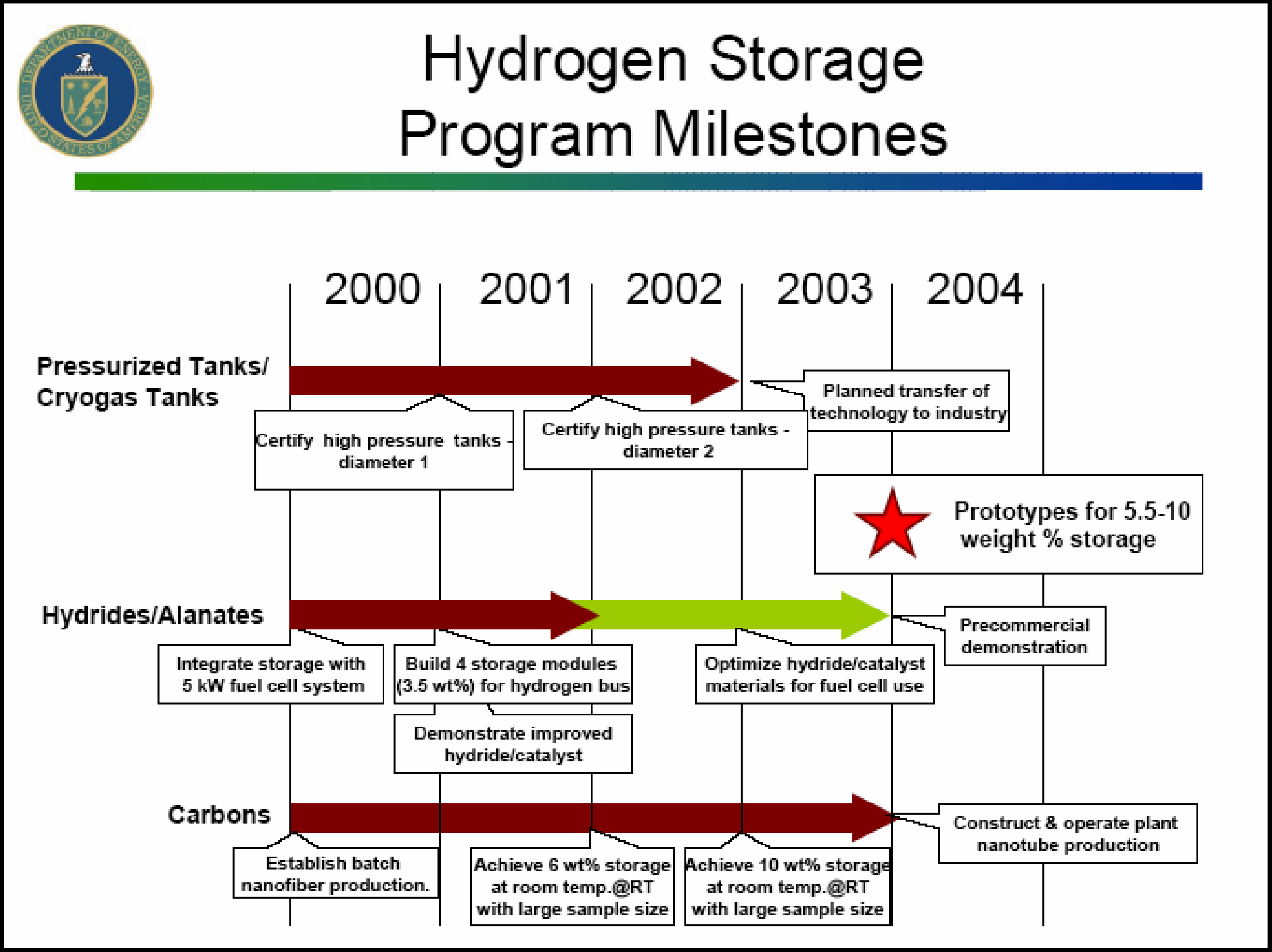
US DOE Targets



DOE Technical Targets: On-Board Hydrogen Storage

	Units	Target	Status Physical Storage	Status Chemical Storage
Storage Weight Percent	%	6	5.2	3.4
Energy Efficiency	%	97	94	88
Energy Density	W-h/L	1100	800	1300
Specific Energy	W-h/kg	2000	1745	1080
Cost	$/kW-h	5	50	18
Operating Temperature	°C	-40–50°C	-40–50°C	-20–50°C
Start-Up Time To Full Flow	sec	15	<1	<15
Hydrogen Loss	scc/hr/L	1.0	1.0	1.0
Cycle Life	Cycles	500	>500	20-50
Refueling Time	min	<5	TBD	TBD
Recoverable Usable Amount	%	90	99.7	>90

US DOE Strategy



Hydrogen Storage Program Milestones

2000 2001 2002 2003 2004

Pressurized Tanks/ Cryogas Tanks

- Certify high pressure tanks - diameter 1
- Certify high pressure tanks - diameter 2
- Planned transfer of technology to industry

★ Prototypes for 5.5-10 weight % storage

Hydrides/Alanates

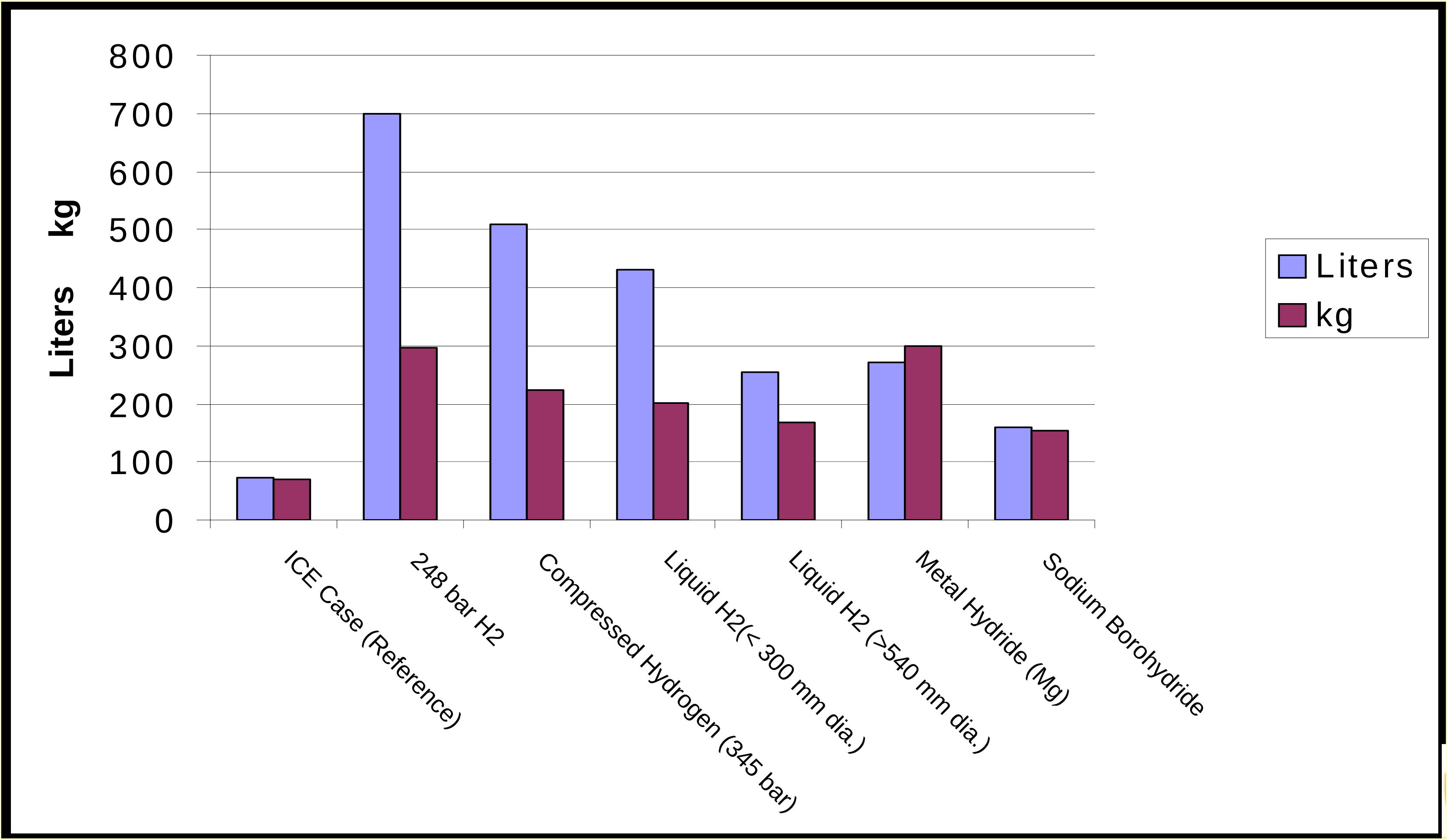
- Integrate storage with 5 kW fuel cell system
- Build 4 storage modules (3.5 wt%) for hydrogen bus
- Demonstrate improved hydride/catalyst
- Optimize hydride/catalyst materials for fuel cell use
- Precommercial demonstration

Carbons

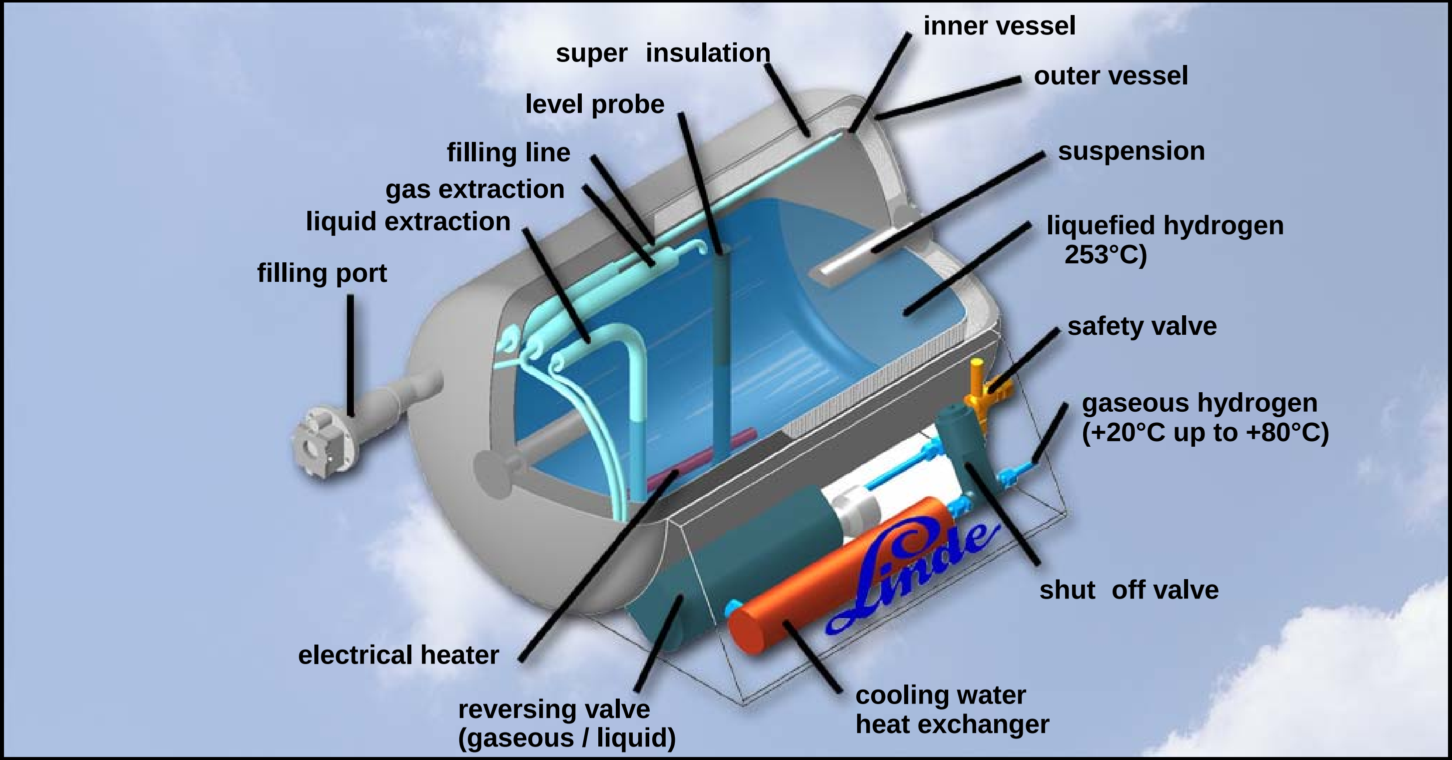
- Establish batch nanofiber production.
- Achieve 6 wt% storage at room temp.@RT with large sample size
- Achieve 10 wt% storage at room temp.@RT with large sample size
- Construct & operate plant nanotube production

FCEV Storage System

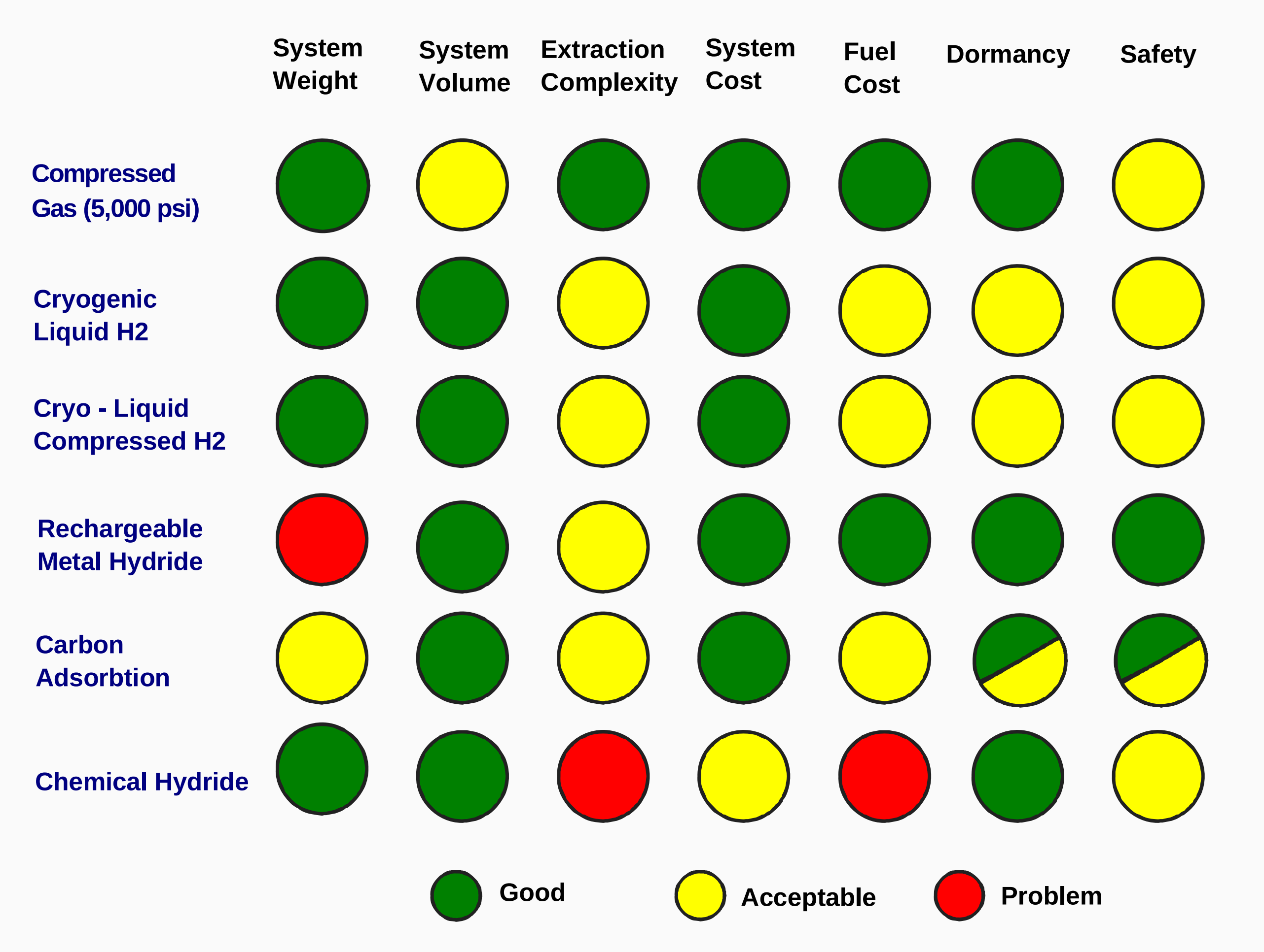
Comparative Volumes and Weights of a FCEV Hydrogen Storage System (Capable of 560 km (350 mi) Range – Compact Sedan)



LH2 Tank Configuration



Storage Systems



	System Weight	System Volume	Extraction Complexity	System Cost	Fuel Cost	Dormancy	Safety
Compressed Gas (5,000 psi)	🟢	🟡	🟢	🟢	🟢	🟢	🟡
Cryogenic Liquid H2	🟢	🟢	🟡	🟢	🟡	🟡	🟡
Cryo - Liquid Compressed H2	🟢	🟢	🟡	🟢	🟡	🟡	🟡
Rechargeable Metal Hydride	🔴	🟢	🟡	🟢	🟢	🟢	🟢
Carbon Adsorbtion	🟡	🟢	🟡	🟢	🟡	🟢/🟡	🟢/🟡
Chemical Hydride	🟢	🟢	🔴	🟡	🔴	🟢	🟡

🟢 Good 🟡 Acceptable 🔴 Problem