Hydrogen Storage - Overview

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*** Most of this presentation has been extracted from George Thomas' invited BES Hydrogen Workshop presentation (May 13-14, 2003)**

H_2 storage is a critical enabling technology for H_2 use as an energy carrier

- The low volumetric density of gaseous fuels requires a storage method which compacts the fuel.
- Hence, hydrogen storage systems are inherently more complex than liquid fuels.
- Storage technologies are needed in all aspects of hydrogen utilization.
  - production
  - distribution
  - utilization

How do we achieve safe, efficient and cost-effective hydrogen storage?

Hydrogen storage development offers many scientific and technical challenges

- Fundamental studies are needed to explore new storage concepts
- There is intense interest in new storage concepts by industry
  - research is closely coupled to applied and developmental areas
- Research areas include:
  - materials science
  - chemical sciences
  - advanced analytical techniques
  - fundamental modeling and simulation

 From George Thomas, BES workshop 5/13/03

Outline

- Storage properties needed in different applications
- Energy densities available from fuels
- Current options for storing hydrogen
  - *gas*
  - *liquid*
  - *solid*

  } *reversible*
  - *chemical hydride systems (non-reversible)*

Where do we go from here?

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Different applications have different hydrogen storage requirements

- **Onboard storage (vehicles)**
  - **FreedomCAR targets based on market needs**
- **Forecourt storage (refueling stations)**
  - **requirements being developed (IHIG)**
- **Distribution storage (delivery trucks)**
  - **high capacity, compact**
- **Production storage (onsite)**
  - **very large quantities**

- **These are also interrelated**

e.g., onsite liquefaction → LH_2 delivery → LH_2 forecourt → LH_2 onboard

Example forecourt requirements

➪ Total hydrogen	<50 te
➪ System volume	<20 m^3/te
➪ Temperature range	-40/60° C
➪ Delivery flow rate	>1 kg/min
➪ Response time (0-90%)	30 sec
➪ Hydrogen purity	99.9
➪ Cycle life (fills)	10,000
➪ Calendar life	15 years
➪ Cost	tbd (US$/te H_2)
➪ Permeation loss	<1 scc/hr/l

Note that there is no weight requirement!

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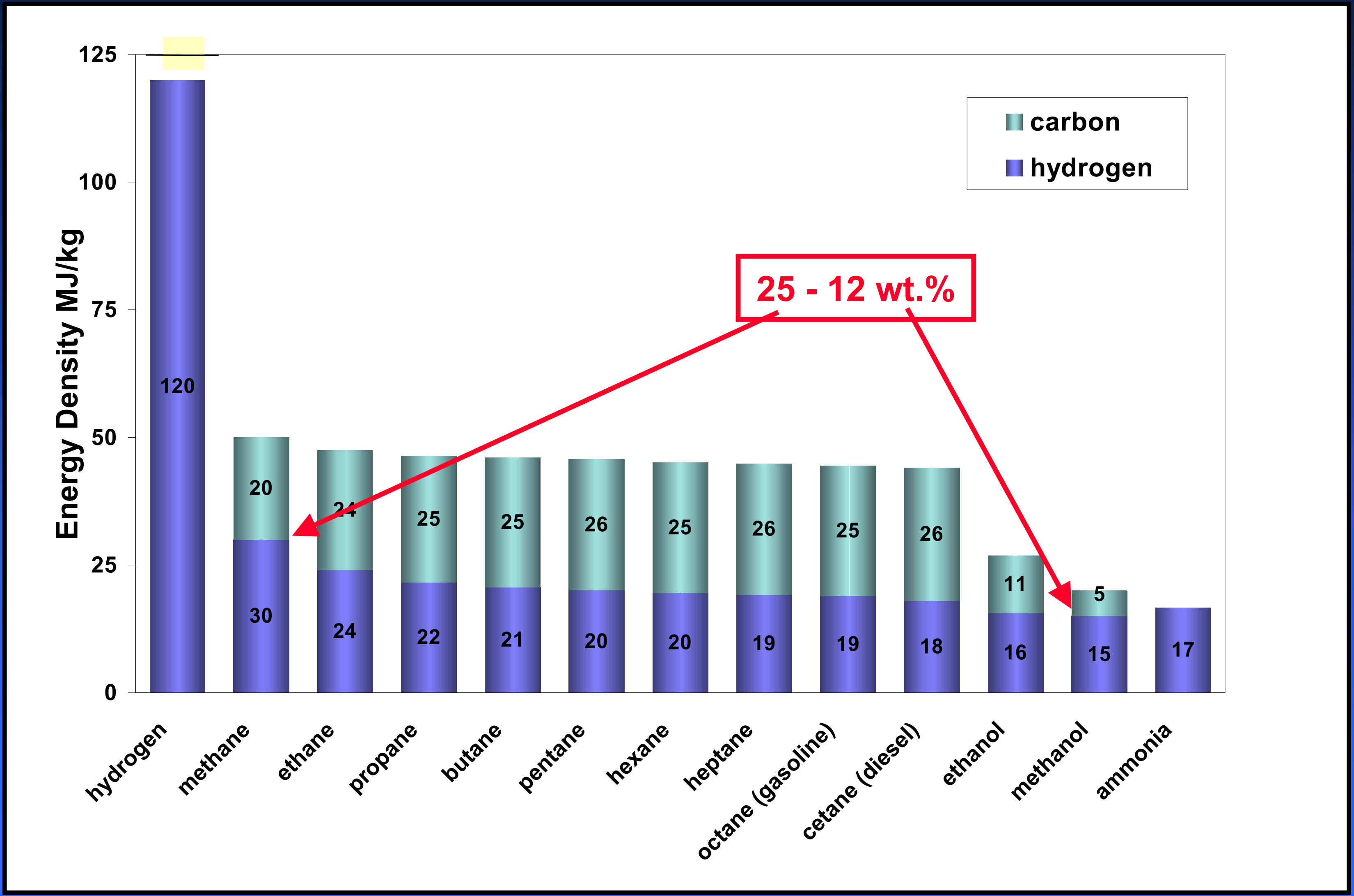
Outline

- ⇨ Storage properties needed in different applications
- ⇨ Energy densities available from fuels
- ⇨ Current options for storing hydrogen
  - gas
  - liquid
  - solid
  - chemical hydride systems (non-reversible)

  (gas, liquid, solid: *reversible*)
- ⇨ Where do we go from here?

Specific energy of fuels (LHV)



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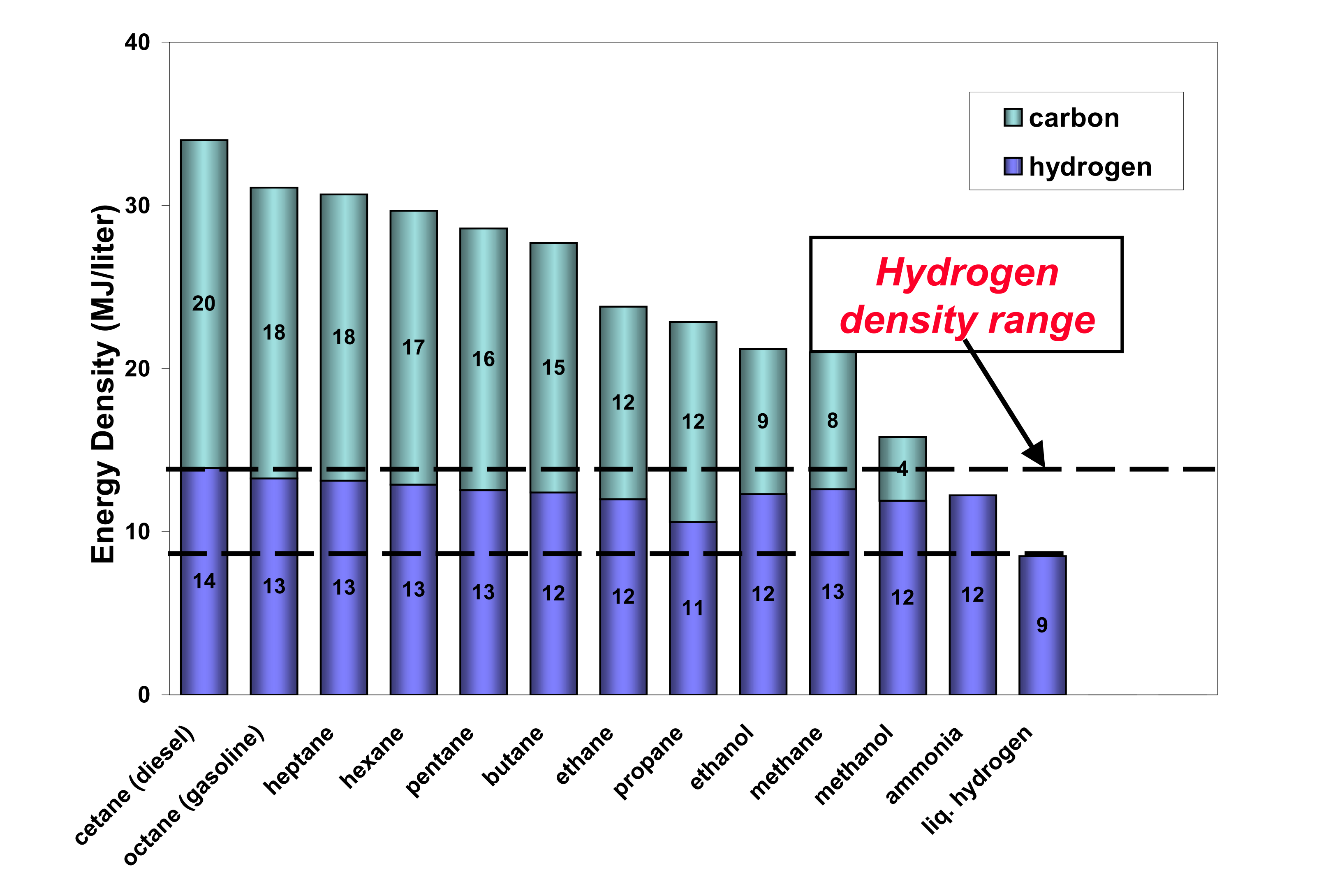
Energy densities (LHV) for fuels in liquid state



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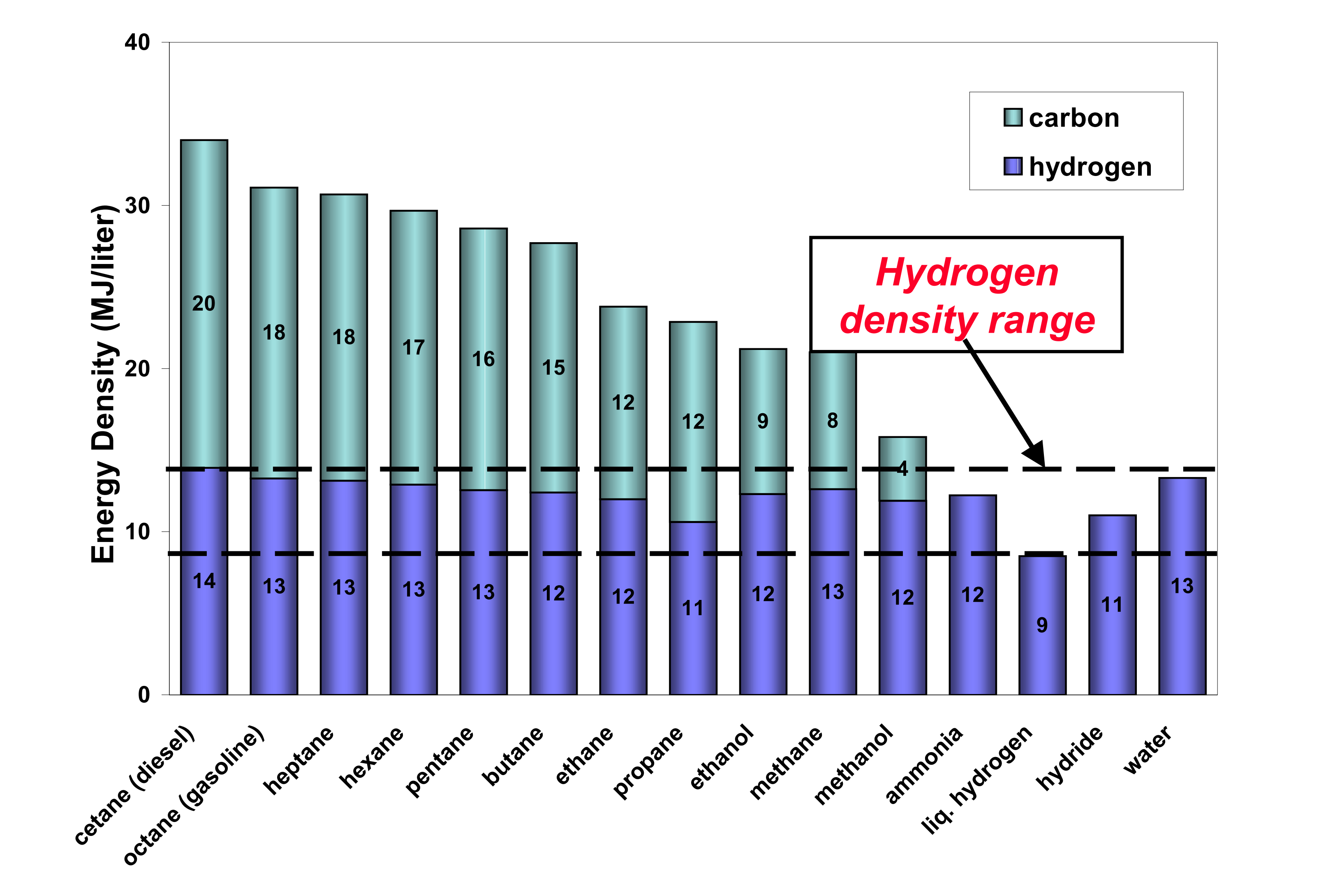

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Outline

- ⇨ Storage properties needed in different applications
- ⇨ Energy densities available from fuels
- ⇨ **Current options for storing hydrogen**
    - *gas*
    - *liquid*
    - *solid*

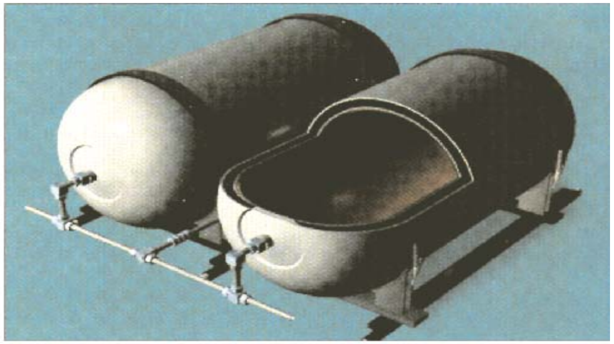
    } *reversible*

    - *chemical hydride systems (non-reversible)*
- ⇨ Where do we go from here?

Reversible Hydrogen Storage Systems

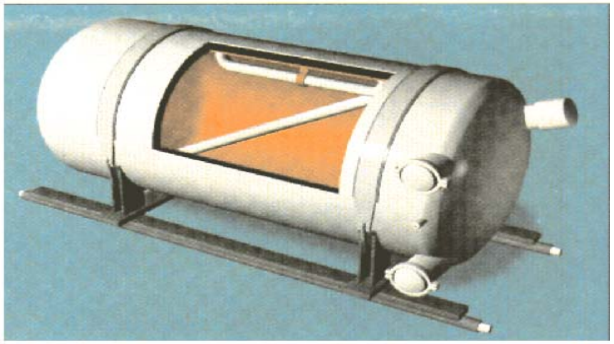
- Pressurized Hydrogen Gas
  - safety (high pressure)
  - volume
  - weight

120 Kg
250 liters
300 bar
25 °C
~200 kWh



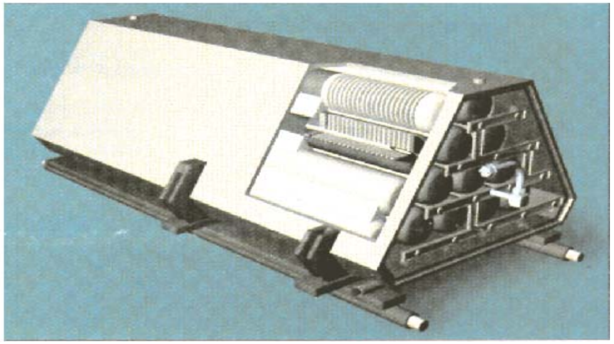
- Cryogenic Liquid Hydrogen
  - safety (low temperature)
  - evaporation losses
  - difficult handling

20 Kg
140 liters
4 bar
-253 °C
~300 kWh



- Metal Hydride - Hydrogen Gas
  - weight
  - cost
  - heat transfer

320 Kg*
170 liters
50 bar
25 °C
105 kWh



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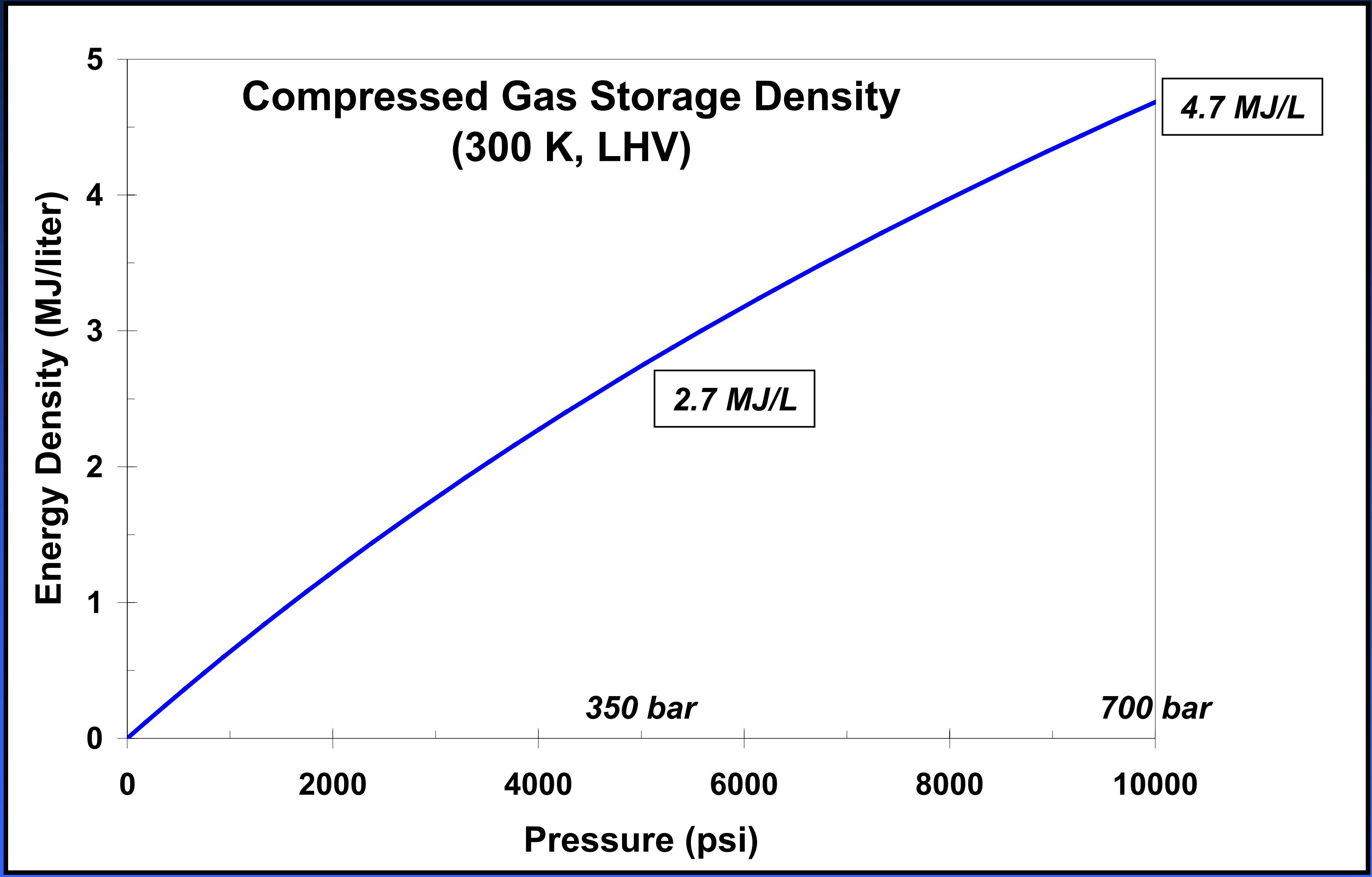
Compressed gas offers a straightforward H_2 storage method



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Composite tanks are robust and lightweight

- 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

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Liquid hydrogen storage requires cryogenic systems

- Equilibrium temperature at 1 bar for liquid hydrogen is ~20 K.

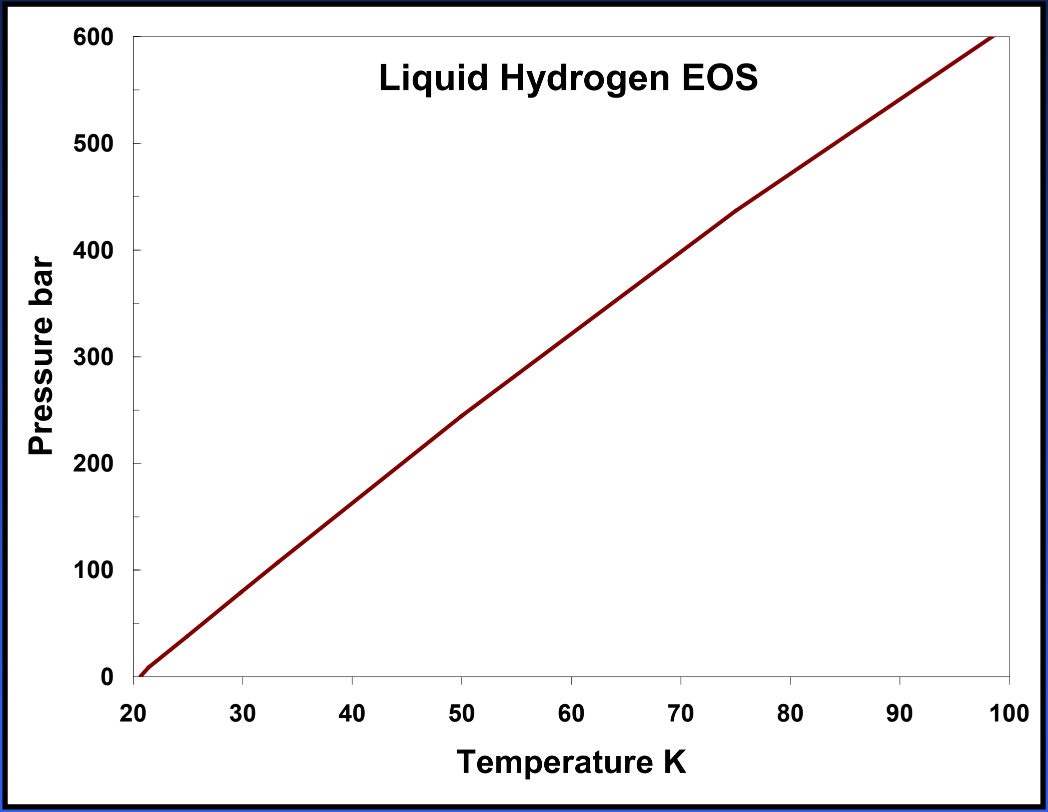
- Estimated storage densities[1]

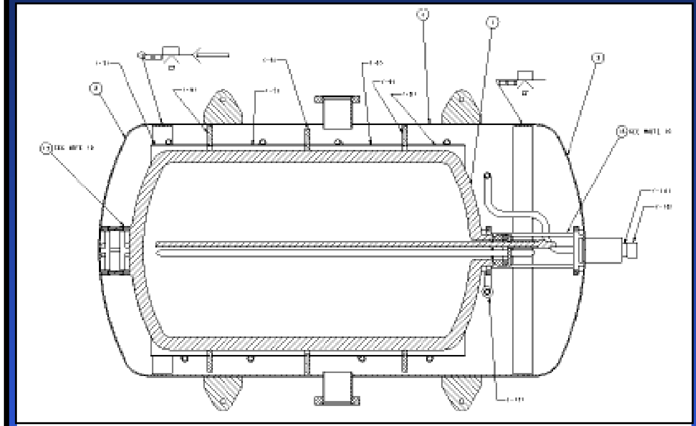
Berry (1998)	4.4 MJ/liter
Dillon (1997)	4.2 MJ/liter
Klos (1998)	5.6 MJ/liter

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

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

High pressure cryogenic tank can reduce temperature requirements





S. Aceves, et al 2002

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

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Another option is to 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

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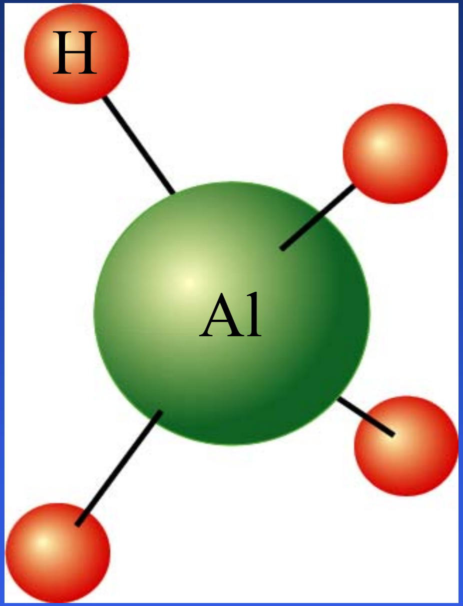
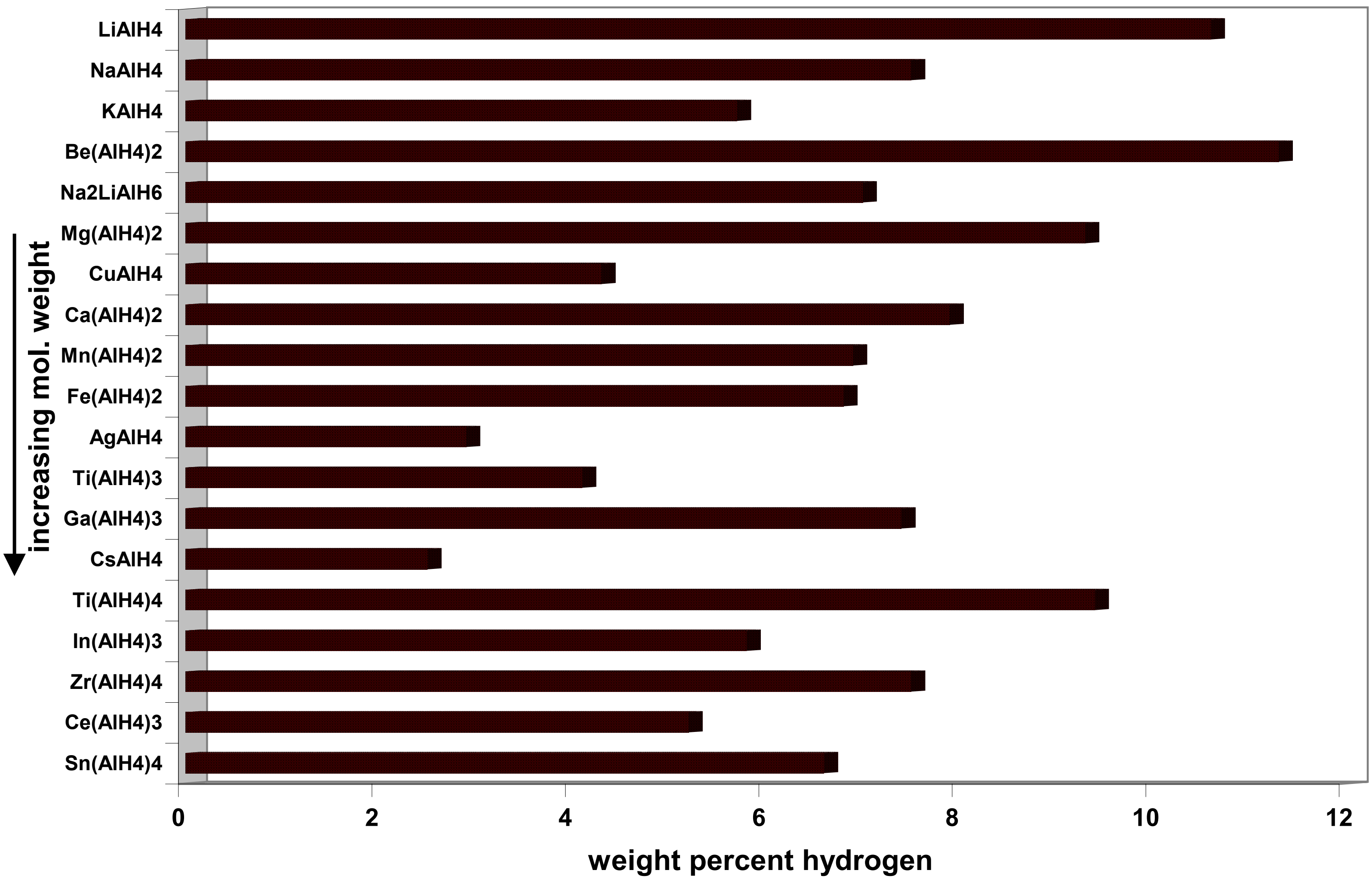
Renewed interest in complex hydrides

- Complex hydrides consist of a H=M complex with additional bonding element(s)
- Reversibility demonstrated in $NaAlH_4$
  By Bogdanovic and Schwickardi (1996)
- Hydrogen complexes include
  - $(AlH_4)^-$ (alanates)
  - $(BH_4)^-$ H with Group VIII elements
- Advantages:
  - Can have lower formation energy
  - Can have high H/M.



173 complex hydrides listed on *hydpark.ca.sandia.gov*

Total hydrogen content of some alanates



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Issues with complex hydrides

- Reversibility
  - Role of catalyst or dopant.
- Thermodynamics
  - Pressure, temperature.
- Kinetics
  - Long-range transport of heavy species
- Capacity

Only $NaAlH_4$ has been studied in detail to date.

- theoretical reversible capacity 5.5 wt.%

- ~ 4-4.5 wt.% demonstrated

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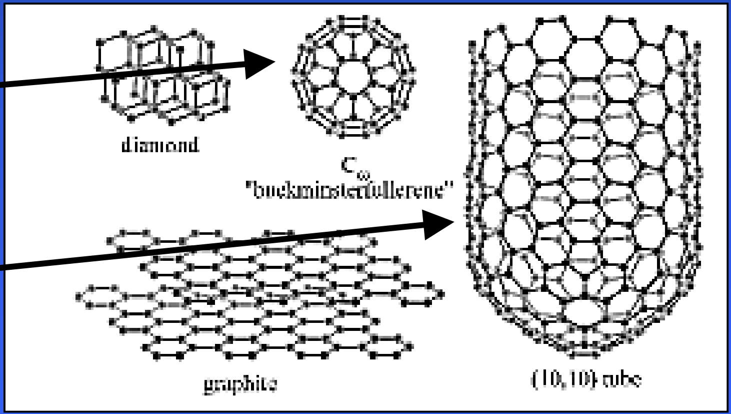
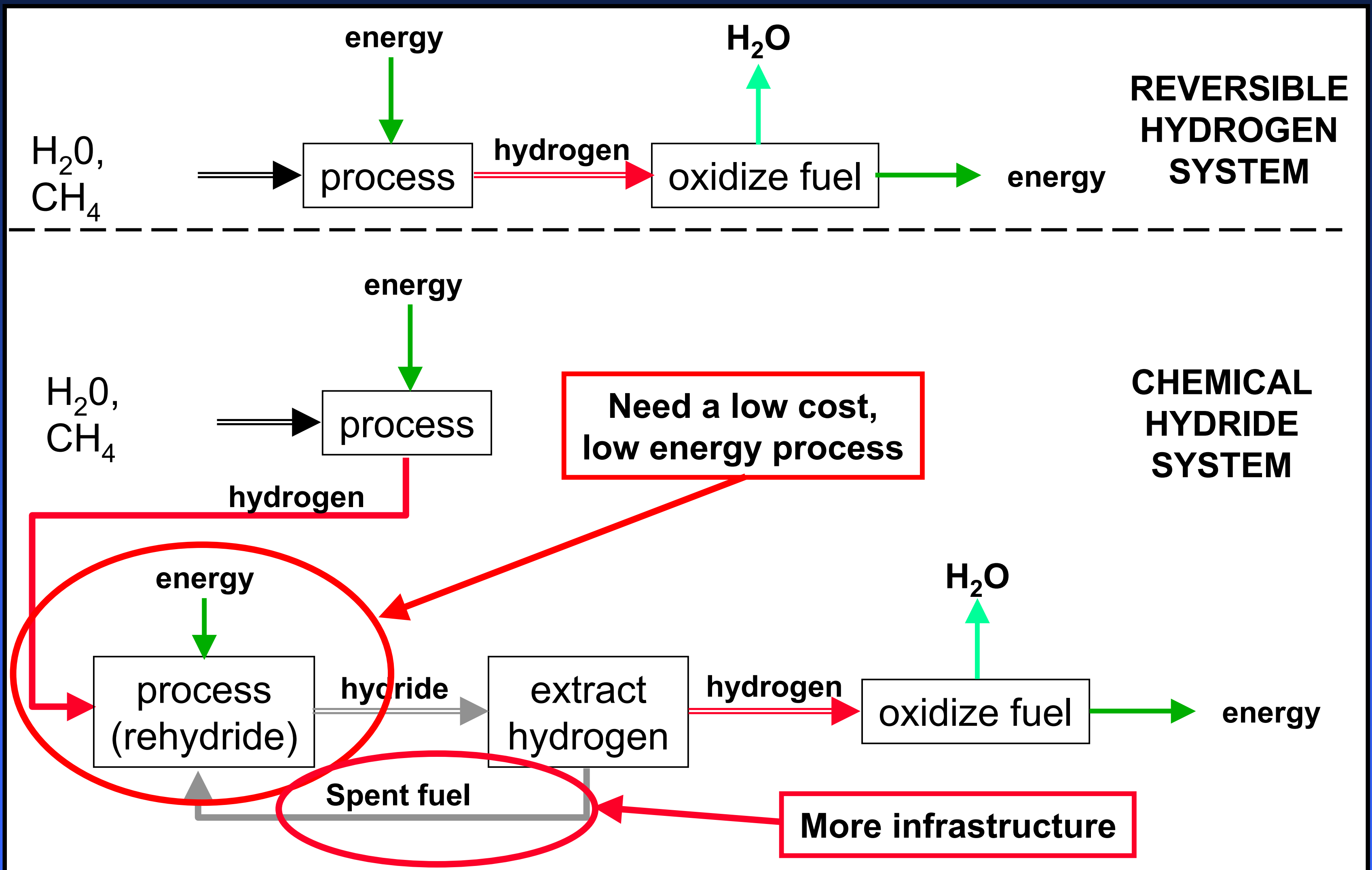
Carbon materials offer an alternative approach to high density storage

- **Hydrogen adsorbs on carbon surfaces.**
  - **liquid hydrogen density on surface.**
  - **Van der Waals bonding (~6 kJ/mol).**
  - **very high surface area needed to achieve sufficiently high packing density.**
- **There are unique carbon structures with high surface area:**
  - **fullerenes.**
  - **activated carbon.**
  - **nanotubes.**
  - **. . .**



Smalley 1996

Chemical hydrogen storage (regenerated off board)



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Where do we go from here?

- Compressed gas
  - greater than 700 bar (10,000 psi)
  - Conformable tanks
  - Microspheres
- Cryogenic storage
  - Improved thermal management
    - Latency
    - Reduced weight, volume
  - High pressure cryogenic
- New solid state or liquid systems
  - New materials
  - Nonthermal systems

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Advanced concepts discussed at H_2 storage workshop in August 2002

Crystalline Nanoporous Materials **Self-Assembled Nanocomposites** **Inorganic – Organic Compounds** **BN Nanotubes** **Hydrogenated Amorphous Carbon** **Mesoporous materials**	*adsorbed hydrogen (surface)*
Advanced Hydrides **Bulk Amorphous Materials (BAMs)** **Nanosize powders**	*absorbed hydrogen (bulk)*
Iron Hydrolysis **Hydride Alcoholysis** **Polymer Microspheres**	*chemical system (nonreversible)*
Metallic Hydrogen	*compressed gas ?*

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High H capacity compounds

ammonia-borane complex
(A. T-Raissi, 2002 APR. Golden, CO)

$H_3BNH_3(l) \rightleftharpoons H_2BNH_2(s) + H_2(g)$ 6.49 wt.% ΔH=-21.7 kJ/mol

$xH_2BNH_2(s) \longrightarrow (H_2BNH_2)_x(s)$ (polymerizes)

$(H_2BNH_2)_x(s) \rightleftharpoons (HBNH)_x(s) + xH_2(g)$ 6.94 wt.%
13.43 wt.% total

$(HBMNH)_x \longrightarrow$ borazine + others $\longrightarrow$ BN + H_2 (>500° C)

Can this system be modified for reversibility?

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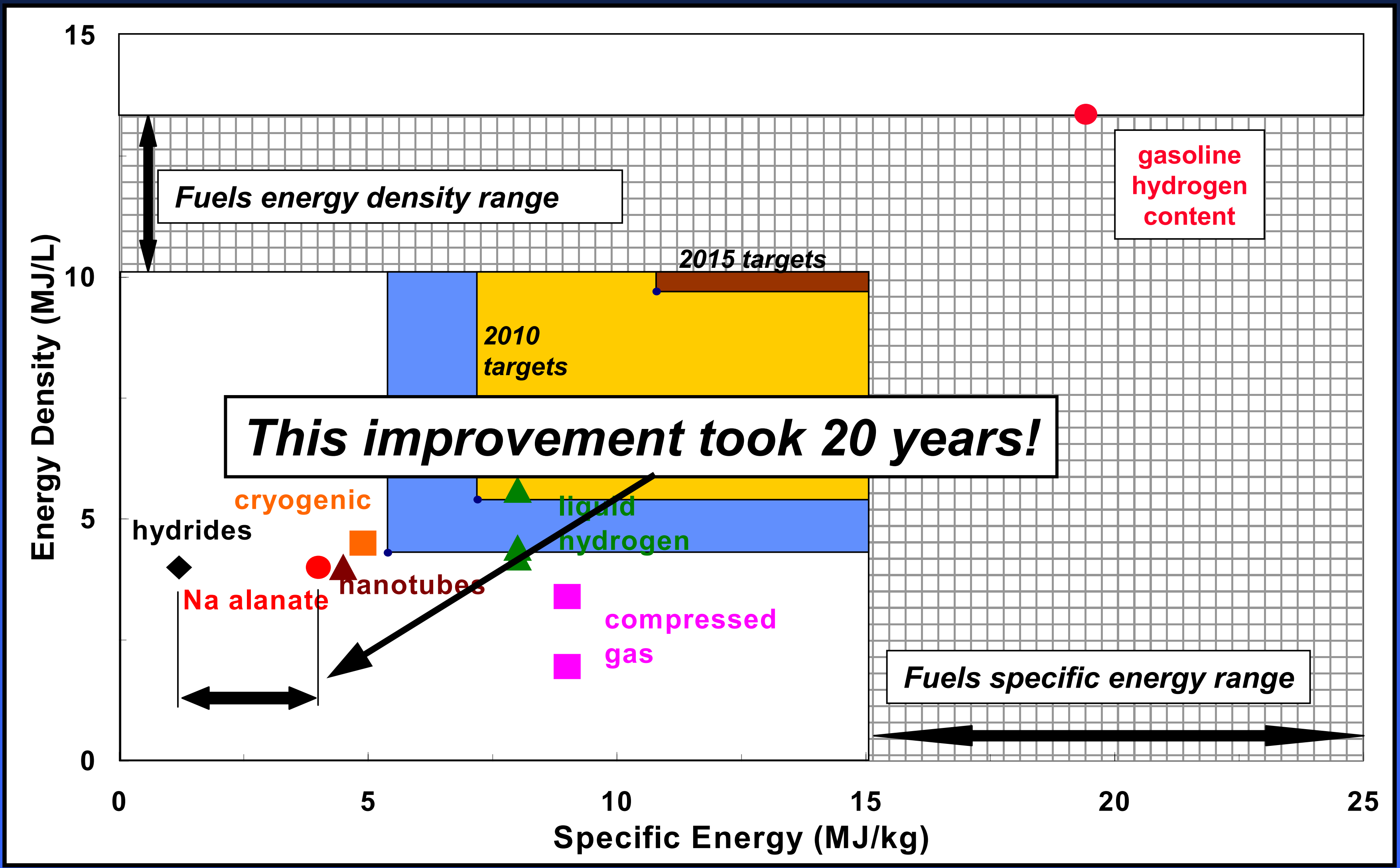
Summary of energy densities



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Outlook

- **Better understanding of reaction mechanisms**
  - **Fundamental studies aid development of advanced materials**
- **Kinetics must be improved**
  - **Advanced catalysts and doping procedures**
- **Second reaction plateau pressure must be increased**
  - **Elemental substitution**
- **Effects of contamination must be investigated**
  - **Further investigation into capacity loss**
- **Reversibility in other complex hydrides must be demonstrated**
  - **Li-alanates, Mg-alanates**
- **Safety issues must be evaluated and addressed**
  - **Engineering design and materials modification**

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