A mobile H_2-solid-state tank based on highly porous nanomaterials for explosion proof storage of large amounts of hydrogen at high density, moderate pressure and room temperature

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Abstract: Hydrogen has the potential to become one of the most important energy sources of the future and will also be a key pillar of the energy transition from fossile to alternative energy sources, due to its high energy content of up to 142 MJ/kg, exceeding that of gazoline by about a factor of 3. Since its combustion product is only pure water, it will make a significant contribution to global CO_2 reduction, and its application will create millions of new jobs and a huge business volume. The production of so-called "green hydrogen" by electrolysis of water using renewable energies is the most sustainable production process. A joint research project, is proposed here, which aims at the development of a light-weight, mobile and operational save tank for the storage of large quantities of hydrogen at very high density in a solid, nano-crystalline material. This new technique will replace the nowadays applied very energy-inefficient and hazardous technology of storage of H_2 gas at the extreme pressure of 700 bar. As novel H_2 storage solid nano-material a 3D-multilayer graphene-on-diamond heterostructure, doped with light elements, has been chosen with especially high thermal conductivity. Due to its very large nano-porosity, corresponding to an extreme specific surface area, this superlight material behaves like a H_2 absorbing sponge, very suitable for its reversible and high-density storage.

Hydrogen is the fuel of the future

<u>**Battery-powered Electric Vehicles (BEV)**</u>

- long refueling time: min. 15 min, max. 8 hours
- limited range: ~200 km (during winter: ~90km)
- emission-free only if *Alternative Energy* (so-called *"Green Energy"*) is used for the production of electrical current.

<u>**H_2-Compressed-Gas powered Fuel-Cell Electric Vehicles (FCEV)**</u>

- fast refueling time: ~ 5 min (6 kg H_2)
- limited range: ~ 300 km (with very large and expensive tanks)
- operational unsafe (risk of explosion !)
- H2-CG storage is very energy inefficient technology
- emission-free only if H_2 is produced by *Alternative Energies.*

<u>**Advantages of FCEV with H_2-Storage Solid Material Tanks**</u>

- large driving range (at least 600 km with volume of gazoline tank)
- operational safe (no risk of explosion !)

HY4 Emission-Free, Light Aircraft (DLR)

L=7.4m,wingspan=21.4m,M=1500kg; 1st flight: 11/29/2016

Toyota Mirai

L = 4.89 m, M = 1850 kg

2x CG-Tanks: p = 700bar

5 kg H_2 → Range ~500km

$V_{tank}=2 \cdot 60$ l , $V_{trunk}=36$ l

114 kW-Battery recharged by FC during driving (7 - 8 l H_2O /100 km).

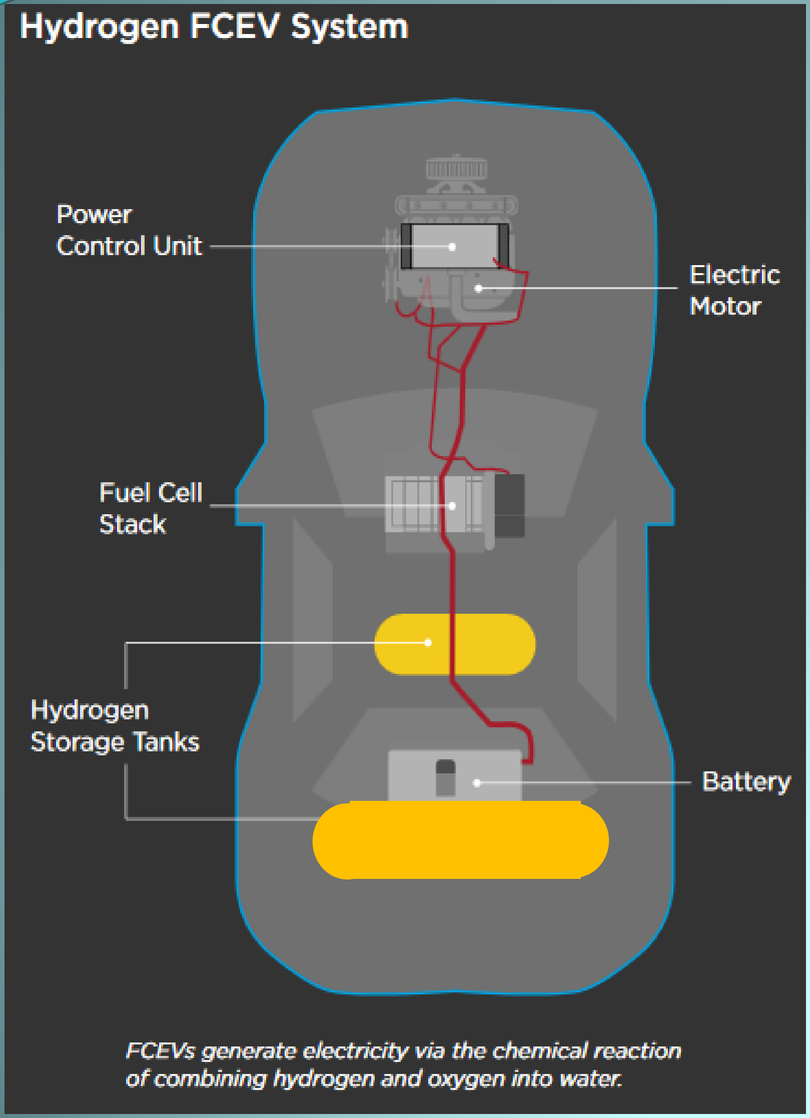
2 high-pressure tanks: p = 350 bar, 8 kg H_2
→ Range: ~750 km

Low-T. – PEM-FC:	45kW	(Co."Hydrogenics")
Li-Ion battery:	21 kWh	4 passengers
E-motor:	80 kW	speed: ≤200 km/h

Not suitable for future air traffic !

The very high E requirement of large aircrafts can only be achieved by explosion-proof H_2 tanks.

The Hydrogen Storage Solid Material Tank



Disadvantages of 700bar-H_2-CG-Tank

- potential hazard due to the high pressure of 700bar-H_2-CG-tanks when used by laymen danger of **oxyhydrogen** & **pressure explosion**,
- low energy density of H_2-Compressed Gas,
- About 30 % of the stored energy are spent for compression of H_2 to high pressures,
- very voluminous and expensive C-fiber tanks.

Advantages of the novel "HySSMat"- Tank

- moderate-pressure tank with H_2 explosion-proof bound in a crystalline lattice structure. For escape of H_2 gas in case of a burst of tank vessel desorption energy is needed.
- HySSMat - Tank has about 6- to 8-times higher energy density than a H_2-CG Tank.
- volume of the HySSMat-Tank is much smaller, about the same size as a normal gasoline tank.

Necessary Properties of a Novel Nanomaterial

Required properties of solid-state storage material:

- **high mech., chem. and thermal stability**
- **solid , inorganic 3-dimensional morphology** (no organic materials, like MOFs)
- **no bulk powder** (with its rather low thermal conductivity)
- **super-light, sponge-like nano-crystalline molecular 3D-structure**
  - consisting of the light carbon atoms
  - cage-like molecular structure
  - nm-porousity and extremely large **SSA** (>1000 $m^2\ g^{-1}$) → superlight
  - very high thermal conductivity of multi-layer graphene storage material and diamond waver as substrate (graphene: ~5000 W/(mK) & diamond: ~2300 W/(mK))
- **As H_2 Storage Solid Material with these optimum properties we have selected a multi-layer Graphene-on-Diamond Heterostructure**

H_2 Storage Materials

Ref: A. Züttel, "Materials for hydrogen storage", materialstoday, Septemper (2003), pp. 18-27

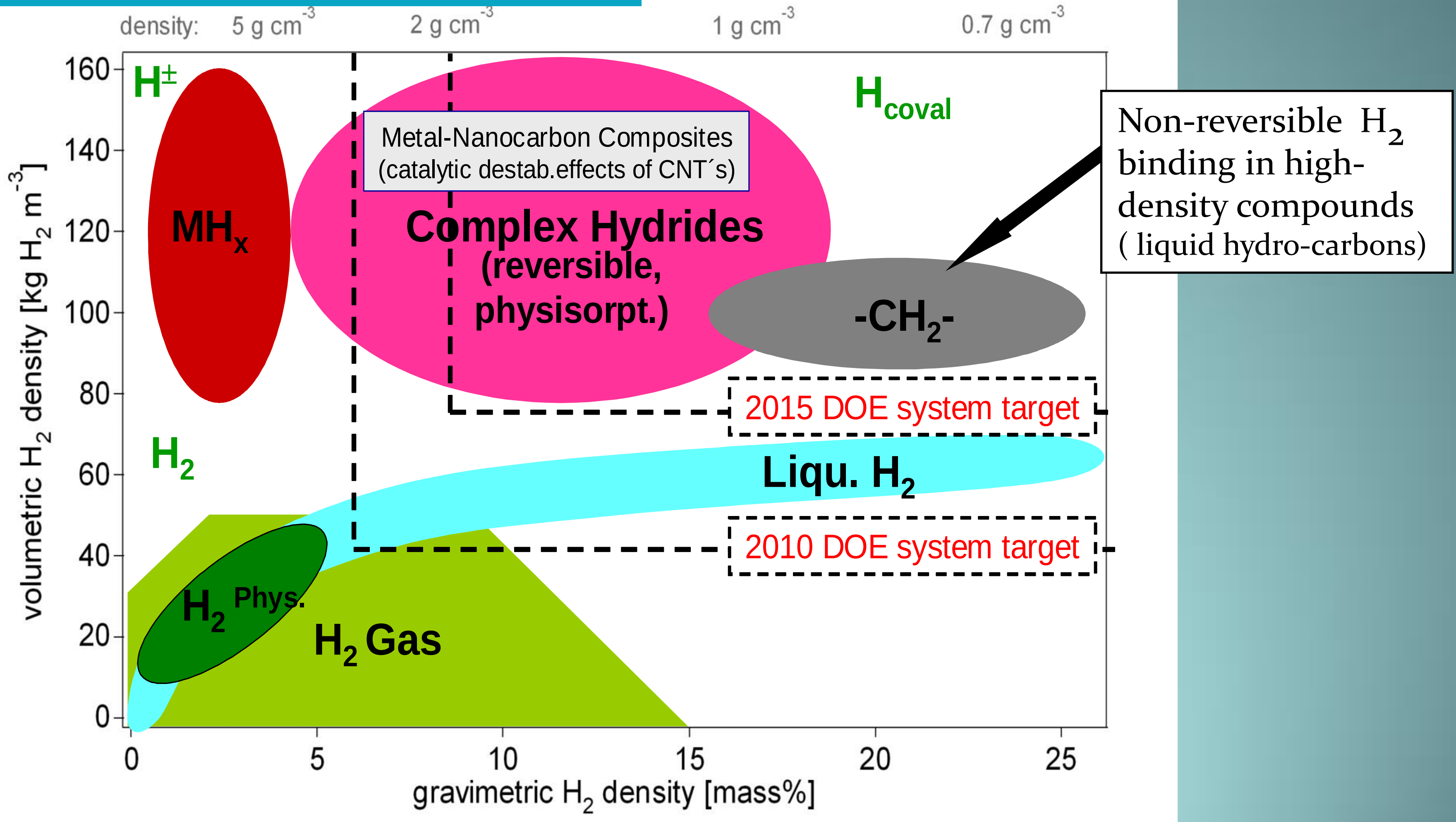
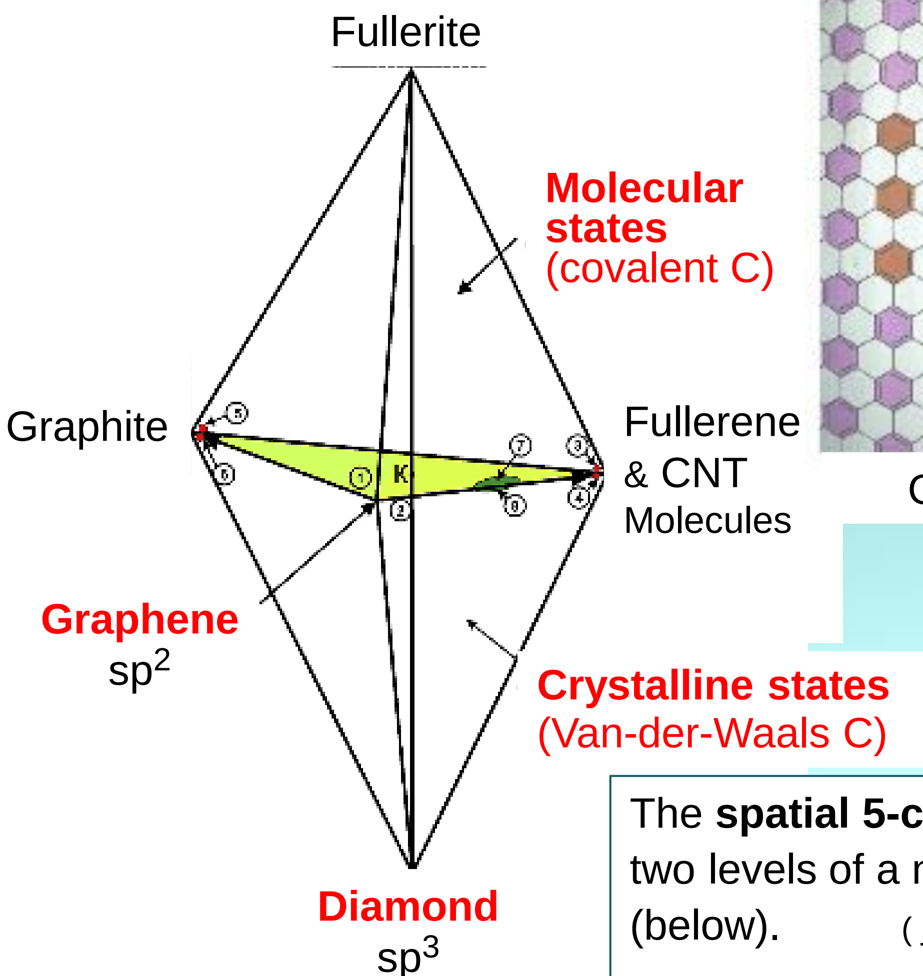
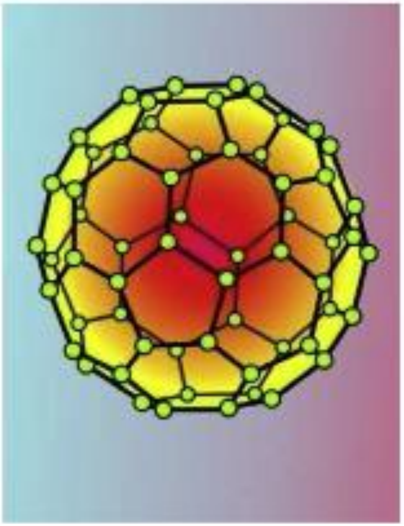


Diagram of Carbon Allotropes



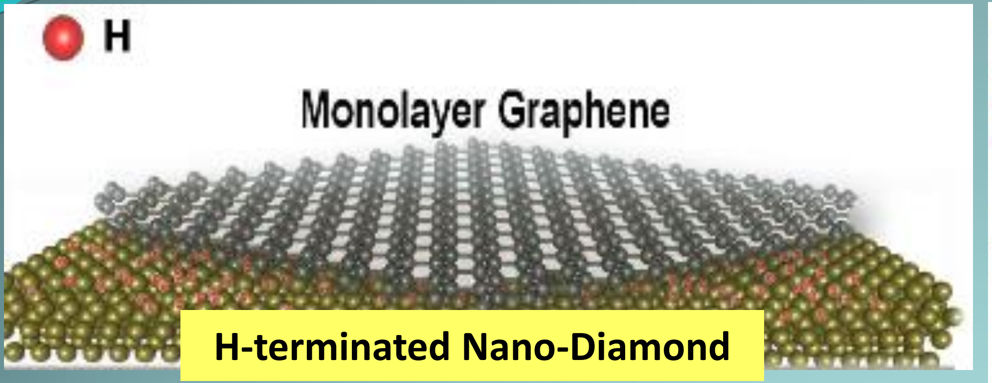


Graphene Nanotubes C_{60} Fullerene

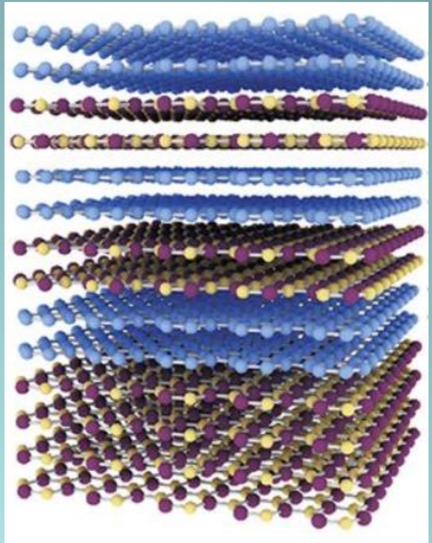
Nano-Crystalline Carbon

The **spatial 5-component state diagram** of carbon allotropes on two levels of a matter morphology, molecular (top) and crystalline (below). (ref. : D.V. Schur et al., in "Carbon nanomaterials in clean energy hydrogen systems, Dordrecht, NL, Springer (2008) p. 67-83.)

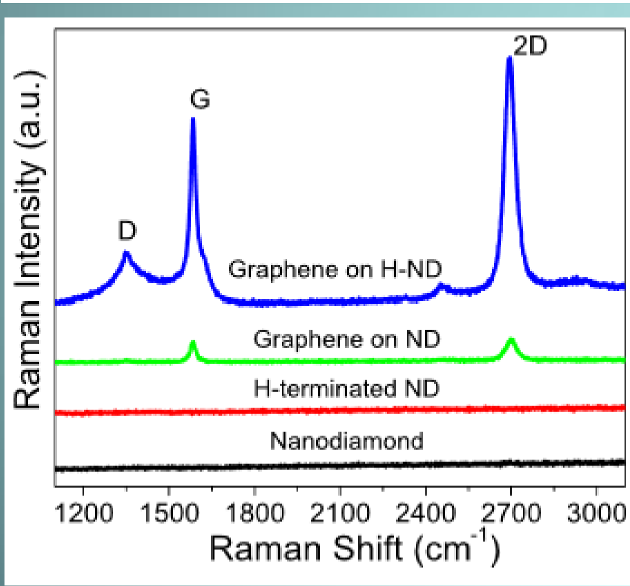
Morphology of van-der-Waals Heterostructures



Graphene on Hydrogen-terminated-Nanodiamond Heterostructure (schematic)
(Fang Zhao, Sci. Reports 5:13771, DOI: 10.1038/srep13771)



Nano-Crystals of layers of graphene held together by **van- der-Waals forces** are deposited by **CVD** on both sides of nano-diamond wavers, forming a 3-dimensional **Graphene-on-Diamond**



Raman spectra

graphene-H-ND

graphene-ND

H-ND

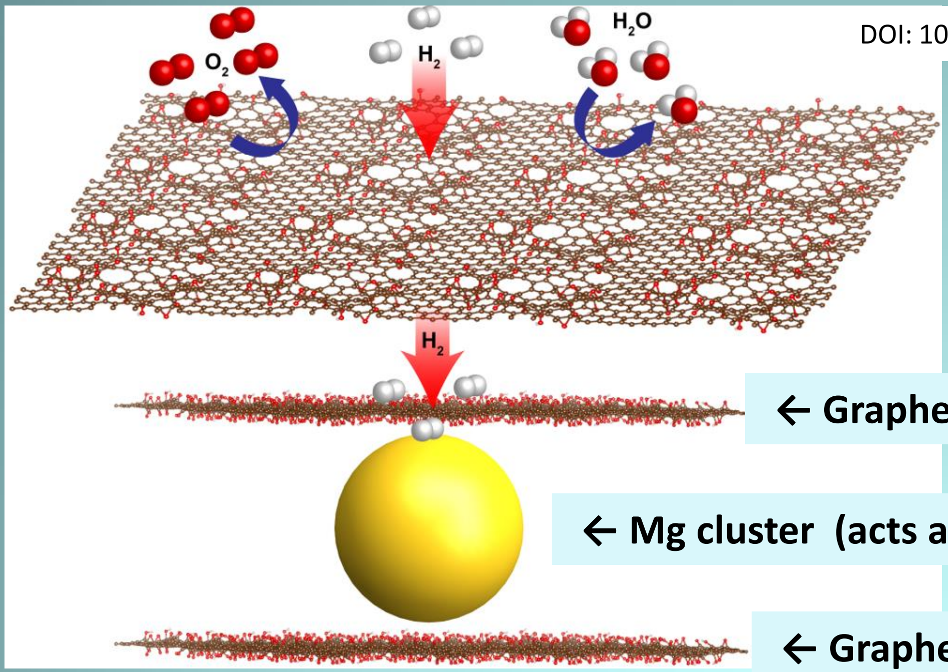
ND

Fig. (left top): Doping of nano-crystalls with light atoms: **carbon atoms** are shown by **blue** spheres, **boron atoms** in **yellow** and **nitrogen** in **purple**.

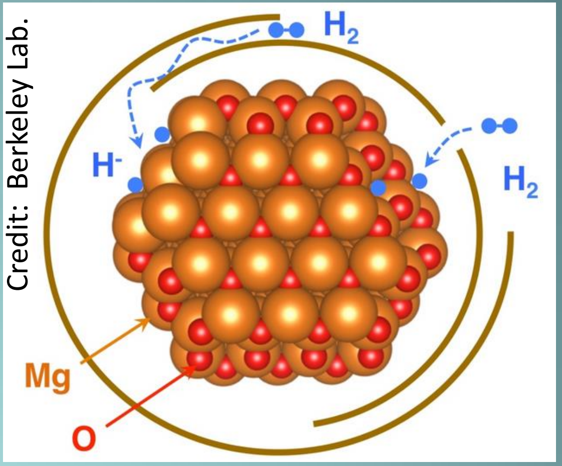
Instead of light elements also alloys or compounds can be intercalated between the C-layers :
(a) hBN layers (hexagonal rings of alternating B and N, with strong covalent sp_2 bonds.
(b) Layered oxides used for alloying, combining layers and intercalating of ions and molecules.

Mg atoms Envelopped by Graphene

O_2 H_2 H_2O *impermeable to graphene*



DOI: 10.1038/ncomms10804



Credit: Berkeley Lab.

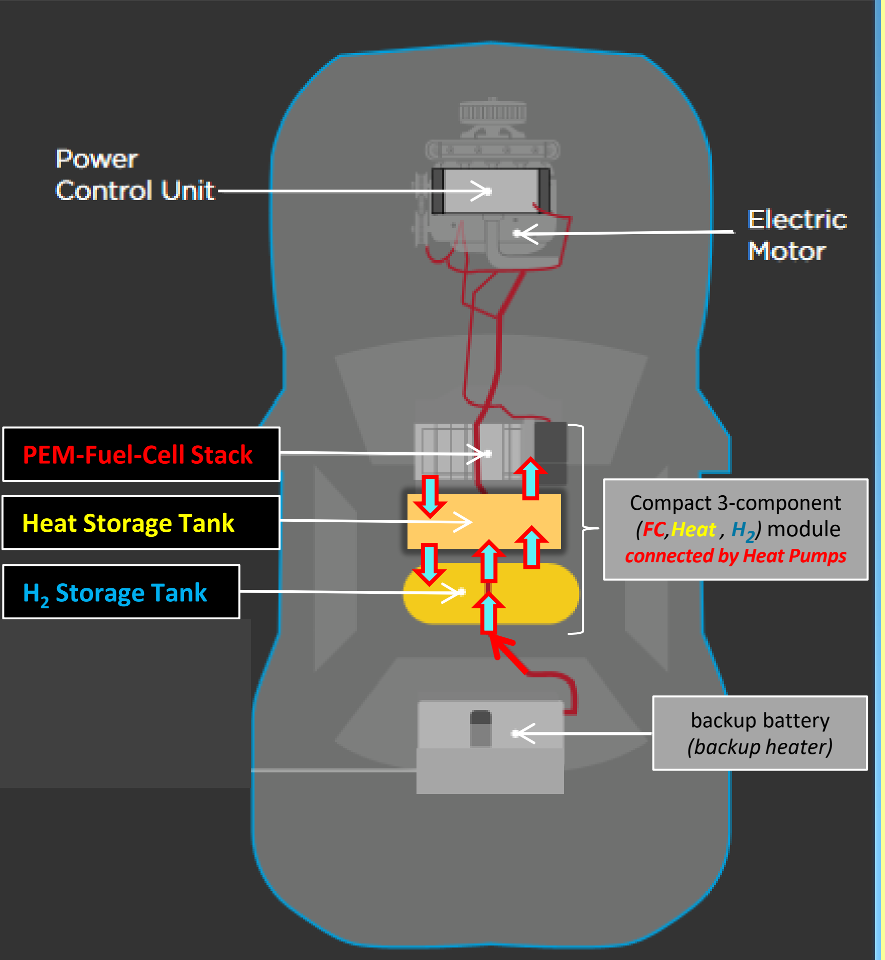
A graphene evelope of Mg prevents **nanoparticles (Mg, B, N)** to react with molecules from the air (H_2O, O_2, CO_2 etc.) which would block H_2 from contacting the Mg surface, whereas the very **thin oxide layer** formed on Mg surface does not hinder MgH_2 formation.

Schematically shown :
H_2 diffusion pathways (blue) through gaps and pores of over-lapping **graphene layers (dark brown)** and through the ultra-thin oxide layer **(O atoms in red)** coating graphene-wrapped **Mg particles (light brown).**

DOI: 10.1021/acs.nanolett.7b02280

Combined Heat & Hydrogen Storage Tanks

Hydrogen-**S**torage **S**olid-**M**aterial Tank Fuel Cell Electric Vehicle



FCEVs generate electricity via the chemical reaction of combining hydrogen and oxygen into water.

Hydrogen Storage Solid-Material Tank

Light-weight aluminum **vessel** with fiber-reinforced liner, filled with a stack of nano-diamond wavers, double-sided coated with multilayers of **Graphene-on-Diamond Van-der-Waals heterostructures** (doped with light-elements, e.g. B, N, Mg).

Heat Storage Tank (Heat buffer)

Latent heat-storage system of light-weight, highly porous, foam-like **Phase Change Nano-Material** (N-**PCM**) with very high thermal conductivity, which absorbs or releases heat very fast, when the PCM changes from solid to liquid and vice versa. Heat conduction is performed by nano-crystalline **heatpipes** with high thermal conductivity.

The purpose of the Heat Tank is two-fold:

(a) the H_2 absorption heat is used either for
- cold start of the FC or
- desorption of H_2 for generating electricity by FC

(b) the FC operation heat
- is stored in the Heat Tank and used for H_2 desorption and generation of electricity by FC.

Summary

A project has been presented for the development of a mobile, explosion proof, solid-state H_2-storage tank based on a light, multi-layer nano-crystalline graphene-on-diamond hybrid-material to efficiently store hydrogen with high density.

Due to the particular morphology and molecular structure of the chosen multi-layer Van-der-Waals-heterostructure material, both, non-covalent physisorption and a strong, covalent chemisorption forces are simultaneously responsible for a sufficiently large H-bond strength. Whereas the Van-der-Waals or nano-capillary forces of physisorption are enhanced by the nm- and sub-nm-enclosures and predicted by A.K. Geim to lead to enormous nano-capillary pressures (as high as 1GPa = ~10,000 atm) on trapped molecules, the strength of the strong, covalent forces causing light-element hydrogen formation can be adjusted by varying the concentration of the doped light elements.

We are looking for partnerships with research institutions and companies, competent in nanomaterial and hydrogen technologies, which are interested in a collaboration.