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Hydrogen Storage

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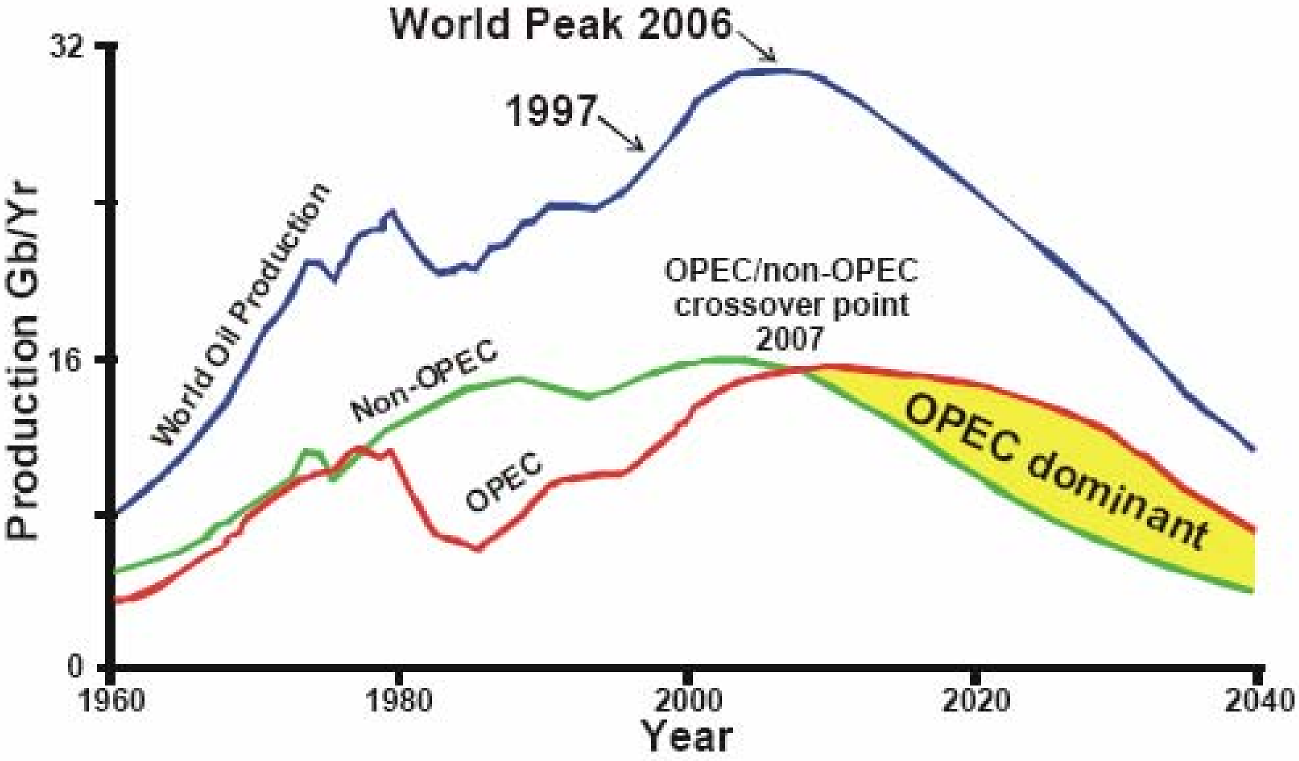


The World Petroleum Life Cycle
R.C. Duncan and W. Youngquist

Pollution and Climate Change

- Average concentration of CO_2 in the Earth's atmosphere has risen from 280 to 370 ppm since mid 19th century.
- Burning Fossil fuels is responsible for 75% of human emissions.
- Average temperatures in Australia increased by 0.7℃ in the 20 th century.
- Greenhouse gases partly responsible for climate change which is predicted to impact greatly on our lifestyle in the next 50 years.

TIME
FOR
CHANGE!

Challenge is to move away from fossil fuels to renewable forms of energy

Alternative Energy Carrier: Hydrogen?

- Hydrogen can be produced from many primary sources.
- Hydrogen has the highest energy to weight ratio (120 kJ/g) of any fuel.
- Hydrogen is oxidised cleanly to water – No carbon products formed!
- Hydrogen is the ideal fuel for fuel cells and can also be used in an internal combustion engine.

Two Major Problems

1. Hydrogen Production
2. Hydrogen Storage

Hydrogen Storage

Hydrogen has ≈ 3 times the energy per unit mass than gasoline

BUT

At STP gasoline has ≈ 3000 times the energy per unit volume

Hydrogen Storage

Four types of storage options:

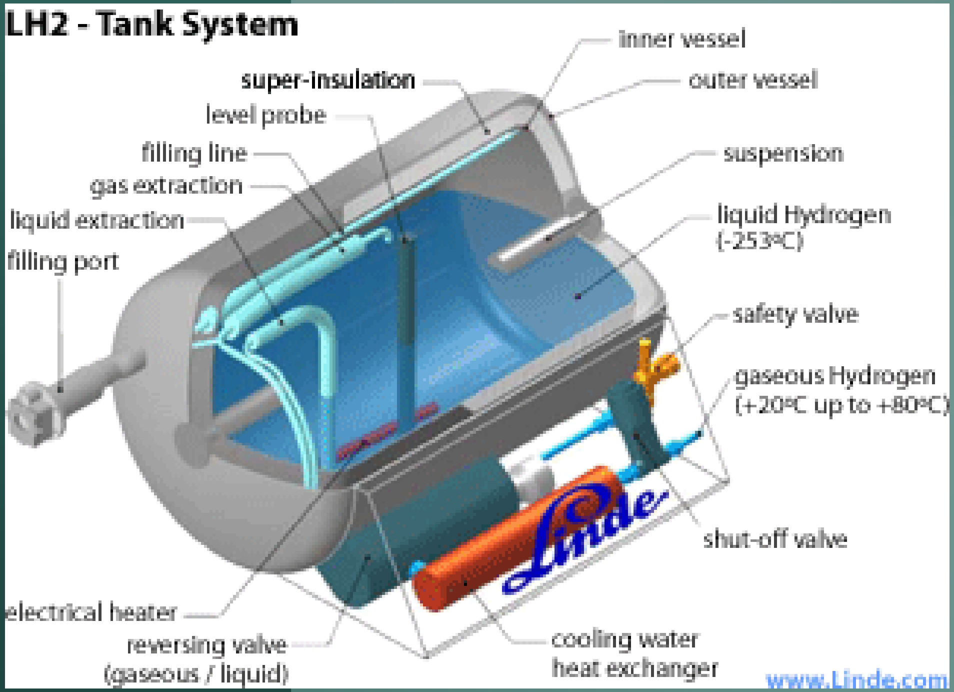
- Liquid Hydrogen
- Gaseous Hydrogen stored under high pressures.
- As a hydride – metal hydrides, complex hydrides, chemical hydrides
- Gas on solid adsorption – carbon nanotubes, inorganic nanotubes, metal organic frameworks → porous materials

Hydrogen Storage

U.S. DOE Targets 2010

- **> 6.5 wt.% hydrogen capacity**
- **Volumetric density > 45 kg H_2 m^{-3} (1.5 $kWhl^{-1}$)**
- **< 100°C**
- **< 2 atm (202 kPa)**
- **1000 hydrogen loading and unloading cycles**
- **Recharging of hydrogen must be feasibly quick**

Liquid Storage

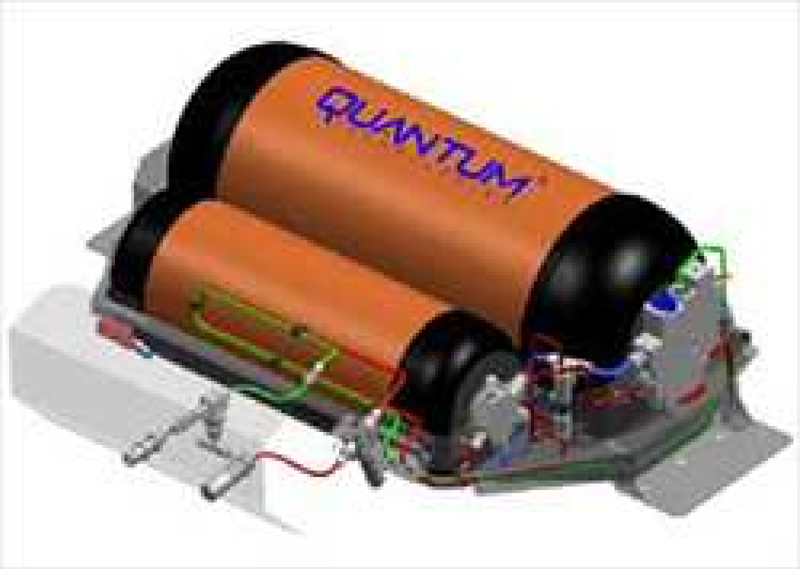


- Low temperature 20 K
- High pressure
- Energy to keep cold, lowers energy density
- Unsafe for transportation??

http://www.eere.energy.gov/hydrogenandfuelcells/storage/hydrogen_storage.html#liquid

Gas Storage

- Very high pressures
- 10,000 psi ~ 680 atm
- Energy required to pressurize
- Unsafe for transportation??
- 157 litre tank at 350 atm required for 3.75 kg H_2 (Honda FCX Concept car)



http://www.eere.energy.gov/hydrogenandfuelcells/storage/hydrogen_storage.html#liquid

GM HydroGen3 Hydrogen Fuel Cell

Specifications

Vehicle: Opel Zafira minivan with hydrogen fuel cell propulsion system

Seating capacity: 5

Fuel storage system: The liquid tank can store 4.6 kg of hydrogen (-253℃)

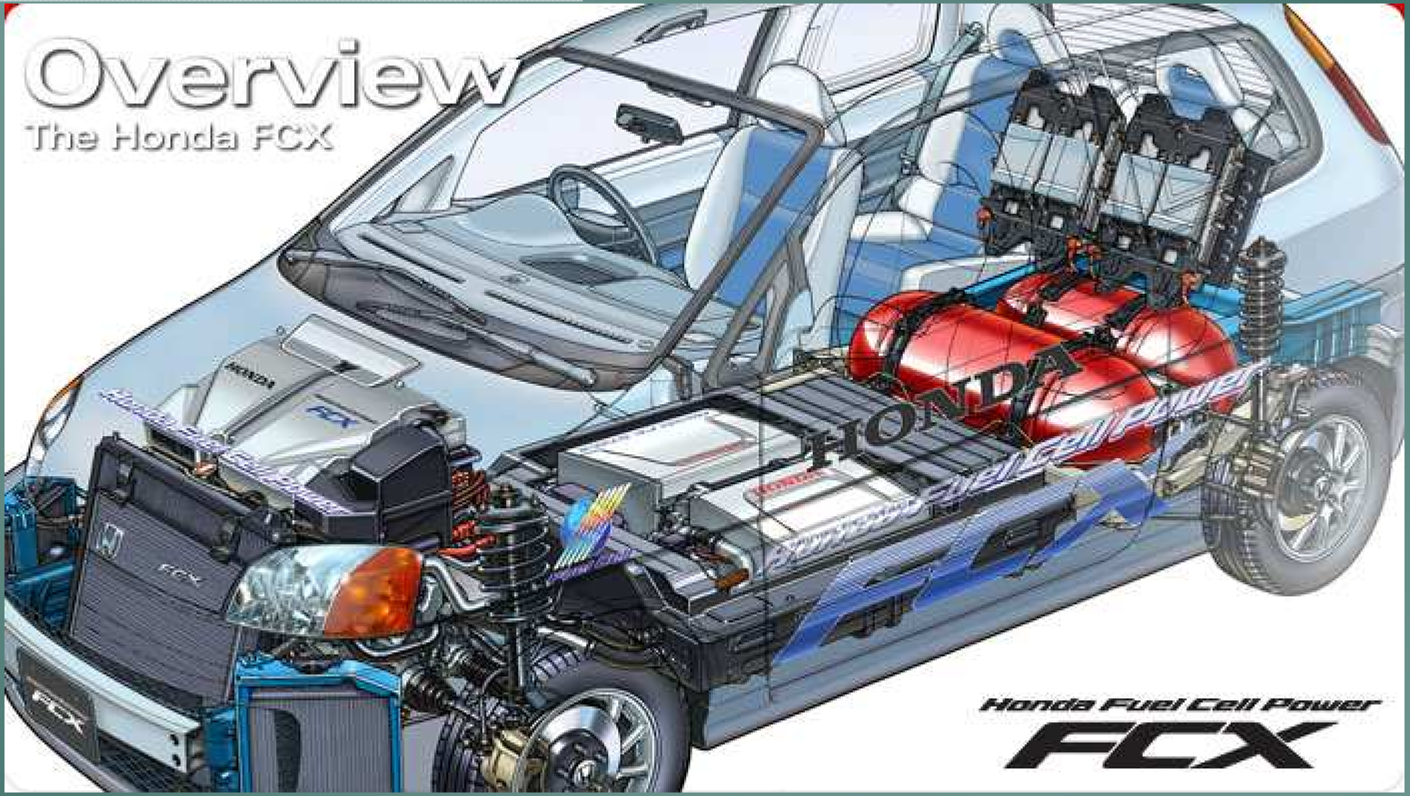
The compressed tank (10,000 psi) can store 3.1 kg of hydrogen

Range: 400 km (liquid storage); 270 km (compressed)

Top speed: 160 kmhr^{-1}

http://www.gm.com/company/gmability/adv_tech/images/fact_sheets/hydrogen3.pdf

Honda FCX Fuel Cell Power



http://world.honda.com/FuelCell/FCX/overview/

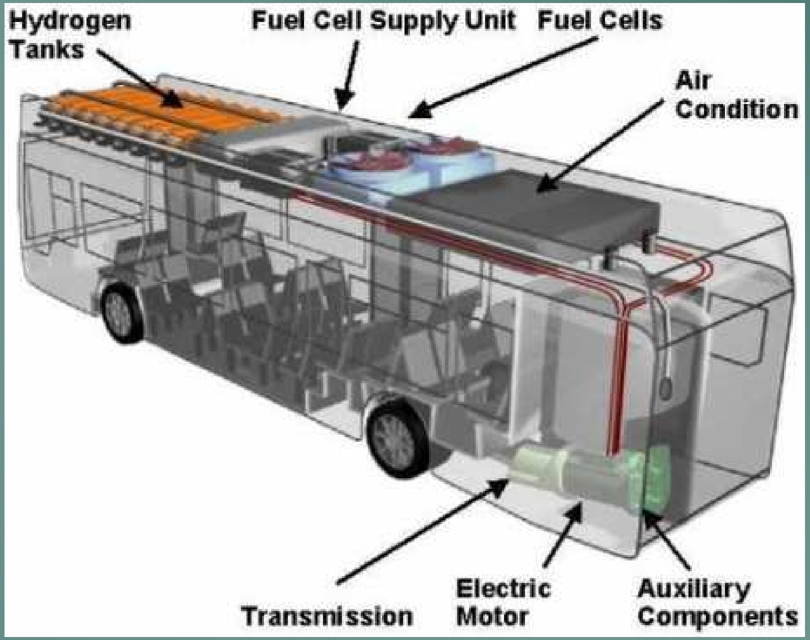
Honda FCX Fuel Cell Power

http://world.honda.com/FuelCell/FCX/overview/

Honda FCX Fuel Cell Power

http://world.honda.com/FuelCell/FCX/overview/

Hydrogen Bus



Perth Hydrogen Bus (Pictures Courtesy: www.dpi.wa.gov.au November 2004)

Metal Hydrides

Advantages

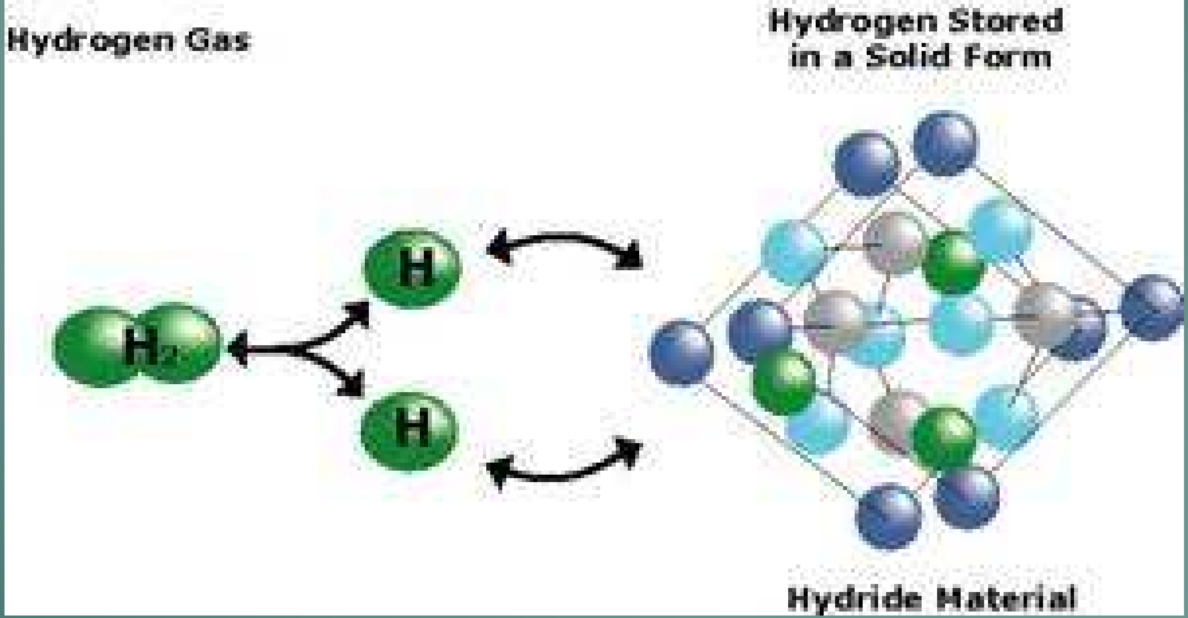
- high hydrogen density at moderate pressure
- all hydrogen desorbed at same pressure
- released hydrogen very pure
- MgH_2 → 7.7 wt%, AlH_3 → 10.1 wt%
- Examples: FeTi, $LaNi_5$, Mg_2Ni

Disadvantages

- best hydrides require impractical ^oC
- to store same amount of energy as a petrol fuel tank → may weigh up to 20 times more!

Metal Hydrides

- Interstitial absorption



$M + H_2 \longrightarrow MH + \text{Heat Out}$

$M + H_2 \longleftarrow MH + \text{Heat In}$

Complex Metal Hydrides [MXH_4]

- **M – Metal E.g. Na, Li, Mg etc.**
- **X – Aluminium or Boron**

Table 1. Maximum theoretical hydrogen storage capabilities of key alanates and borohydrides (Ritter et. al. Materials Today, Sept. 2003)

Hydride	Max. Wt% Hydrogen
Sodium Alanate ($NaAlH_4$)	7.5
Magnesium Alanate ($Mg(AlH_4)_2$)	9.3
Lithium Alanate ($LiAlH_4$)	10.6
Sodium Borohydride ($NaBH_4$)	10.6
Lithium Borohydride ($LiBH_4$)	18.5

Alanates ($MAlH_4$)

- **Model System $NaAlH_4$ represents only reversible system under reasonable conditions**

$$3NaAlH_4 \overset{\text{Catalyst}}{\leftrightarrow} Na_3AlH_6 + 2Al + 3H_2 \quad \text{[3.7 wt\%]} \quad (1)$$

$$Na_3AlH6 + 2Al + 3H_2 \overset{\text{Catalyst}}{\leftrightarrow} 3NaH + Al + 3/2H_2 \quad \text{[1.9 wt\%]} \quad (2)$$

Thomas et al. www.eere.energy.gov/hydrogenfuelcells Jan 2004

Alanates ($MAlH_4$)

- Both $LiAlH_4$ and $Mg(AlH_4)_2$ have not yet been observed as reversible
- Similar effects on all systems with dopants, catalysts and ball-milling, results in loss of 1-2 wt.%

Borohydrides (MBH_4)

- Model system is $NaBH_4$
- Not yet reversible under reasonable conditions (Amendola et al. Int J. Hydrogen Energy **25** (2000) p. 969 – 975)

$$NaBH_4 + 2H_2O \xrightarrow{\text{Catalyst}} 4H_2 + NaBO_2{}^{\alpha} + \text{HEAT (300) kJ}$$

α This product can be replaced by, or occur in conjunction with $NaB(OH_4)$ under certain conditions of temperature and pressure. The characteristics of both are fairly similar.

Borohydrides (MBH_4)

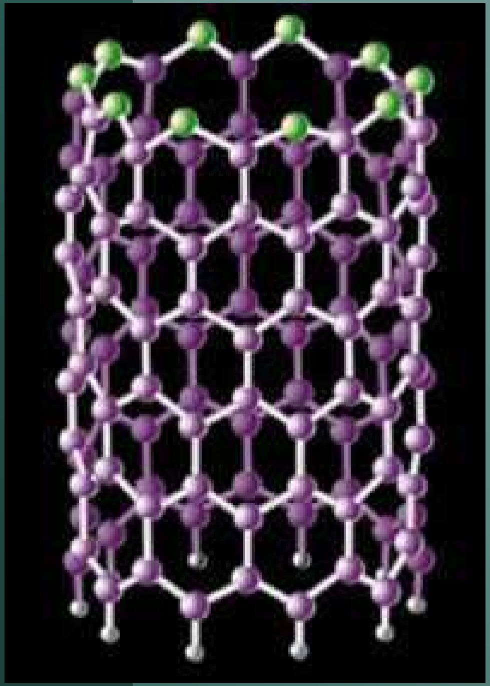
- Exhibits Good Capacity (~7.0 wt%)
- Ruthenium catalyst allows easy control, near instantaneous reaction
    - 5 mol% ion exchange resin beads
- Exothermic reaction allows direct coupling with PEM fuel cell
- $NaBO_2$ must be re-processed off site
- Costs around $80/kg

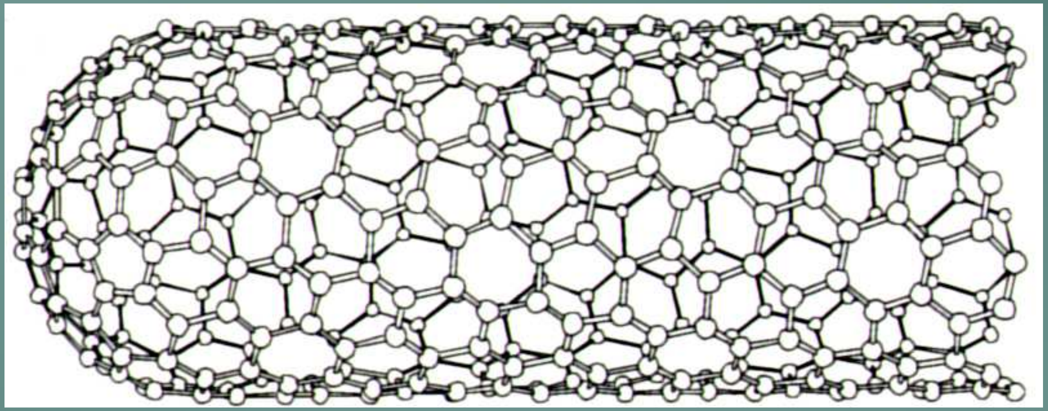
Borohydrides (MBH_4)

- If $NaBH_4$ can be made reversible, focus will shift to higher capacity $LiBH_4$ (18.5 wt%)
- $NaBH_4$ is already in use, Hydrogen on Demand™ by Millennium Cell Inc. (www.millenniumcell.com/investor/science.html Jan 2004)

High Surface Area Materials

- **Metal Organic Frameworks**
- **Carbon Nanotubes**





Graphite layer rolled into a cylinder
→ capped by half a fullerene

Hydrogen Storage at Curtin

- Curtin (Buckley and Gale) awarded $285 K from $2.1 M CSIRO NHMA Hydrogen Storage Stream grant.
- Buckley Project Leader of Project 4: Hydrogen storage in porous materials.
- Magnesium, Aluminium.
- Porous materials: Mesoporous Materials, Carbon aerogels.

Magnesium

- MgH_2 theoretical storage capacity of 7.7 wt.%, high reversibility and low cost.
- Slow desorption kinetics and desorption temperature of 573 – 714 K, depending on the pressure, doping and milling conditions.
- Although the alloying or doping of Mg in some cases has resulted in a lower desorption temperature, this has been offset by a lower hydrogen storage capacity due to the added weight.
- The challenge remains to lower the thermodynamic stability of Mg and its alloys and hence lower desorption temperature without decreasing the wt.%.

Magnesium

- A theoretical study using ab-initio Hartree-Fock and DFT calculations has been conducted by Wagemans et al. to investigate the effect of crystal grain size on the thermodynamic stability of magnesium and magnesium hydride.

- They showed that the hydrogen desorption energy decreases significantly when the MgH_2 cluster size is < 1.3 nm, leading to a desorption temperature of 473 K for a cluster size of 0.9 nm, a reduction of 100 K to that measured for the bulk.

Magnesium

- We intend to synthesise and stabilise nanosized MgH_2 particles comprised of sub-nanometre MgH_2 clusters, in an effort to lower the desorption temperature of MgH_2.

- The effect of organic additives such as benzene and cyclohexane to the milling process on the structural properties of the nanosized Mg particles will be investigated

Aluminium

- AlH_3 theoretical storage capacity of 10.1 wt.%. Low cost and low decomposition temperature in range T = 333 – 473 K.

- Volumetric capacity of 0.074 kg H_2/l, more than 60% higher than the 2010 volumetric DOE target of 0.045 kg H_2/l.

- H_2 gas pressures > 2.5 GPa are required to rehydride Al back to AlH_3.

Aluminium

- If AlH_3 is to be used as an onboard hydrogen storage system, a yet to be developed low cost method for off board regeneration of spent Al back to alane is required.
- Klingler et al. have suggested that alane might be made at lower temperatures and pressures using nanoparticulate aluminium.

Aluminium

- Klingler et al. varied temperature and pressure conditions, and determined that the equilibrium hydrogenation pressure for 100 nm aluminium particles was 34.2 MPa at 338 K.

- This combination of temperature and pressure is well within the range of interest for automotive applications, where 35 MPa gas cylinders are presently used, even for these relatively large aluminium nanoparticles.

Aluminium

- Using DFT, Yarovsky and Goldberg have predicted that nanosized aluminium clusters of 13 atoms could absorb 42 H atoms forming $Al_{13}H_{42}$ resulting in 10.5 wt% of H_2.

- They also noted that the activation energy for dissociative chemisorption of H_2 on Al_{13} is not high and can be overcome by thermal energy or by adding a catalyst.

- Further DFT calculations on Al similar to that conducted by Wagemans et al. on Mg will be done in an effort to determine the particle size that will produce the lowest absorption pressure.

Aluminium

- Experimentally we propose to hydrogenate smaller aluminium nanoparticles (< 100 nm), synthesised via ball milling (Sadi et al.), with the aim of decreasing the hydrogenation pressure further.

- Mechanochemical Process (McCormick et al.)

- Novel chemical routes for synthesising aluminium nanoparticles will also be investigated.

- For example, solution phase decomposition of $H_3Al.NMe_3$ (Me ≡ Methyl) can be controlled with surface-active additives to produce oxide-free aluminium nanoparticles.

Conclusion

- **Hydrogen will be a future energy carrier**

- **Breakthroughs are occurring annually concerning production and storage issues**

- **The search for a lightweight, low pressure Hydrogen Storage material is ongoing.**

References

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