Nanomaterials for Hydrogen Storage Applications

Presented by:
Dr. Ramesh Kumar K
Assistant Manager-Nanotechnology
HPCL Green R&D Centre

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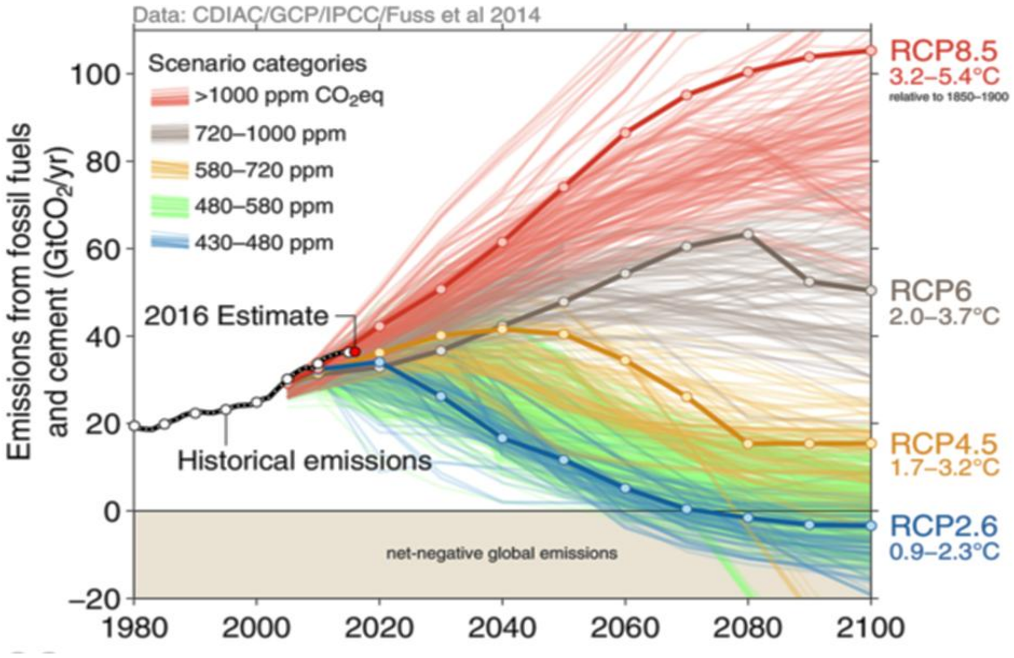
Introduction

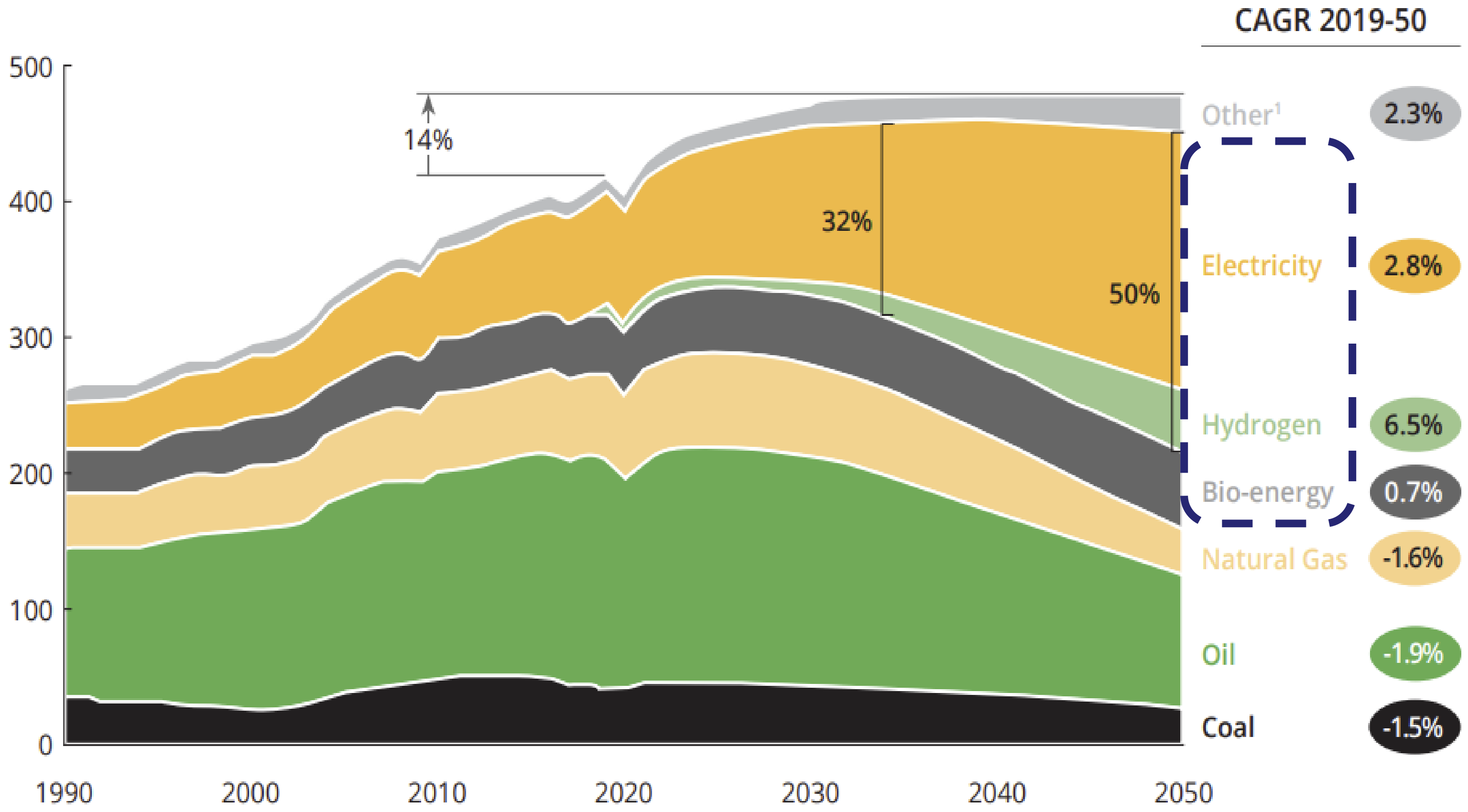
source: tradingeconomics.com

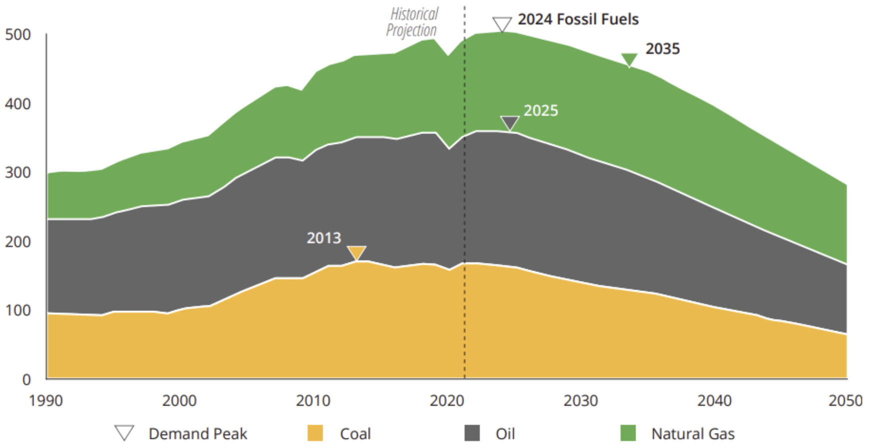


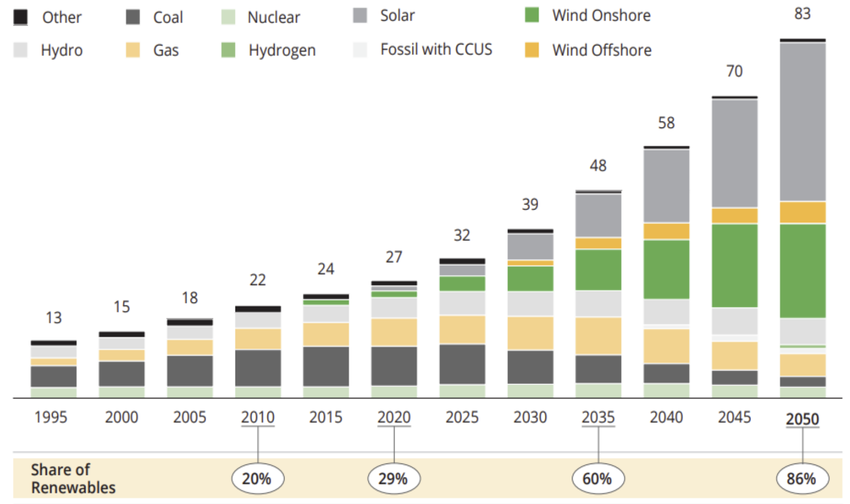
Data: CDIAC/GCP/IPCC/Fuss et al 2014

- ✓ Motor vehicles create approximately one-third (30%) of all carbon dioxide (CO_2) emissions
- ✓ CO_2 emissions from burning of fossil fuels are a significant contributor to global warming and climate change

Global Energy Mix



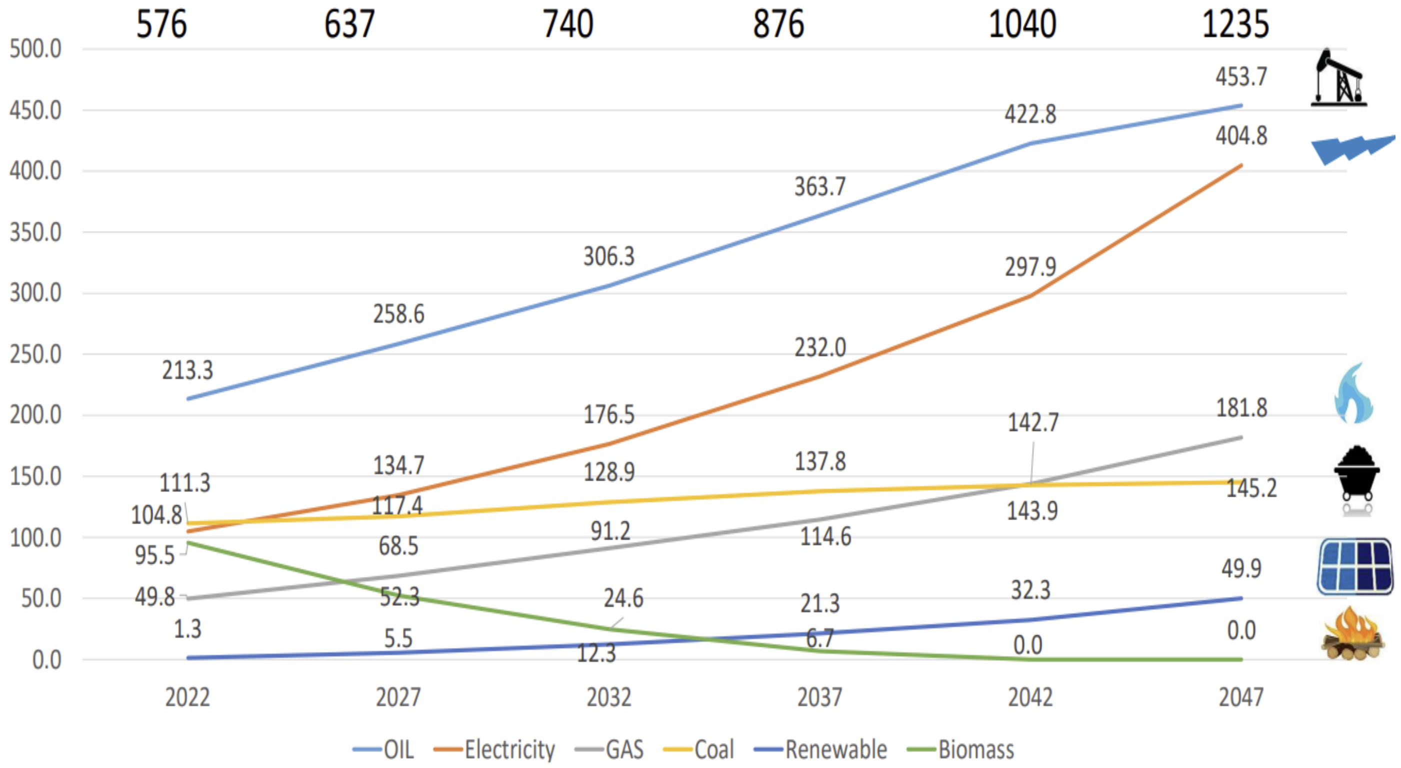




Downward trend of fossil fuels post 2030

Source: The Green S

Indian Energy Mix/Fuel Scenario



- Energy demand doubles by 2047
- Oil grows on same lines. Gas quadruples
- Renewables etc. scale up multiple
- Coal declines in share but grows in volume
- Biomass tails off to nil

Source: Energy Demand Evaluation Outlook Report 2022-2047, PPAC ENDEVOUR`2022

Introduction

- ✓ Among the renewable energy sources, hydrogen can **replace the existing fossil fuels** and can provide solutions to the world's increasing energy demands and climate change, since it has **high calorific value** (142 MJ/ kg) and also clean and environmentally compatible that do not generates greenhouse gases

- ✓ On-board hydrogen **storage** continues to be challenging because gaseous hydrogen should be contained within a small volume without adding significant weight to a vehicle

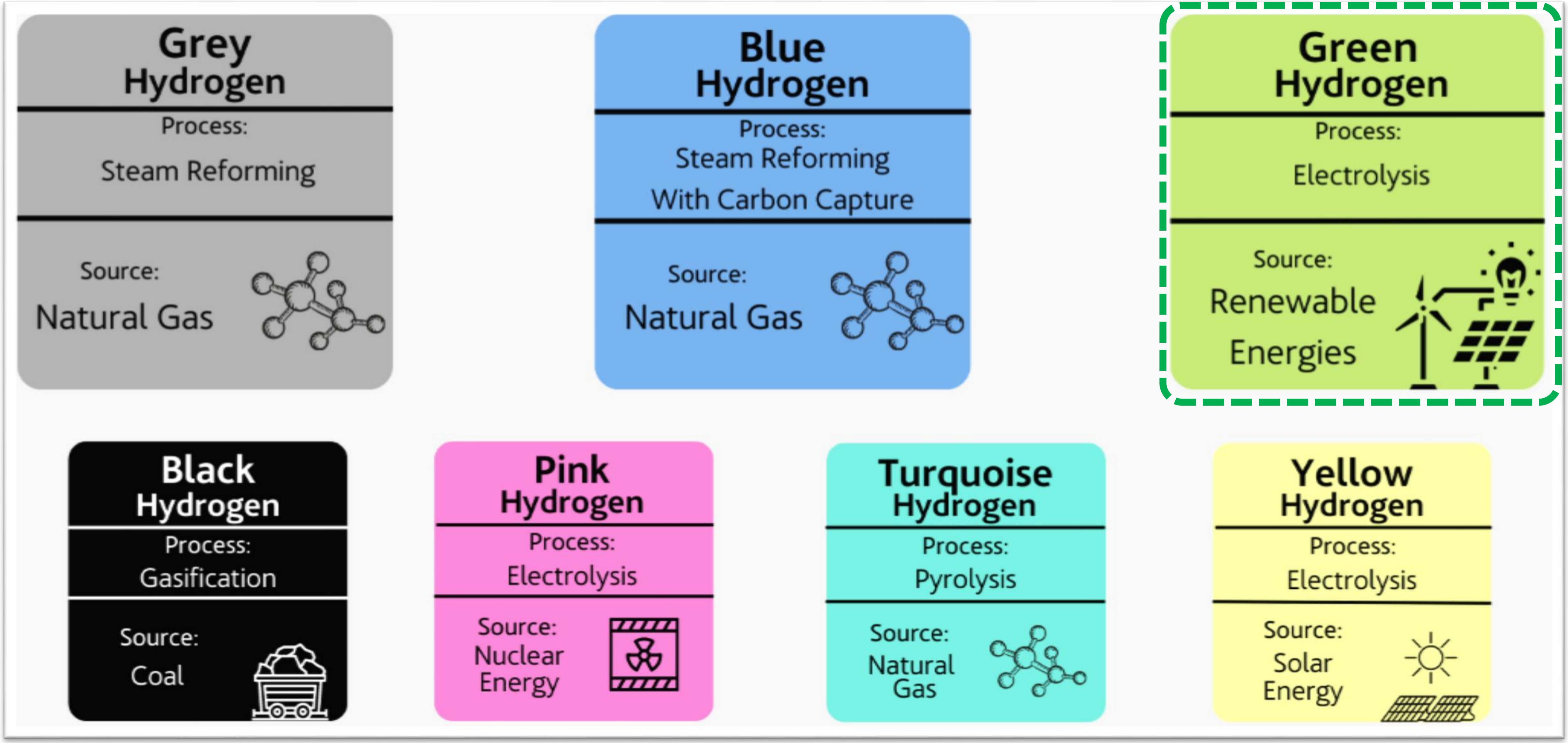
H_2 Advantages:

- High energy density (120-142 MJ/kg)
- Low density (0.09 kg/m^3 at STP)
- Zero emission fuel source

H_2 Challenges:

- Explosive
- Storage problems
- Transportation problems

Types of Hydrogen



Grey Hydrogen
Process:
Steam Reforming
Source:
Natural Gas

Blue Hydrogen
Process:
Steam Reforming
With Carbon Capture
Source:
Natural Gas

Green Hydrogen
Process:
Electrolysis
Source:
Renewable Energies

Black Hydrogen
Process:
Gasification
Source:
Coal

Pink Hydrogen
Process:
Electrolysis
Source:
Nuclear Energy

Turquoise Hydrogen
Process:
Pyrolysis
Source:
Natural Gas

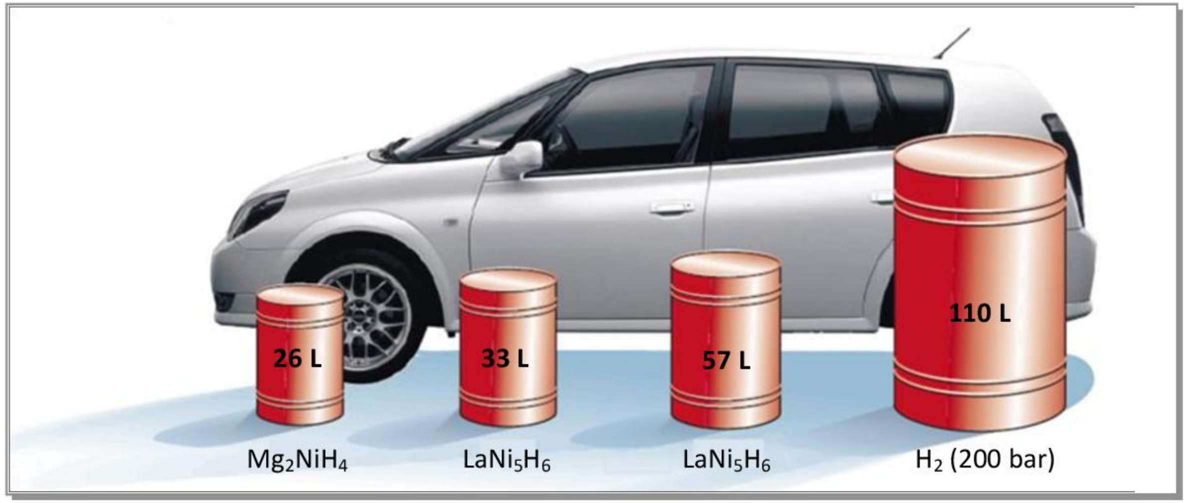
Yellow Hydrogen
Process:
Electrolysis
Source:
Solar Energy

Targets

- US DoE targets production of green Hydrogen **10 MMTPA by 2030**, **20 MMTPA by 2040** and **50 MMTPA by 2050**
- DoE's targets to produce hydrogen at **$2/kg by 2026** and **$1/kg by 2031** ($1 per 1 kilogram in 1 decade ("1 1 1"))
- India's National Green Hydrogen Mission has set a target of producing **5 MMTPA** of green hydrogen by **2030**

- The US DoE has set **hydrogen storage** targets for light-duty automobiles. The targets are:
  - **5.5 wt %** for **2025**
  - **6.5 wt %** as the ultimate target

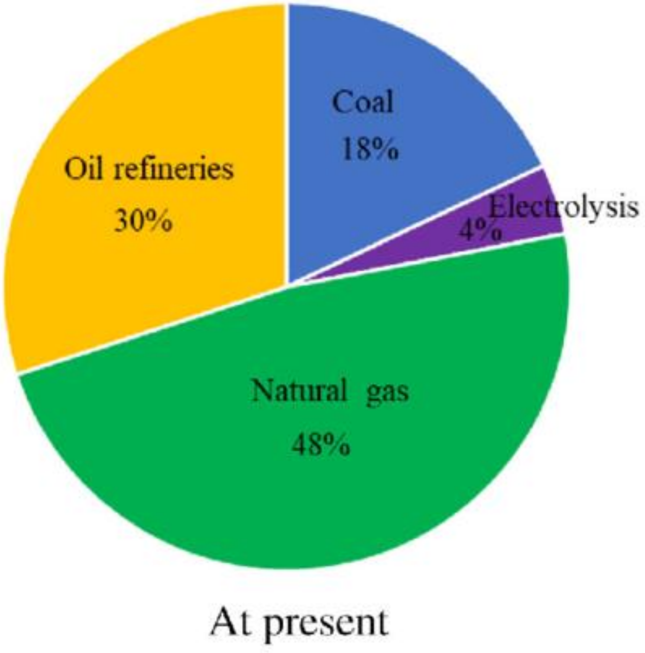
- For realistic driving distances, typically 4 kg of H_2 is required, which occupies nearly 44 m^3 at ambient pressures and temperature conditions



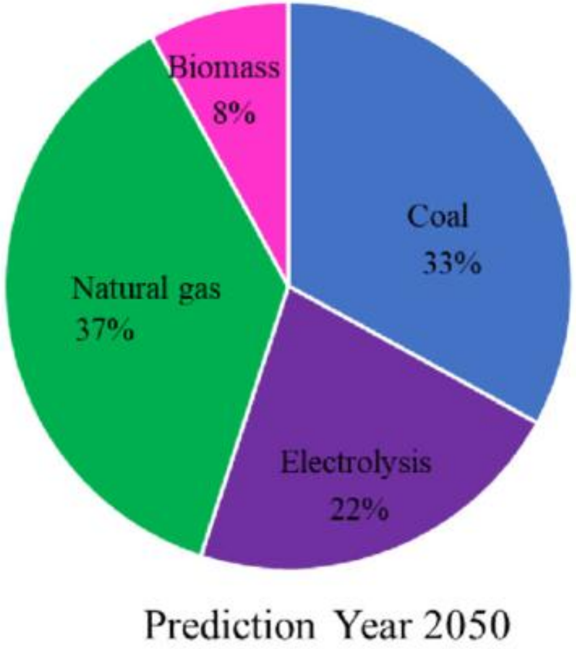
Why Hydrogen Storage?

Hydr

Sources of Hydrogen



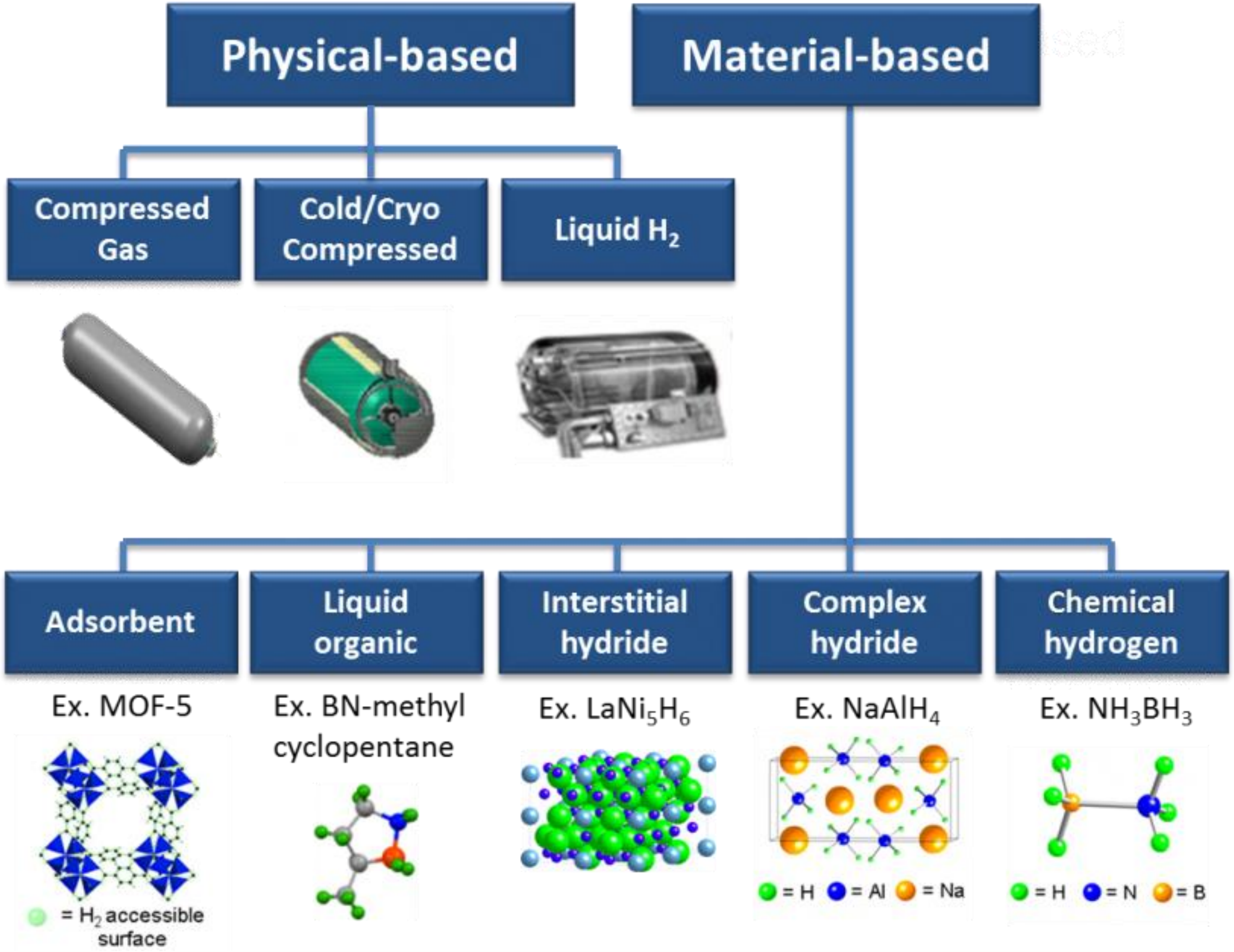
At present



Prediction Year 2050

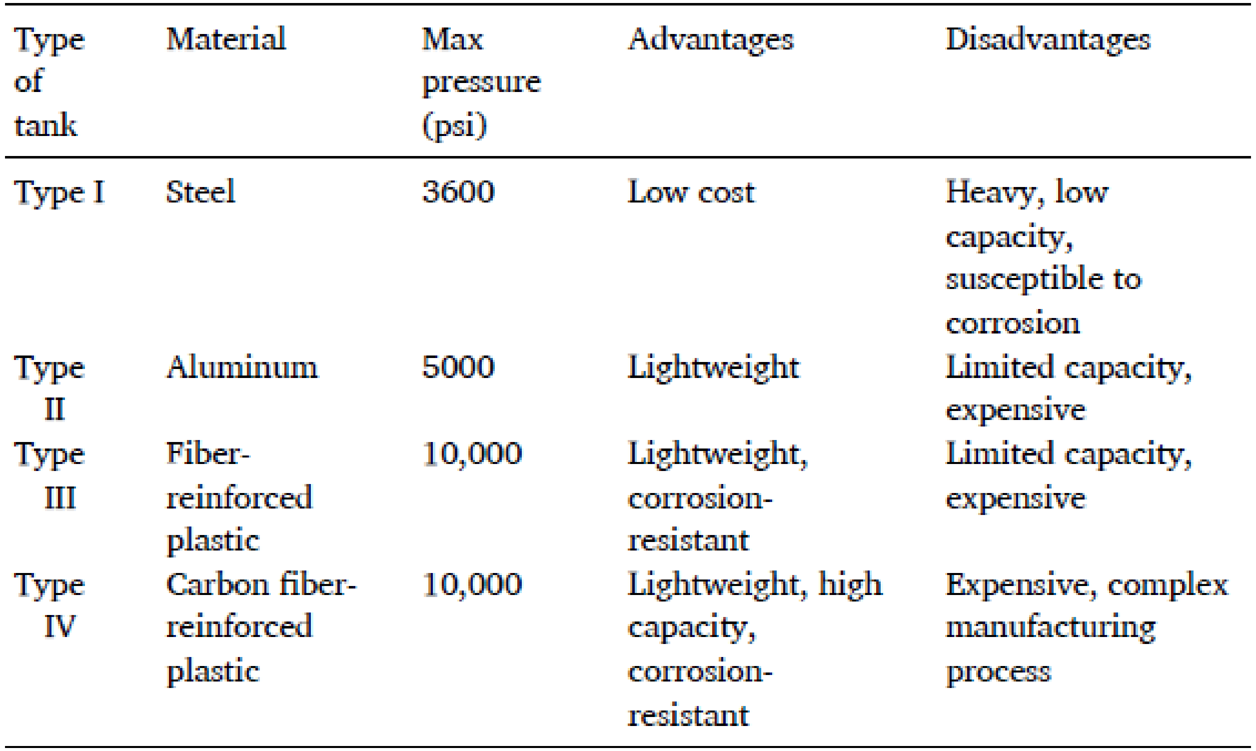
- **Renewable sources**: Wind, solar, geothermal, and biomass
- **Electricity:** From the grid or from renewable sources
- **Other resources:** Water, Nuclear power & Biogas

How Hydrogen is Stored?

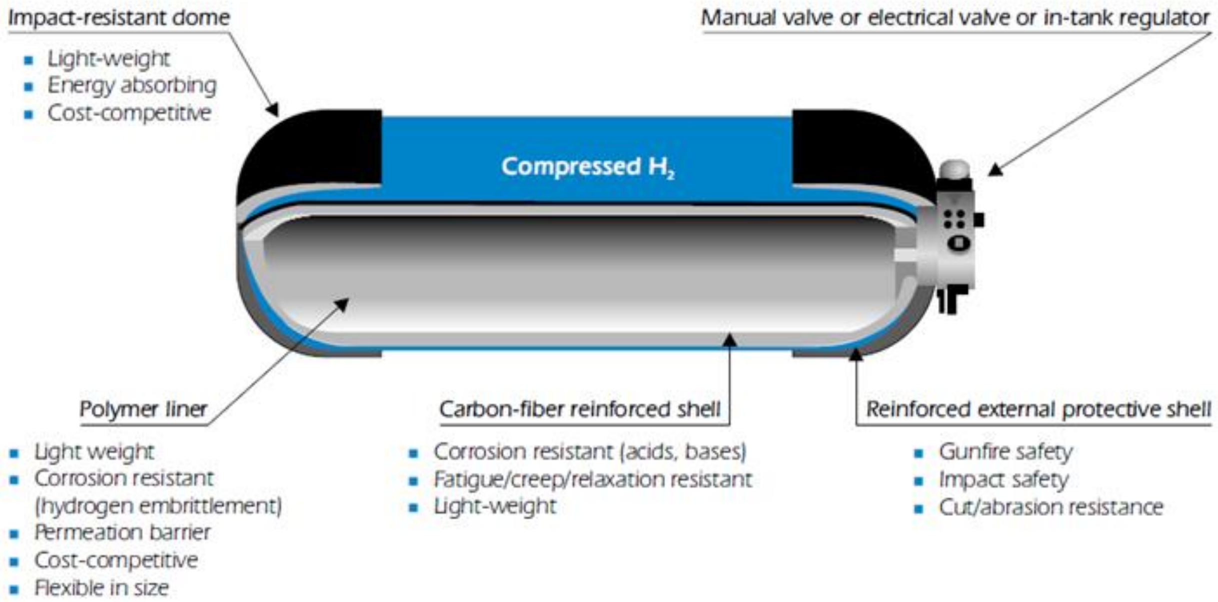


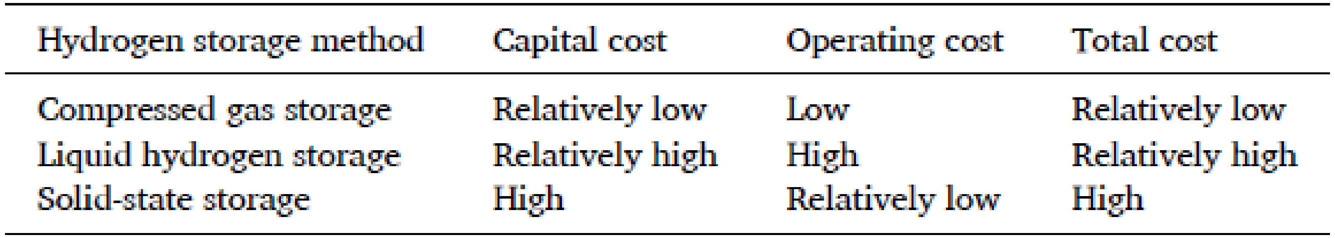
- Physical-based
  - Compressed Gas
  - Cold/Cryo Compressed
  - Liquid H_2
- Material-based
  - Adsorbent: Ex. MOF-5
  - Liquid organic: Ex. BN-methyl cyclopentane
  - Interstitial hydride: Ex. $LaNi_5H_6$
  - Complex hydride: Ex. $NaAlH_4$
  - Chemical hydrogen: Ex. NH_3BH_3

Storage Methods

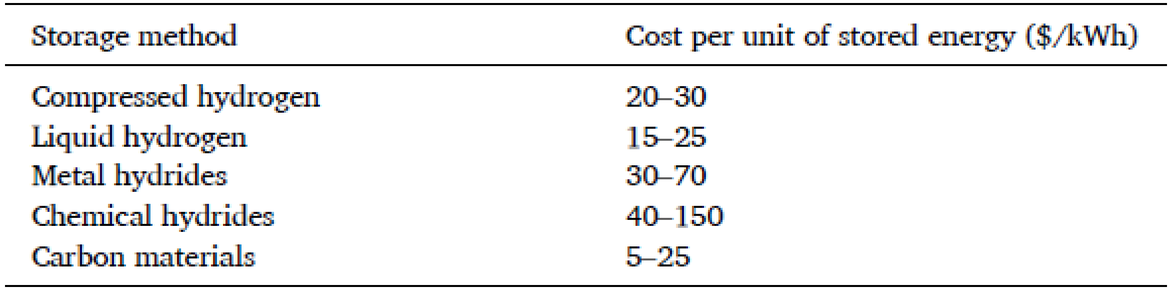


Type of tank	Material	Max pressure (psi)	Advantages	Disadvantages
Type I	Steel	3600	Low cost	Heavy, low capacity, susceptible to corrosion
Type II	Aluminum	5000	Lightweight	Limited capacity, expensive
Type III	Fiber-reinforced plastic	10,000	Lightweight, corrosion-resistant	Limited capacity, expensive
Type IV	Carbon fiber-reinforced plastic	10,000	Lightweight, high capacity, corrosion-resistant	Expensive, complex manufacturing process





Hydrogen storage method	Capital cost	Operating cost	Total cost
Compressed gas storage	Relatively low	Low	Relatively low
Liquid hydrogen storage	Relatively high	High	Relatively high
Solid-state storage	High	Relatively low	High



Storage method	Cost per unit of stored energy ($/kWh)
Compressed hydrogen	20–30
Liquid hydrogen	15–25
Metal hydrides	30–70
Chemical hydrides	40–150
Carbon materials	5–25

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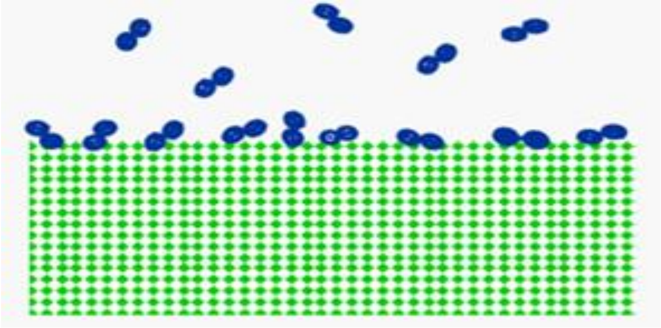
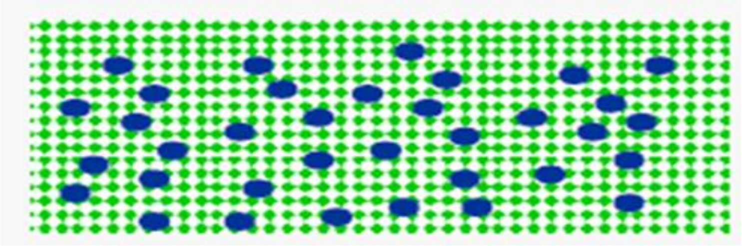
Hydrogen Storage by Adsorption/Absorption

- In adsorption, hydrogen is **attached to the surface of a material** either as hydrogen molecules or as hydrogen atoms.

- In absorption, hydrogen is dissociated into H-atoms, and then the hydrogen atoms are **incorporated into the solid lattice framework**.



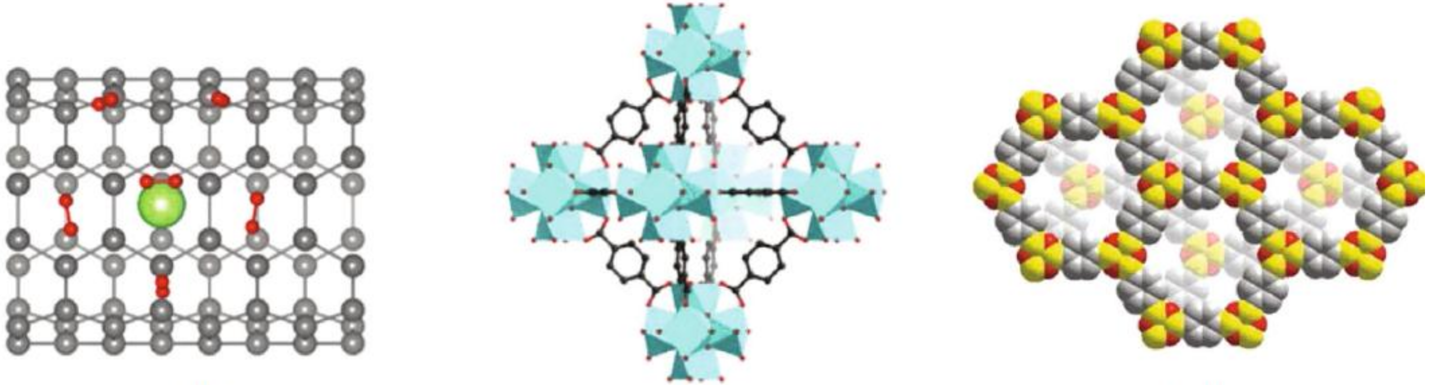
Adsorption of hydrogen



Absorption of hydrogen

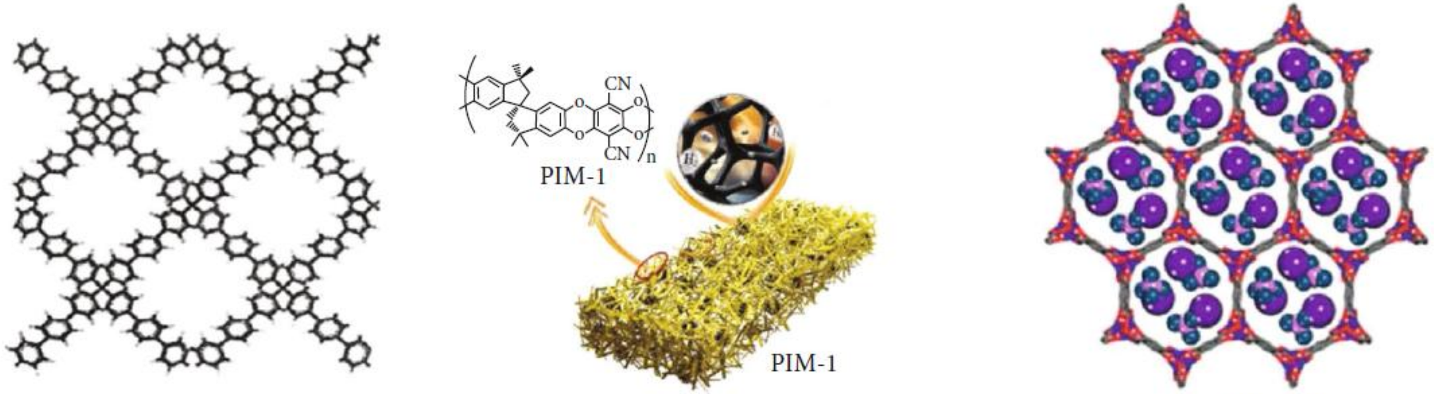
Because of weak interaction, significant physisorption is only observed at low temperatures (<273 K). Due to weakness of the van der Waals bonding**, low temperatures and elevated pressures** must be applied to achieve significant hydrogen storage densities using adsorption.

Nanomaterials for Hydrogen Storage



CNT MOF COF-1

(a) (b) (c)

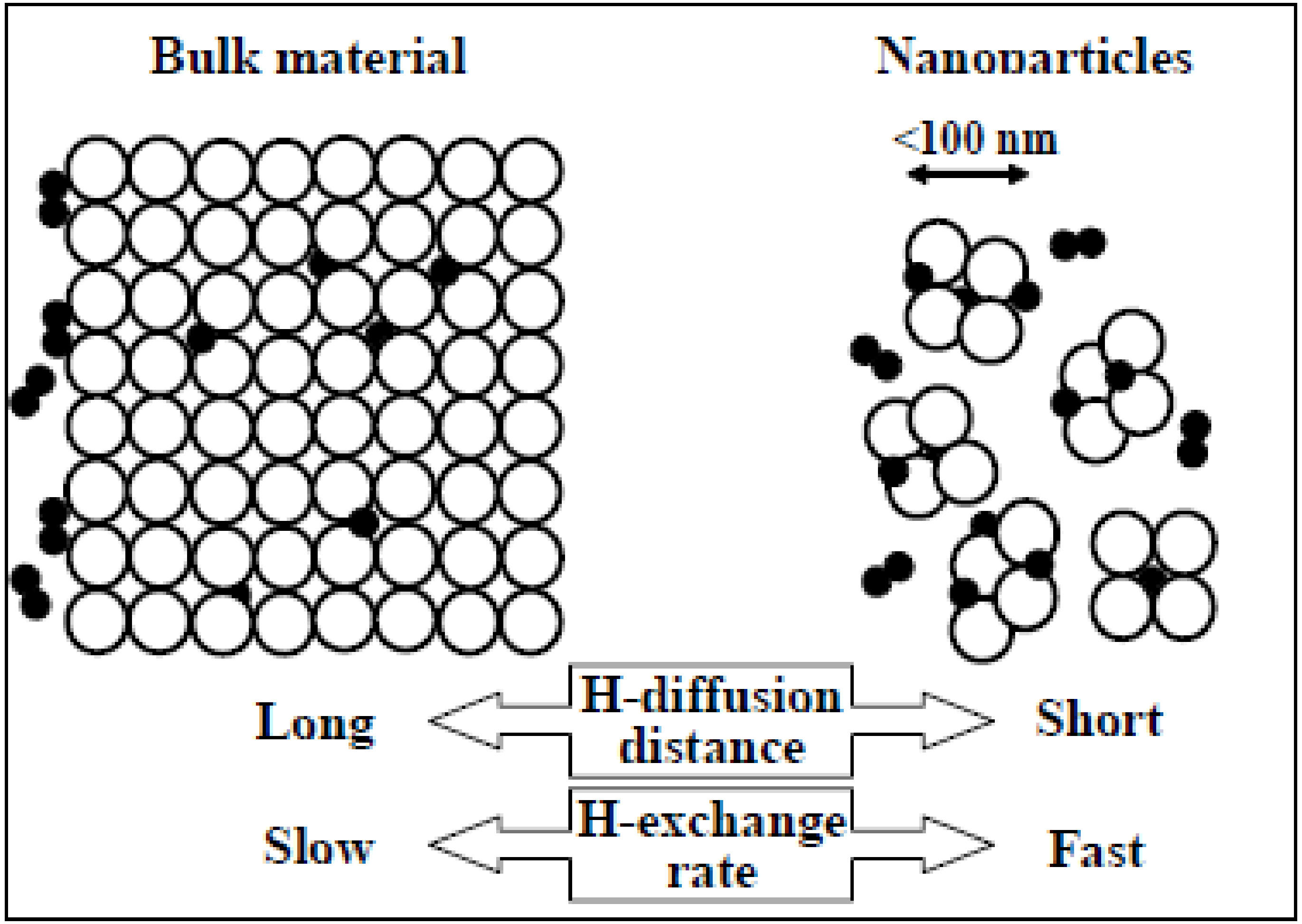


PAF-1 Composite Nano-NaAlH$_4$@MOF-74

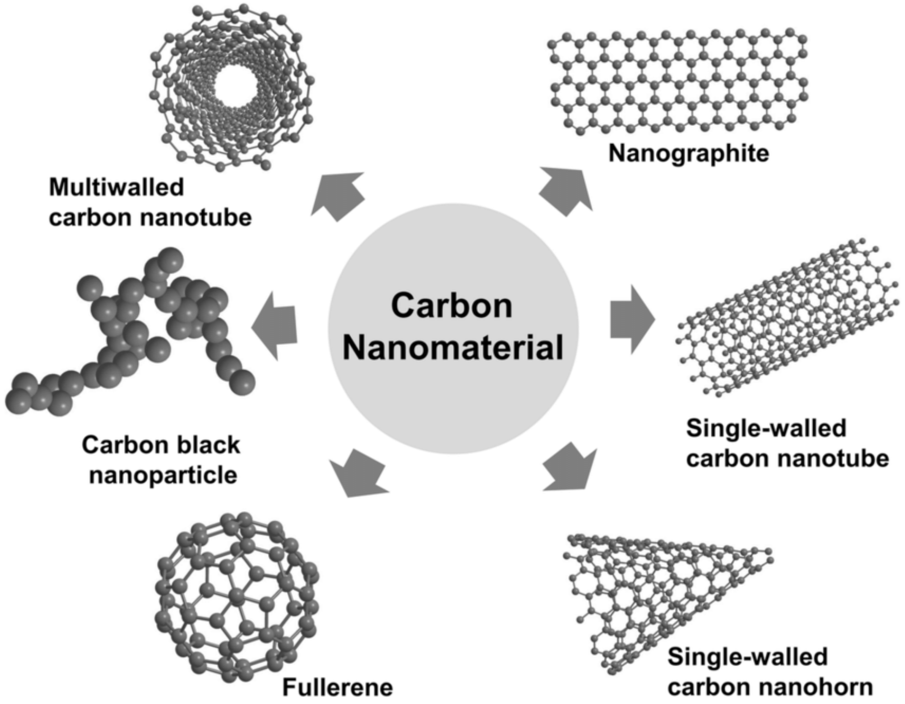
(d) (e) (f)

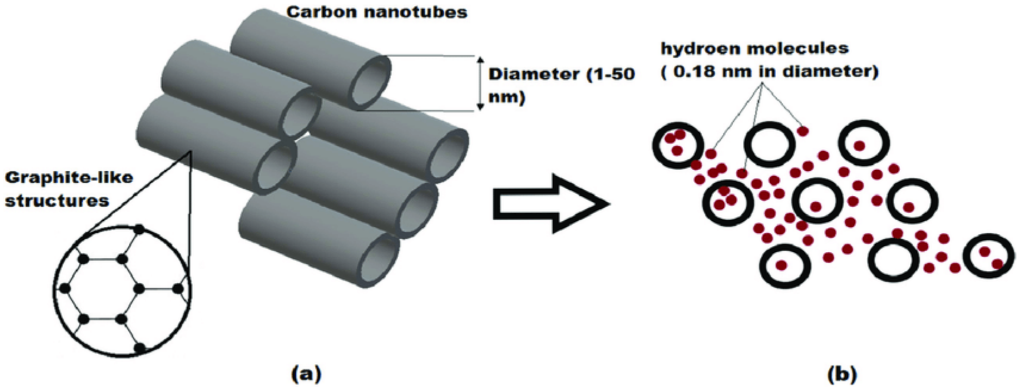
Nanomaterials for Hydrogen Storage

Nanomaterials are superior to macroscopic bulk materials due to higher surface area



Carbon-Based Nanomaterials





Carbon material	Storage conditions Temp. (K)/Press. (bar)	BET surface area ($m^2\ g^{-1}$)	Hydrogen capability (wt%)
AC (Maxsorb)	77/30	3306	5.70
AC (Maxsorb)	303/100	3306	0.67
AC (AX-21)	77/60	2745	10.80
AC (KOH-treated)	298/100	2800	0.85
AC (KOH-treated)	77/20	3190	7.08
AC (KOH-treated)	77/20	2770	6.20
AC (KOH-treated)	77/20	3000–3500	7.03
AC (KOH-treated)	77/19	687	2.14
AC (Pt-doped)	298/100	2033–3798	1.10
AC (Pd-doped)	298/80	2547	5.50
AC ((Ni-B)-doped)	77/1.0	976	1.80
SWCNT	133/0.4	–	5–10
CNT	273–295/1.0	290–800	≤1.0
CNT (film)	298/10	–	8.0
MWCNT	298/148	–	6.3
CNT (Li-doped)	653/1.0	130 (specific)	20
CNT (K-doped)	343/1.0	130 (specific)	14
MWCNT (Ca-doped)	– (electrochemical)	–	0.3
MWCNT (Co-doped)	– (electrochemical)	–	1.05
MWCNT (Fe-doped)	– (electrochemical)	–	1.5
MWCNT (Ni-doped)	– (electrochemical)	–	0.75
MWCNT (Pd-doped)	– (electrochemical)	–	0.4
CNF	298/120	51	6.54
CNF (KOH-treated)	77/40	1500–1700	3.45
CNF (N-doped)	298/100	870 (specific)	2.0
CNF (Ni-doped)	298/100	1310	2.2

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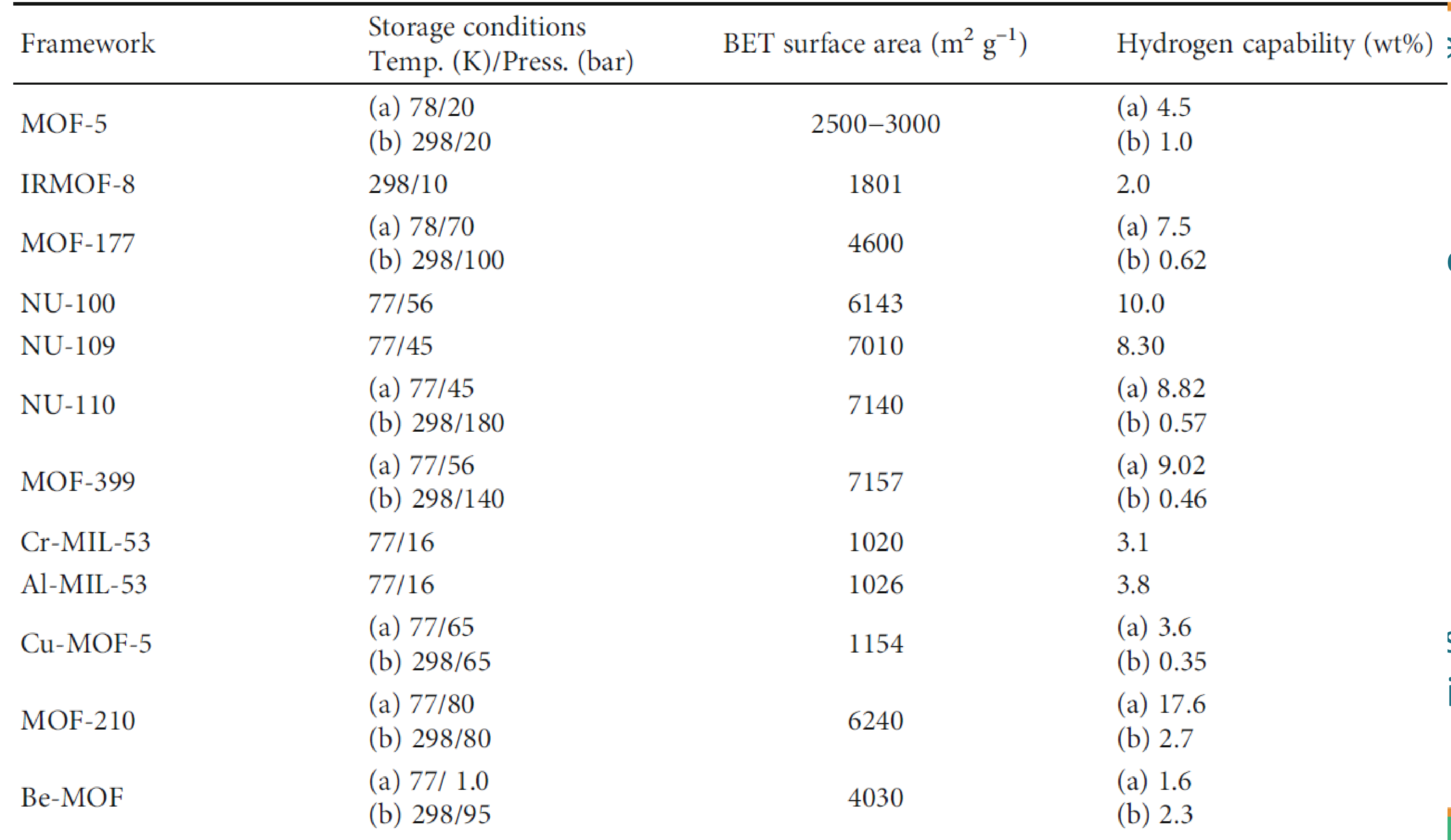
MOFs for Hydrogen Storage

- Metal … that c … molec … aterials … 'linker'

- Due t … e area … (tunal … s … ity



Framework	Storage conditions Temp. (K)/Press. (bar)	BET surface area (m^2 g^{-1})	Hydrogen capability (wt%)
MOF-5	(a) 78/20 (b) 298/20	2500–3000	(a) 4.5 (b) 1.0
IRMOF-8	298/10	1801	2.0
MOF-177	(a) 78/70 (b) 298/100	4600	(a) 7.5 (b) 0.62
NU-100	77/56	6143	10.0
NU-109	77/45	7010	8.30
NU-110	(a) 77/45 (b) 298/180	7140	(a) 8.82 (b) 0.57
MOF-399	(a) 77/56 (b) 298/140	7157	(a) 9.02 (b) 0.46
Cr-MIL-53	77/16	1020	3.1
Al-MIL-53	77/16	1026	3.8
Cu-MOF-5	(a) 77/65 (b) 298/65	1154	(a) 3.6 (b) 0.35
MOF-210	(a) 77/80 (b) 298/80	6240	(a) 17.6 (b) 2.7
Be-MOF	(a) 77/ 1.0 (b) 298/95	4030	(a) 1.6 (b) 2.3

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Metal hydrides for Hydrogen Storage

- Metal hydrides and complex hydrides offer high gravimetric capacity. However, the **high operating temperature** and **low reversibility** hindered the practical implementation

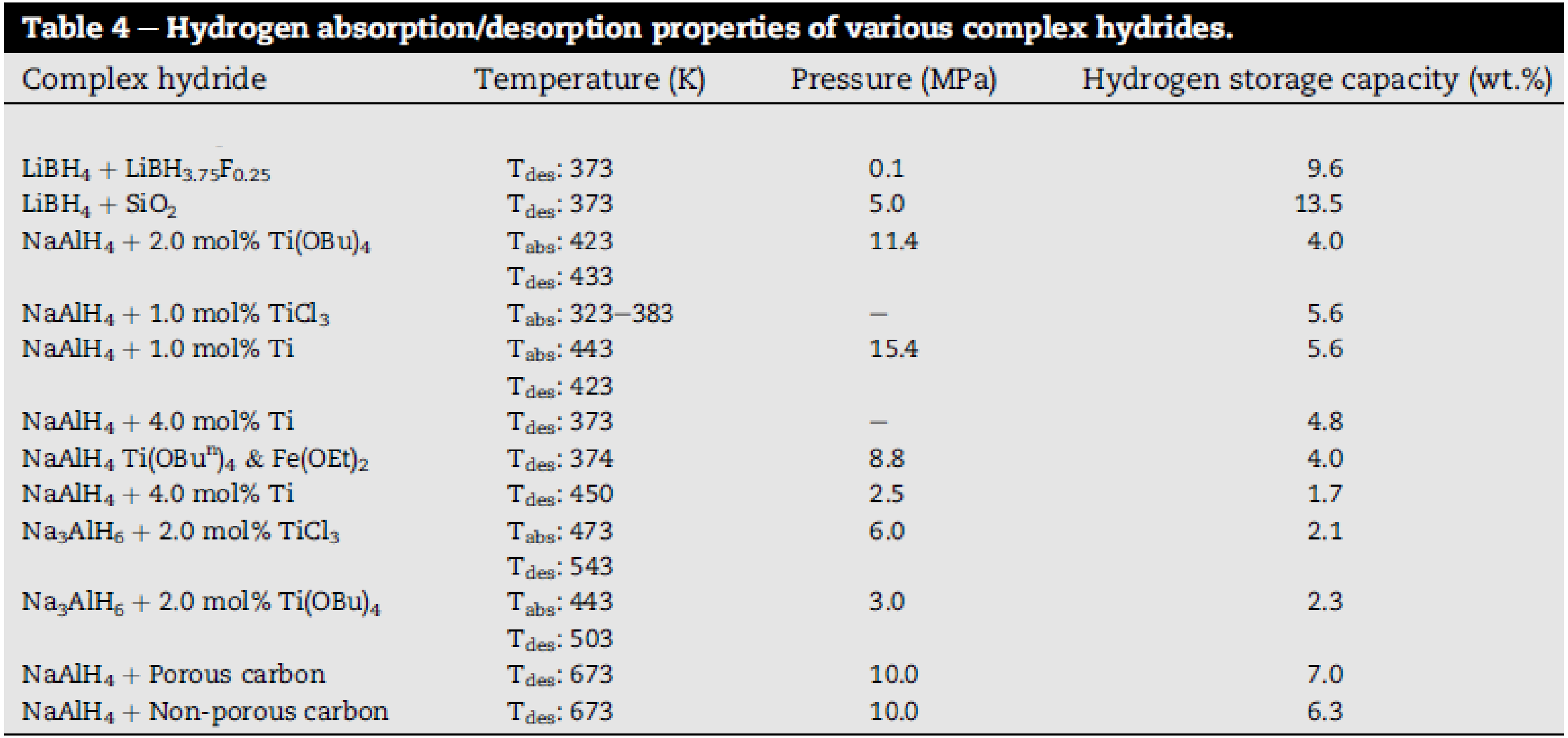
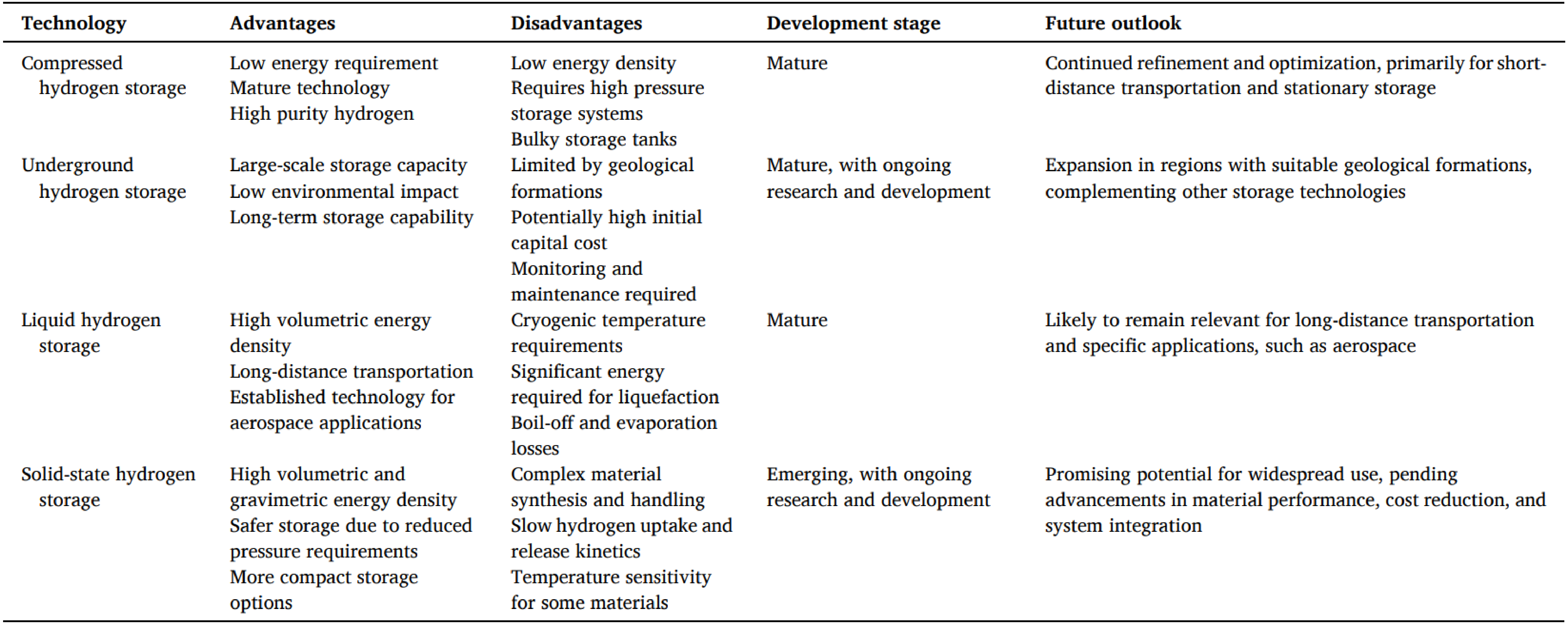


Table 4 – Hydrogen absorption/desorption properties of various complex hydrides.

Complex hydride	Temperature (K)	Pressure (MPa)	Hydrogen storage capacity (wt.%)
$LiBH_4 + LiBH_{3.75}F_{0.25}$	T_{des}: 373	0.1	9.6
$LiBH_4 + SiO_2$	T_{des}: 373	5.0	13.5
$NaAlH_4$ + 2.0 mol% $Ti(OBu)_4$	T_{abs}: 423 T_{des}: 433	11.4	4.0
$NaAlH_4$ + 1.0 mol% $TiCl_3$	T_{abs}: 323–383	–	5.6
$NaAlH_4$ + 1.0 mol% Ti	T_{abs}: 443 T_{des}: 423	15.4	5.6
$NaAlH_4$ + 4.0 mol% Ti	T_{des}: 373	–	4.8
$NaAlH_4$ $Ti(OBu^n)_4$ & $Fe(OEt)_2$	T_{des}: 374	8.8	4.0
$NaAlH_4$ + 4.0 mol% Ti	T_{des}: 450	2.5	1.7
Na_3AlH_6 + 2.0 mol% $TiCl_3$	T_{abs}: 473 T_{des}: 543	6.0	2.1
Na_3AlH_6 + 2.0 mol% $Ti(OBu)_4$	T_{abs}: 443 T_{des}: 503	3.0	2.3
$NaAlH_4$ + Porous carbon	T_{des}: 673	10.0	7.0
$NaAlH_4$ + Non-porous carbon	T_{des}: 673	10.0	6.3

Hydrogen Storage Technologies



Technology	Advantages	Disadvantages	Development stage	Future outlook
Compressed hydrogen storage	Low energy requirement Mature technology High purity hydrogen	Low energy density Requires high pressure storage systems Bulky storage tanks	Mature	Continued refinement and optimization, primarily for short-distance transportation and stationary storage
Underground hydrogen storage	Large-scale storage capacity Low environmental impact Long-term storage capability	Limited by geological formations Potentially high initial capital cost Monitoring and maintenance required	Mature, with ongoing research and development	Expansion in regions with suitable geological formations, complementing other storage technologies
Liquid hydrogen storage	High volumetric energy density Long-distance transportation Established technology for aerospace applications	Cryogenic temperature requirements Significant energy required for liquefaction Boil-off and evaporation losses	Mature	Likely to remain relevant for long-distance transportation and specific applications, such as aerospace
Solid-state hydrogen storage	High volumetric and gravimetric energy density Safer storage due to reduced pressure requirements More compact storage options	Complex material synthesis and handling Slow hydrogen uptake and release kinetics Temperature sensitivity for some materials	Emerging, with ongoing research and development	Promising potential for widespread use, pending advancements in material performance, cost reduction, and system integration

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Hydrogen-Future Prospective

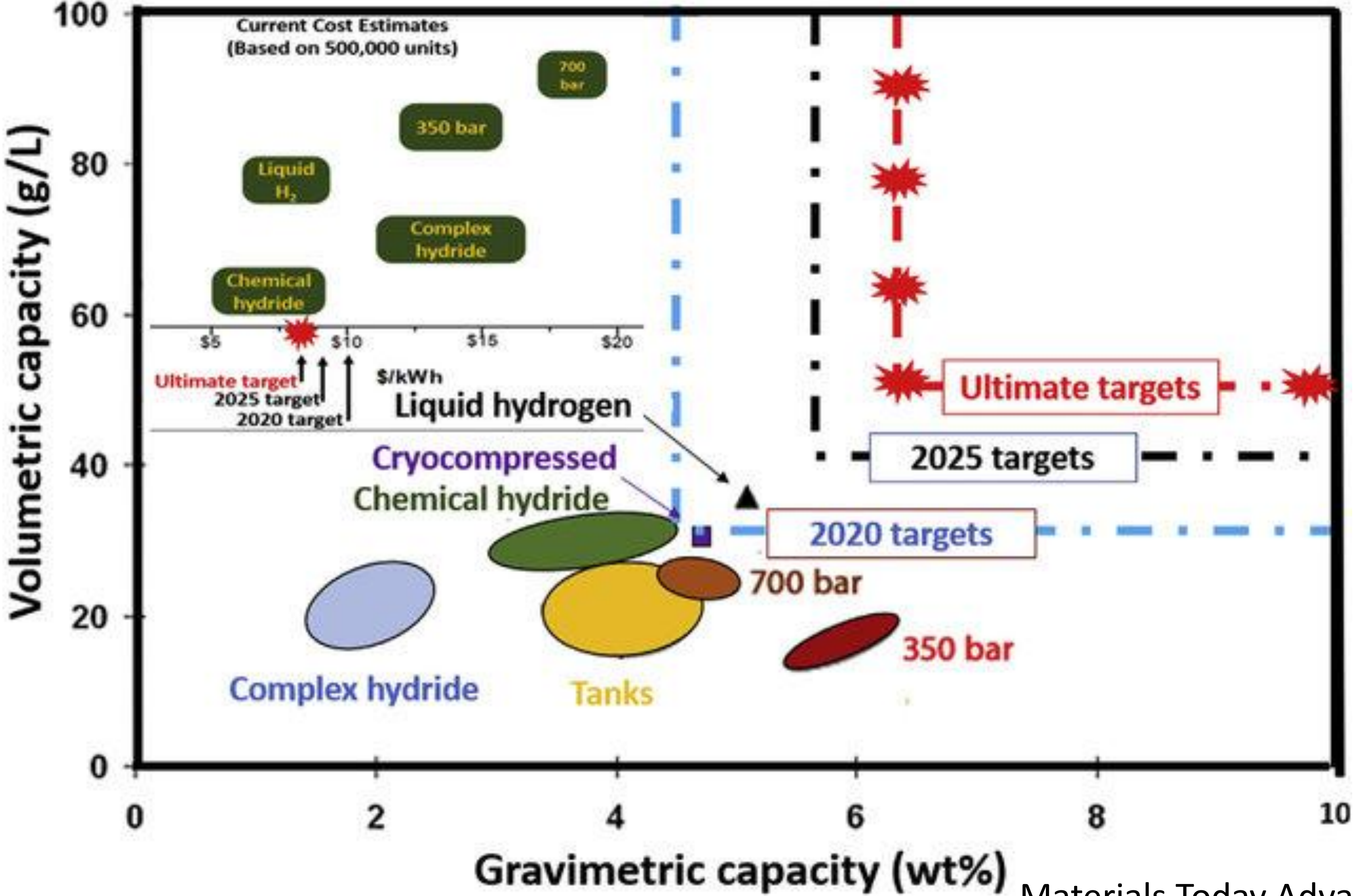
- Long-term, reliable policies adoption to encourage novel technologies and market growth
- Advanced Hydrogen production, purification and storage technologies
- Improved and low-priced electrolyzers
- Entire **hydrogen industry** chain such as hydrogen production, storage and transportation, fuel cells, hydrogen refueling stations and other scenarios should be accelerated. Besides, in-depth **integration and coordination** with the **oil and gas industry** needs more attention, which will rapidly promote the high-quality development of the hydrogen industry system

Team

Dr. Ramesh Kumar K, Dr. Madhavi Konni, Dr. Abinaya K, Dr. Prashant Mishra, Dr. T.A. Rajiv Kumar, Dr. B. Ramachandra Rao, Shri. Vipul Kumar Maheshwari and Dr. Raman Ravishankar

Thank you

Hydrogen Storage Systems-Current Status



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