Hydrogen Storage – Dream or Reality ?

Ph.D Seminar - I

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Why alternate fuels?

- **Growing demand**
- **Awareness for equidistribution**
- **Environmental concerns**
- **Economy and processibility**

Seth Dunn, Tech Monitor, Nov-Dec (2001) 14

Why Hydrogen?

- **Heat and energy content**
- **Perfectly renewable**
- **Light and gas at NTP conditions**

M.Conte *et al* J.Power Source, **100** (2001)171

Comparison of fuel properties

Properties	**Hydrogen (H_2)**	**Methane (CH_4)**	**Gasoline (-CH_2-)**
Lower heating value($kWhKg^{-1}$)	33.33	13.9	12.4
Self ignition temperature (°C)	585	540	228-501
Flame temperature (°C)	2045	1875	2200
Ignition limits in air (Vol %)	4-75	5.3-15	1.0-7.6
Minimal Ignition energy (mWs)	0.02	0.29	0.24
Flame propagation in air (ms^{-1})	2.65	0.4	0.4
Diffusion coefficient in air (cm^2s^{-1})	0.61	0.16	0.05
Toxicity	No	No	High

L. Schlapbach *et al.*, Nature, **414** (2001) 353.

Transistion to hydrogen

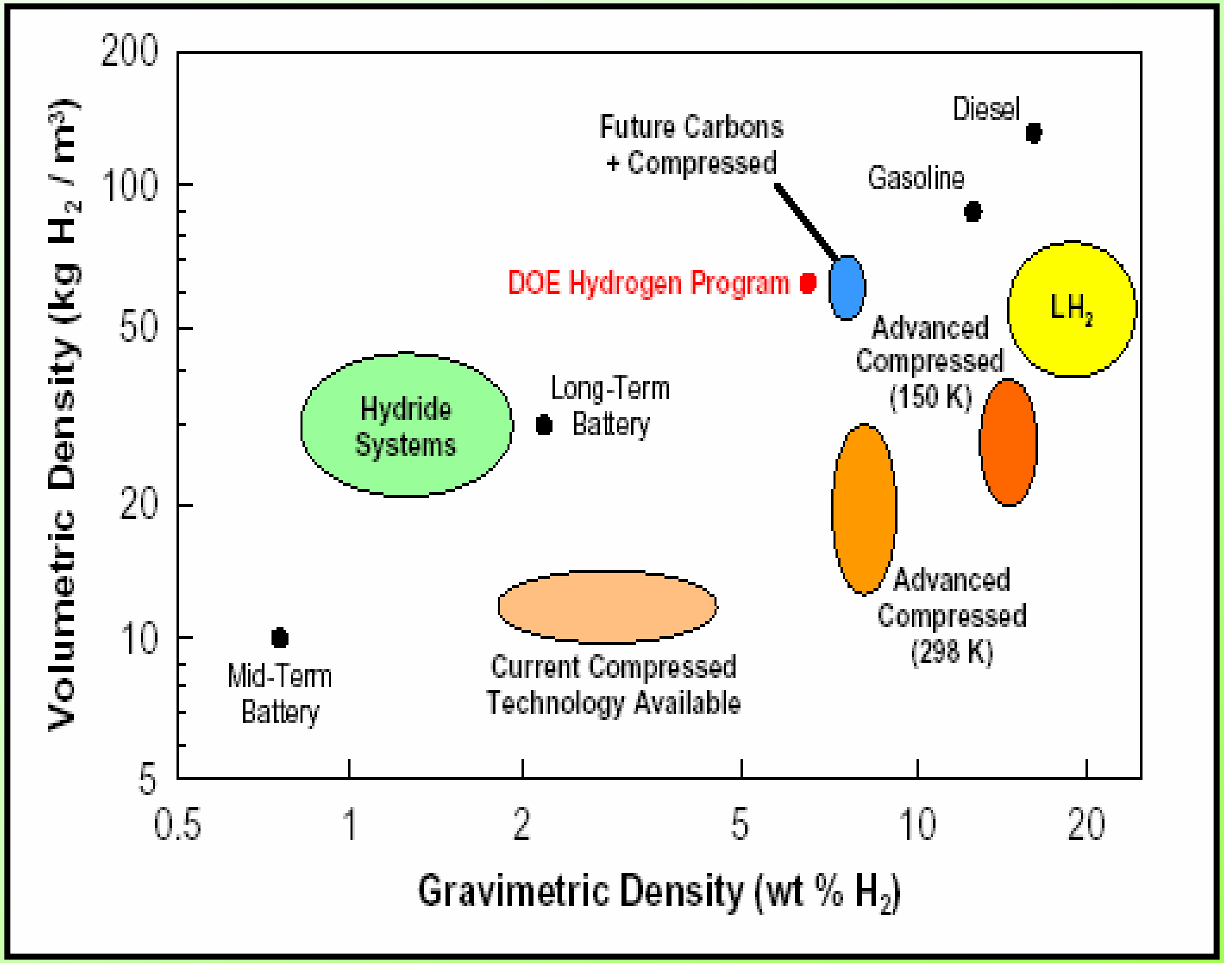
- Production
- Storage
- Distribution

Production of hydrogen

- **Electrolysis**
- **Thermochemical**
- **Biochemical**
- **Solar**

Technology awaited

Why 6.5 wt%?



S.Hynek *et al.*, Int.J.Hydrogen Energy, **22** (1997) 601

Storage

- **Gas/liquid**
- **Solid**

  - Metal, intermetallics, alanates

  - Porous materials

  - Carbon materials

Direction ?

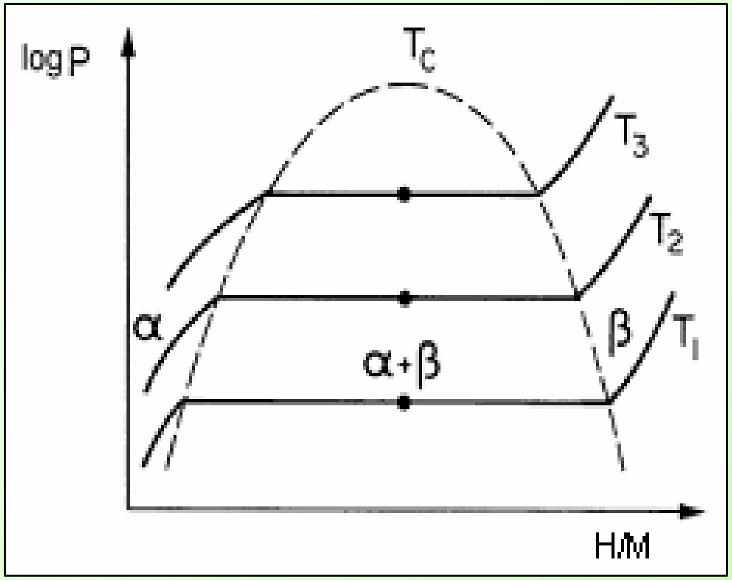
U.Bunger *et al.*, Appl. Phys A, **72** (2001)147

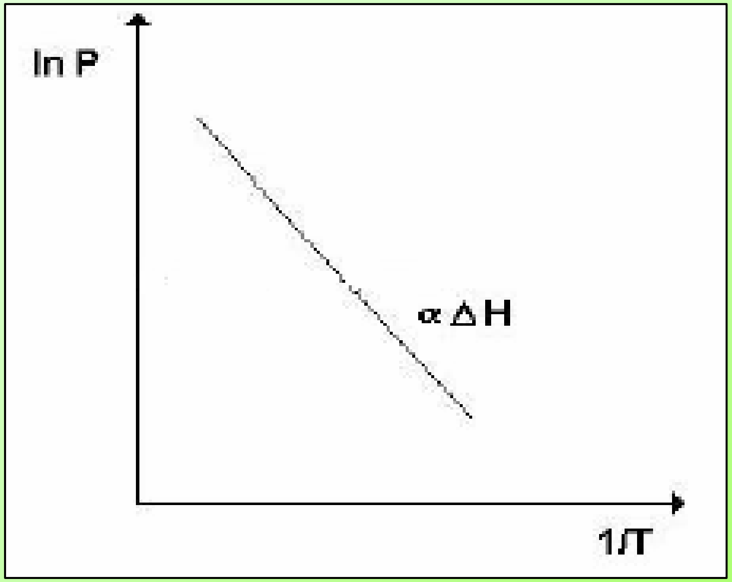
Metal hydrides

- Maximum storage capacity 3 wt%
- Experimental parameters not favourable
- Recycling not feasible
- Cost and weight

G.Sandrock *et al.*, J.Alloys Comp., **293-295**(1999)877

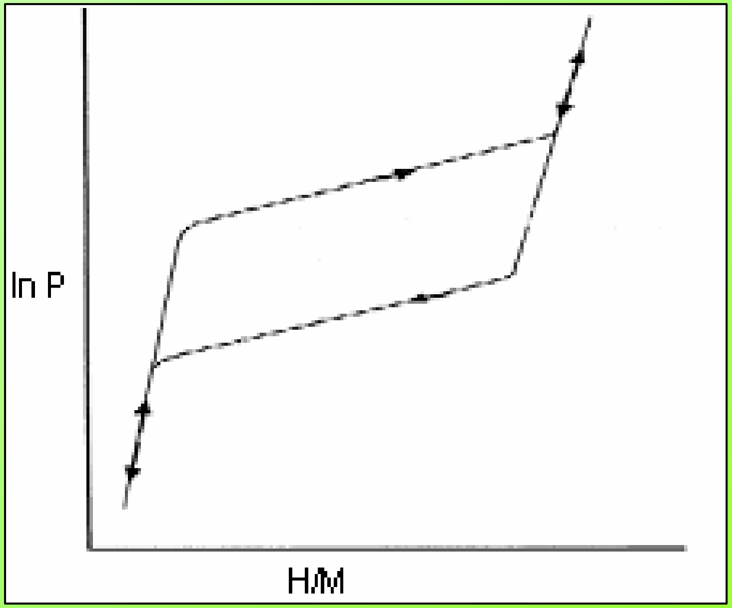
P-C-T isotherm





Sievert's law $H/M = Ks\ P^{1/2}$

$$\ln (K_2/K_1) = -\Delta H/R\ (1/T_2 - 1/T_1)$$

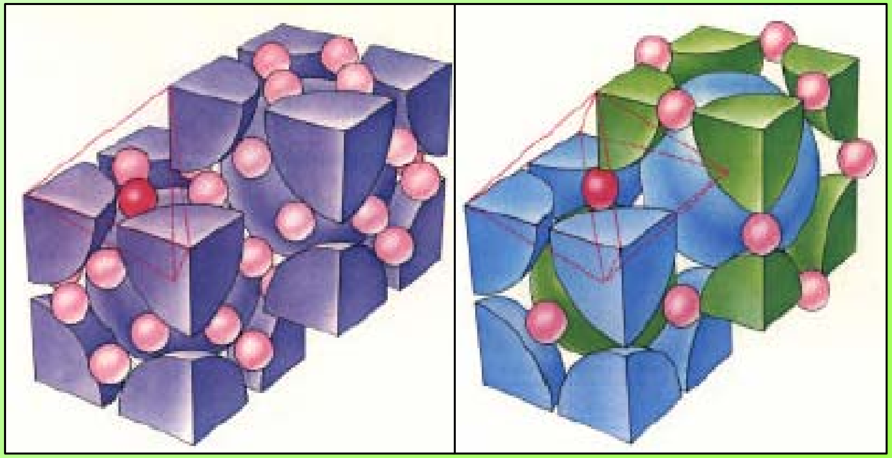


Intermetallics

- **Maximum storage capacity <3 wt%**
  AB (FeTi), A_2B (Mg_2Ni, ZrV_2), AB_5 ($LaNi_5$)

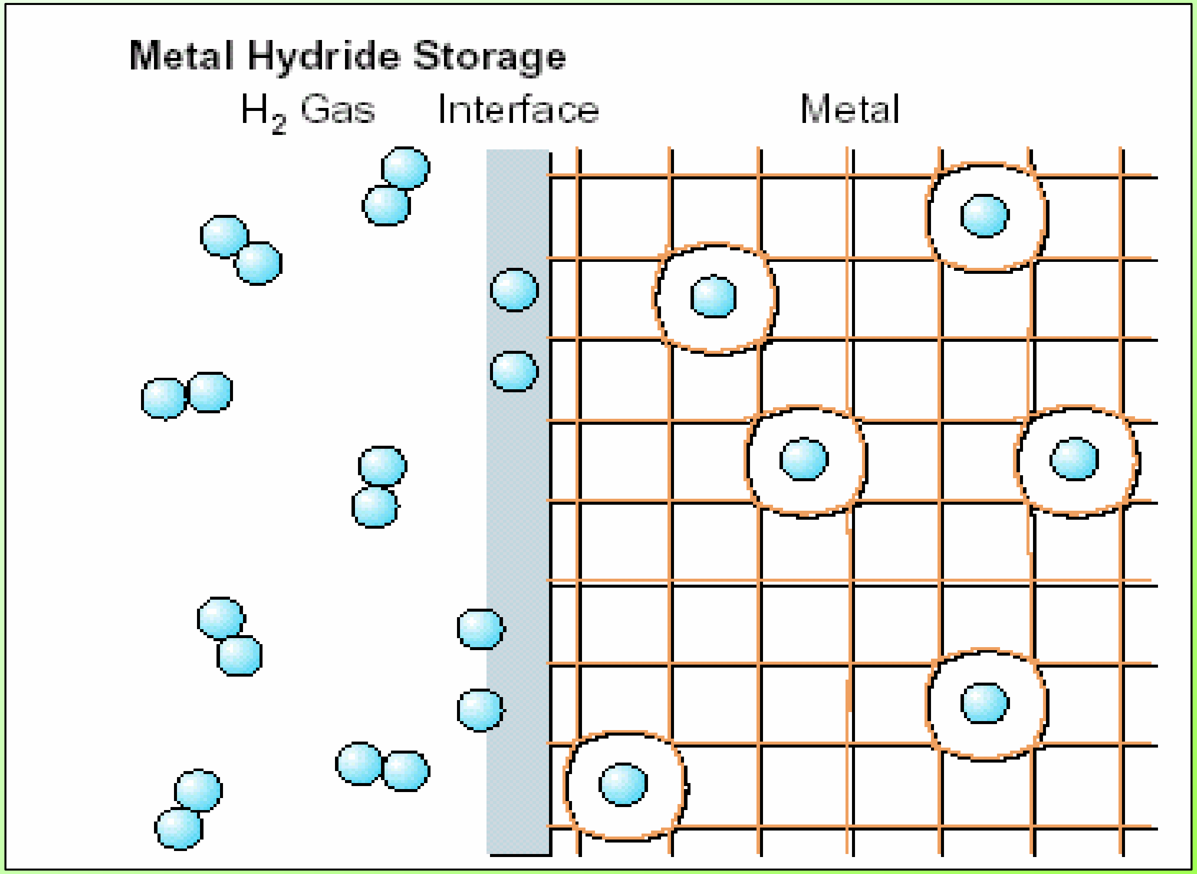
- **Hydrogen activator?**

- **Hydrogen absorber?**



Choice limited

Schematic representation of hydrogen storage in Metal Hydrides



Storage capacity of metal hydride and intermetallics

Material	P_{des} (atm)	T (K)	H-atoms per cm^3 (x 10^{22})	weight % of hydrogen
MgH_2	~10^{-6}	552	6.5	7.6
Mg_2NiH_4	~10^{-5}	528	5.9	3.6
$FeTiH_2$	4.1	265	6.0	1.8
$LaNi_5H_6$	1.8	285	5.5	1.3

Why not ?

P.Dantzer *et al.*, Material Science and Engineering A,**329-331** (2002)313

Alanates

- **Favourable hydrogen storage capacity**
- **Formation**
- **Bonding**
- **Experimental conditions**
  (catalyst, multi step decomposition, poor kinetics)

Feasibility ?

K.J.Gross *et al.*, J.Alloys.Comps **330-332** (2002) 683

Porous materials

- **Possibilities**

  (zeolites,glass microspheres)

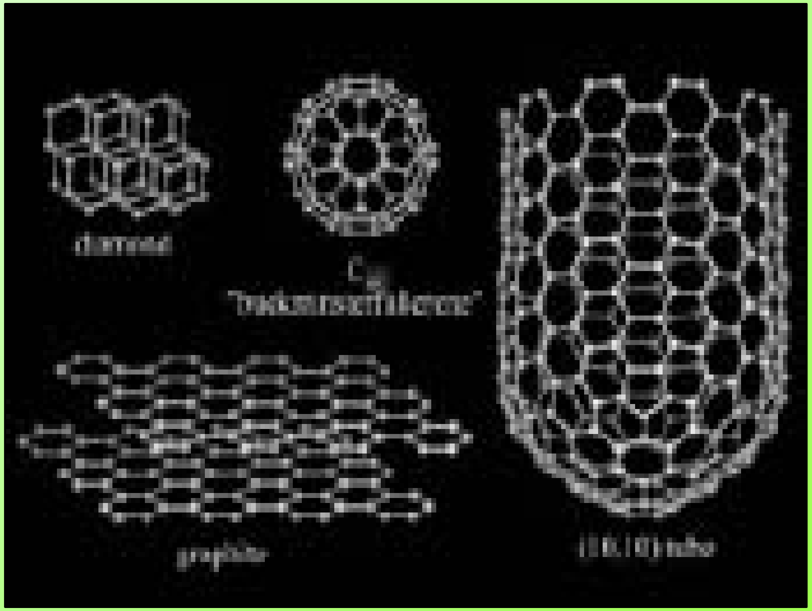
- **Experimental parameter not favourable**

- **Storage capacity**

Not promising

Why carbon?

- ✶ **Nature's process**
- ✶ **Light mass and low cost**
- ✶ **Optional possibilities**



Requirement of UCR >1 why?

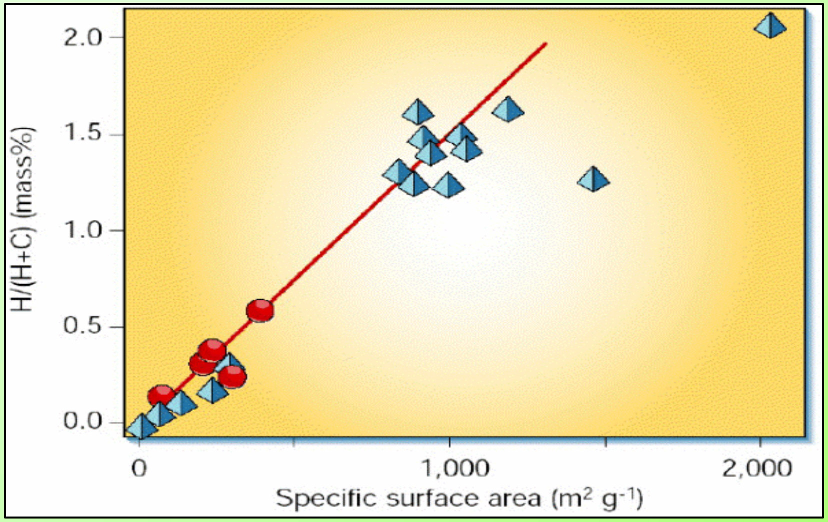
- **UCR:- Storage capacity with adsorbent to storage capacity without adsorbent**
- **Storage capacity of adsorbent – high**
- **How to achieve?**

Q.Wang *et al.*, J.Phys.Chem. B, **103** (1999) 4809

Activated carbon

* **Typically UCR>1**

* **Storage is αSA(pore volume)**



* **Storage only at low T and High P**
  ---5.2 wt% at 65K &42 atm

M.G.Nijkamp *et al.*, Appl.Phys, A, **72**(2001)619

Fullerenes

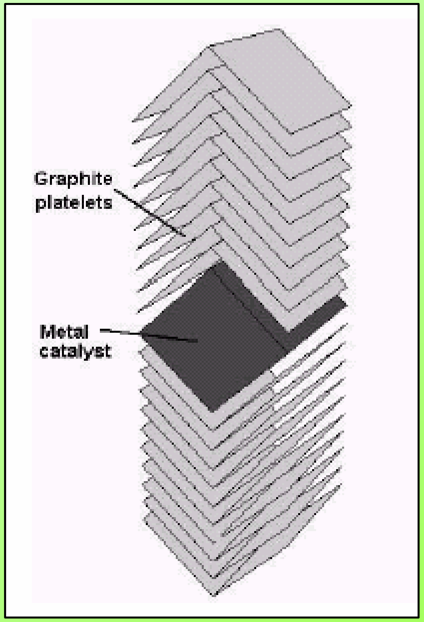
- **Stable stochiometric hydrides**
- **Electrochemical charging**
- **Activation by alkali metal**
- **Strong bonding**

D.V.Schur *et al.*, Int.J.hydrogen Energy **27** (2002) 1063

Carbon Nanomaterials

Herringbone

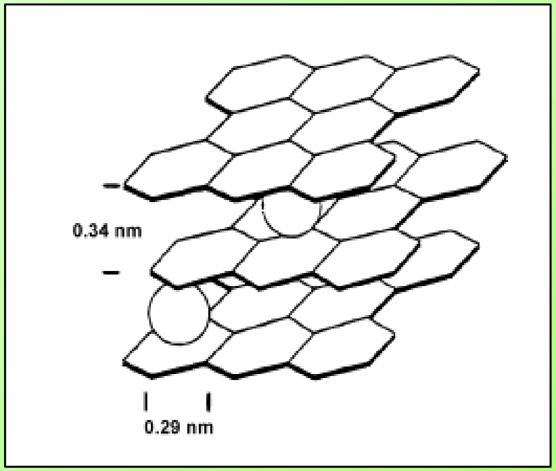
- ✧ Inter planar spacing (0.335 nm)
- ✧ Storage capacity   (67 wt %)
- ✧ Production and recyclibility.



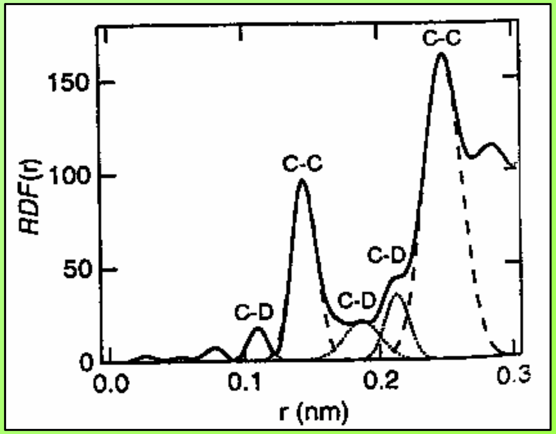
A.Chambers *et al*., J.Phys.Chem. B, **102** (1998) 4253

Platelet

- **Storage capacity (53.68 wt%)**



- **Production and recyclibility**



S.Orimo *et al.*, Appl.Phys.Lett., **75** (1999) 3093

Hydrogen Storage capacity of Graphitic nanofiber

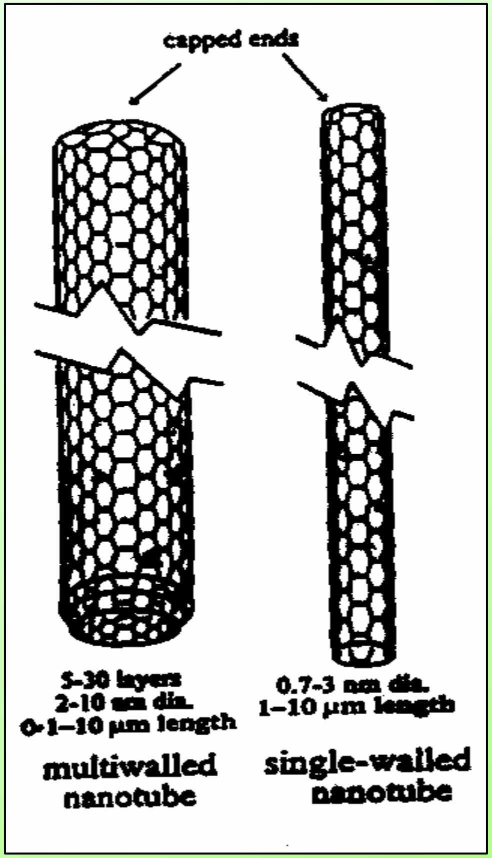
Materials	Pressure (MPa)	Temperature (K)	Wt % of H_2
GNFs (herring bone)	12	298	67.55
GNFs (platelet)	12	298	53.68
GNFs (tubular)	12	298	11.26
GNFs (Heat treatment)	12	298	1.1 - 1.4
CNFs	10	300	~5

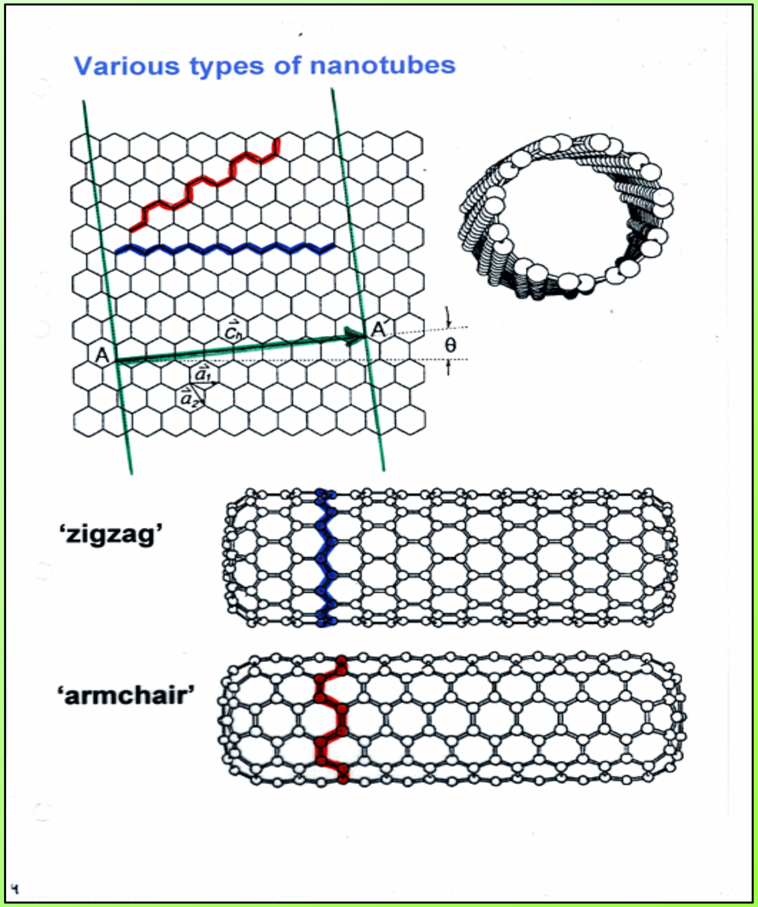
H.M. Cheng *et al*., Carbon **39** (2001)1447

Carbon nanotubes

Possibilities

(Arc/Laser/CVD)

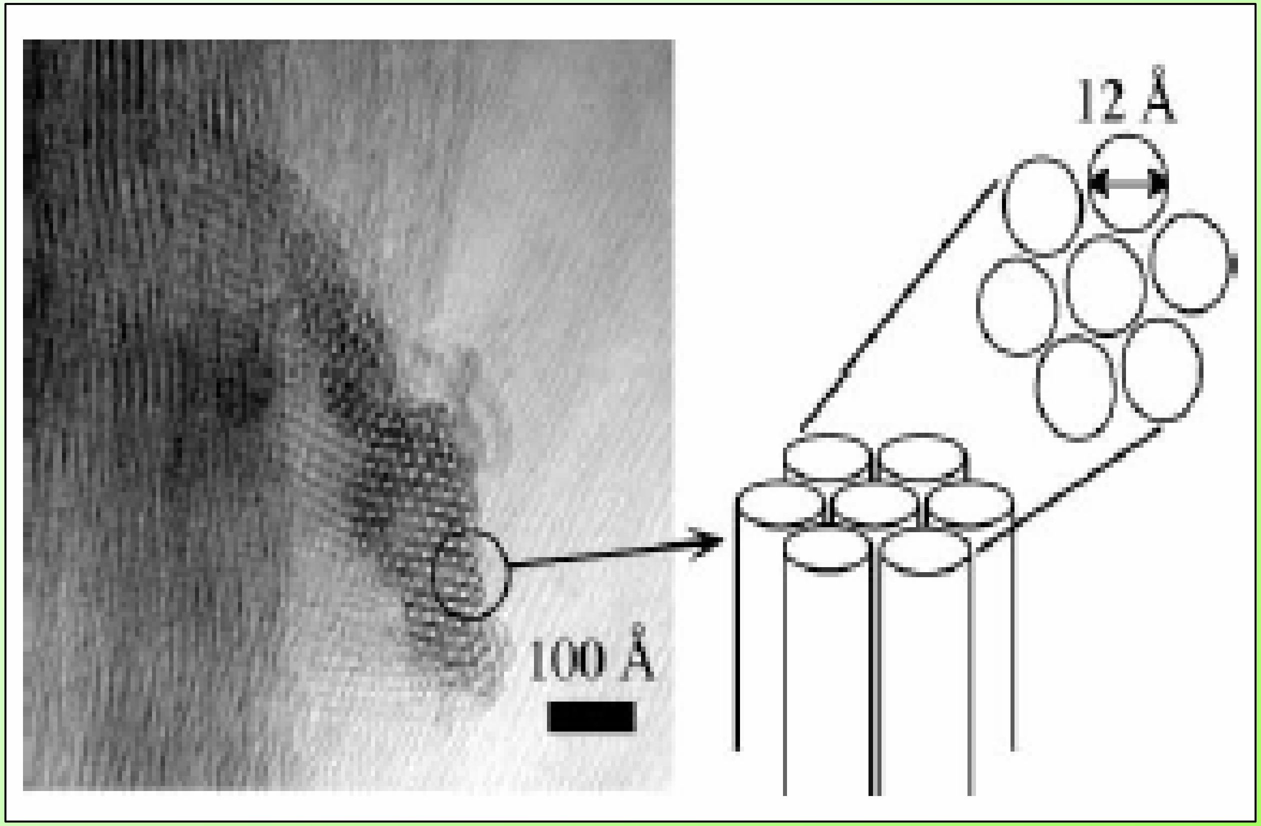




Storage capacity 5-10 wt%

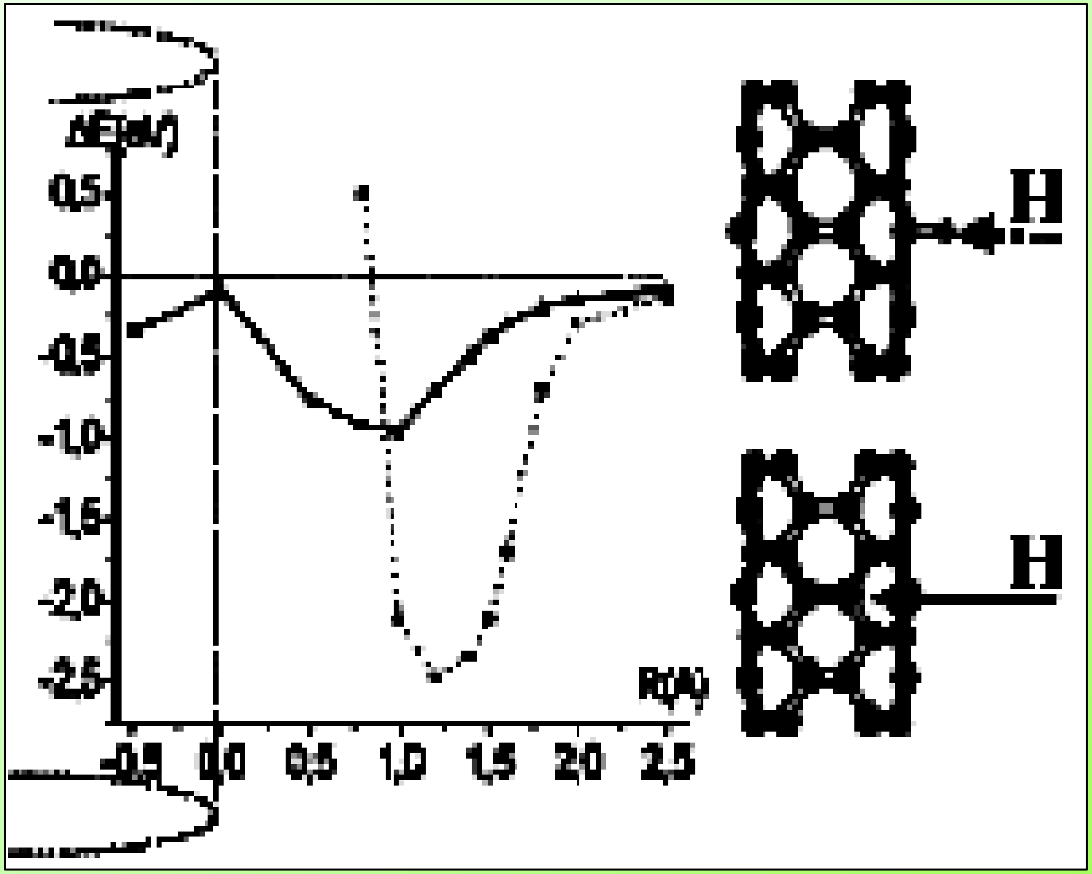
F.Lamari Darkrim *et al.*, Int.J.Hydrogen Energy, **27**(2002)193

TEM picture of single walled carbon nanotube



A.C. Dillon, *et al*., Appl. Phys. A, **72** (2001) 133

Interaction of Hydrogen in Carbon Nanotube



G.E.Froudakis *et al.*, Nano Lett., **1** (2001) 179

Hydrogen storage capacity of SWNTs & MWNTs

Materials	Pressure (MPa)	Temperature (K)	Wt % of H_2
SWNTs	0.04	133	**5-10**
SWNTs (pure)	0.067	Ambient	**3.5-4.5**
SWNTs ~50 %	10	300	**4.2**
SWNTs (pure)	12	80	**8.2**
MWNTs	Ambient	300-700	**0.25**
MWNTs (aligned & opened)	4	80	**1.97**

Modification of nanotubes

- ✶ **Addition of metals and alloys**
- ✶ **Addition of metal oxides**

R.T.Yang, Carbon **38**(2000) 623

Hydrogen storage in modified carbon nanotubes

Materials	P(MPa)	T(K)	Max Wt% H_2
Li-CNT	0.1	473-673	21 (Wet H_2) 1.8 (Dry H_2)
K-CNT	0.1	313	12 (Wet H_2) 2.5 (Dry H_2)
Li-CNT	0.1	473-663	0.73-.42
SWNT -Fe	0.08	Ambient	<0.005
SWNT-$TiAl_{0.1}V_{0.04}$	0.067	Ambient	~7
SWNT – Ti-6Al-4V	0.08	Ambient	1.47
SWNT – NiO-MgO	Ambient	600	0.65

Hydrogen storage capacity of different storage methods

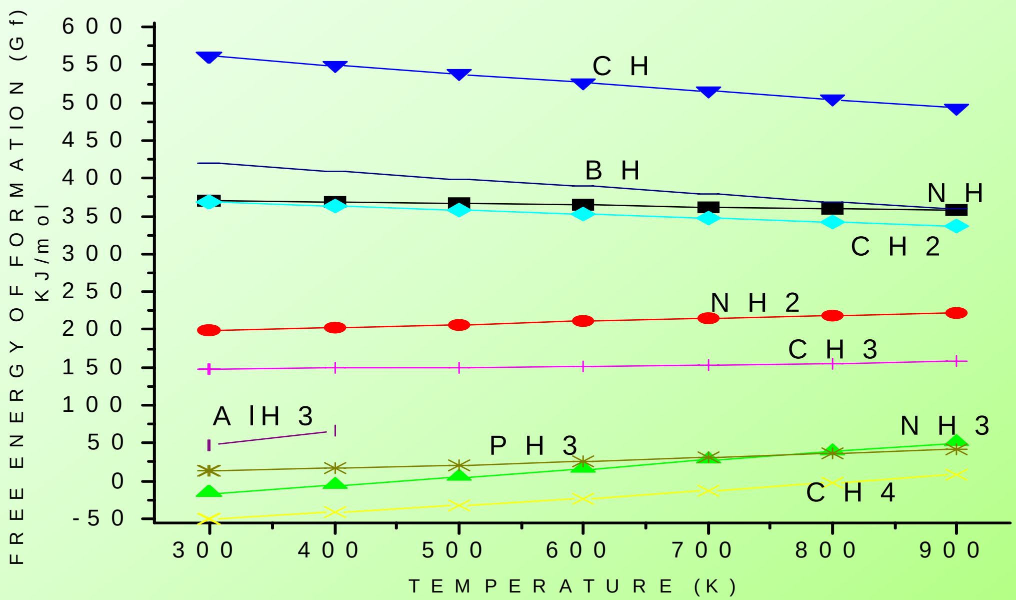
Storage method	**Hydrogen capacity (Wt %)**	**Energy capacity (KW/Kg)**	**Possible application areas**
Gaseous H_2	**11.3**	6.0	TR,CHP
Liquid H_2	**25.9**	13.8	TR
Metal hydride	**~2-6.6**	0.8-2.3	PO,TR
Activated carbon	**6.2**	2.2	-
Zeolites	**0.8**	0.3	-
Glass spheres	**8**	2.6	-
Nanotubes	**4.2-7**	1.7-3.0	PO,TR
Fullerenes	**~8**	2.5	PO,TR

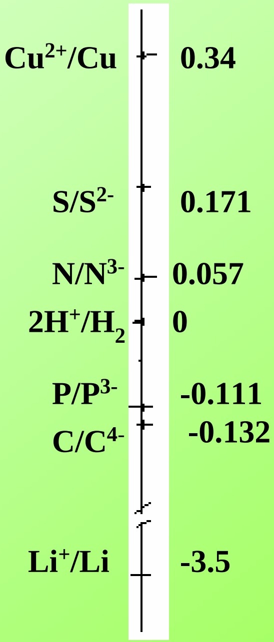
TR-Transportation, PO- Portable, CHP- Power production.

What alternative?

- Revert back to Nature – Heteroatom?
- Heteroatom containing nanomaterials?
- Activation of hydrogen by heteroatom?

Ellingham diagram of the various Species

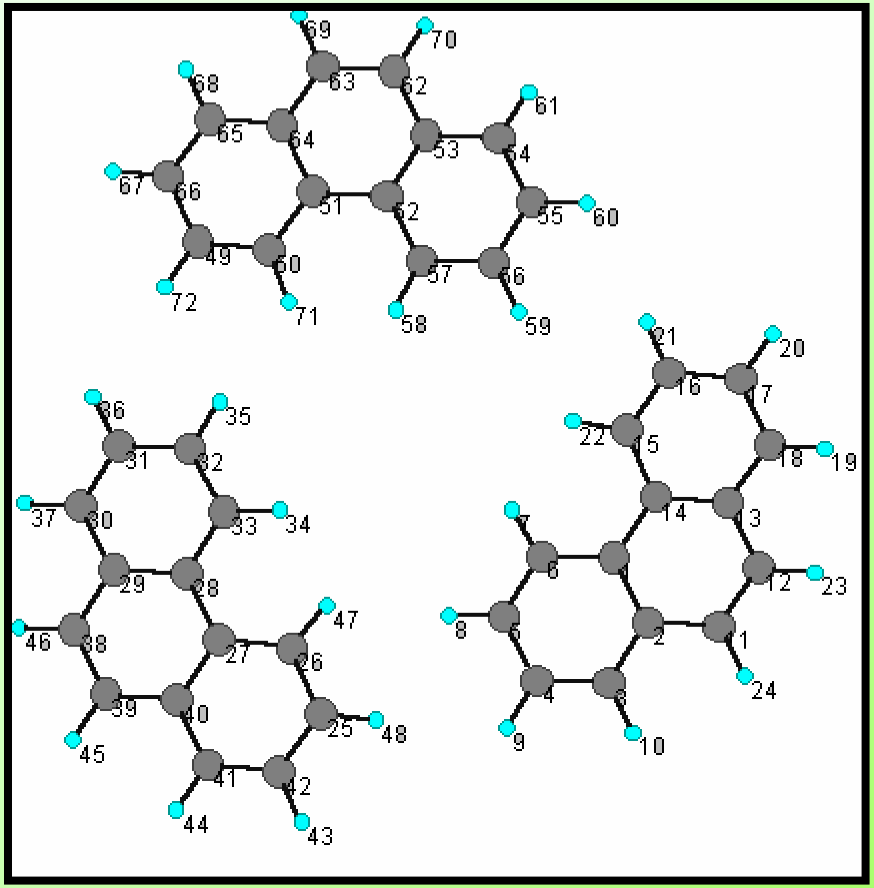




Standard redox potential in volts of various species

Model

Cluster model (the heteroatoms are substituted in positions 26,33,50,57,15 and 6)



Methods:

Energy minimization – UFF 1.02

Single point energy – DFT B3LYP/6-31G(d)

Results

Heteroatom	Mode of substitution	H_2 Energy (eV)	Bond length (H-H) Å	H_2 Dissociation energy (eV)
Hydrogen	-	-31.96	0.708	4.74
Unsubstituted CNT	-	-31.97	0.708	4.76
Nitrogen substituted CNT	1 N + 1 H_2	-26.90	0.84	0.31
(Each ring 1N)	3 N + 1 H_2	-26.89	0.84	0.32
	3 N + 3 H_2	-26.88	0.84	0.33
(Each ring 2N)	6 N + 1 H_2	-27.78	1.08	0.56
	6 N + 3 H_2	-27.70	1.08	0.50
Phosphorus substituted CNT	1 P + 1 H_2	-29.27	0.81	2.06
(Each ring 1P)	3 P + 1 H_2	-28.57	0.82	1.36
	3 P + 3 H_2	-28.72	0.82	1.51
Sulphur substituted CNT	1 S + 1 H_2	-27.48	0.81	0.27
(Each ring 1S)	3 S + 3 H_2	-28.24	0.81	1.03
	3 S + 3 H_2	-27.46	0.81	0.25

Variation in bond length, hydrogen energy and dissociation energy

Conclusions

- Critical components still await development
- Scientific understanding immature
- Possibilities seem promising.