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LODZ UNIVERSITY OF TECHNOLOGY

EDUCATION, RESEARCH, INNOVATION

Graphene nanocomposite for reversible hydrogen storage

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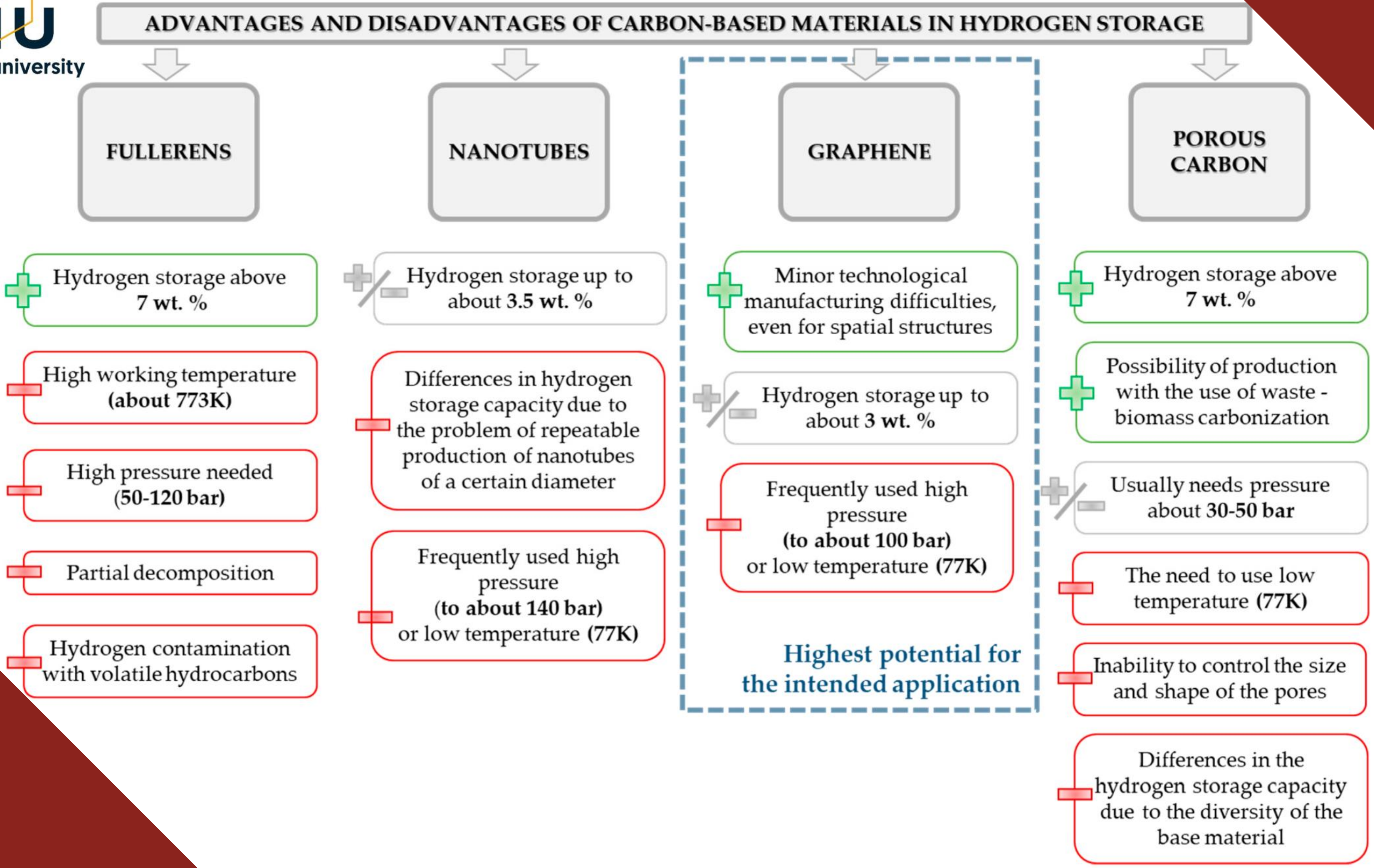
What promotes hydrogen-based economy?

1. Society concerns about the decreasing local air quality
2. Aspects of growing awareness of the sustainable development needs
3. Growth in the field of technological innovations
4. Increasing environmental problems globally
5. Needs for energetic security

What inhibits hydrogen-based economy?

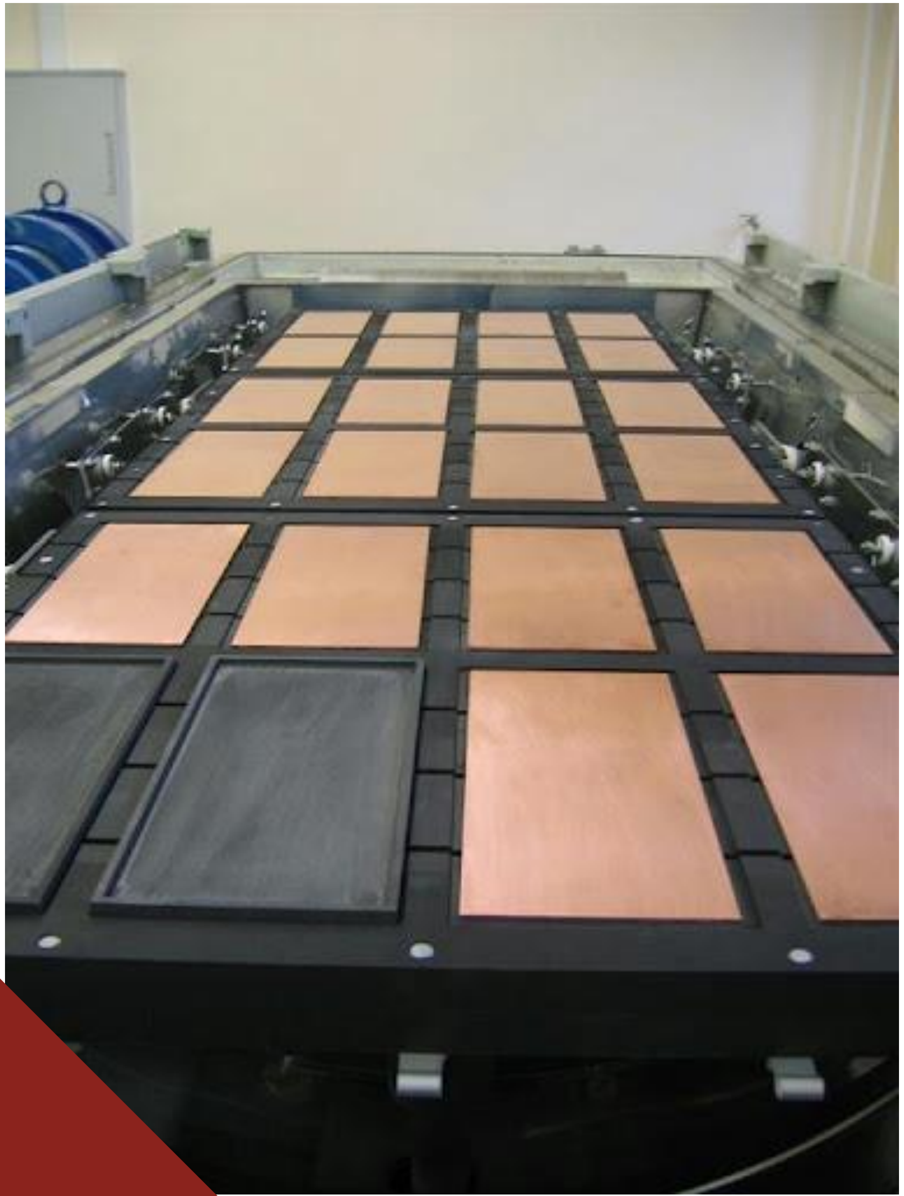
1. Improvements in the field of combustion engines
2. Global economy dependence on fossil fuels
3. High investments needed
4. Reliability and durability of traditional fuel cel vehicles
5. Long viability and realitively low cost of traditional fuel cel vehicles

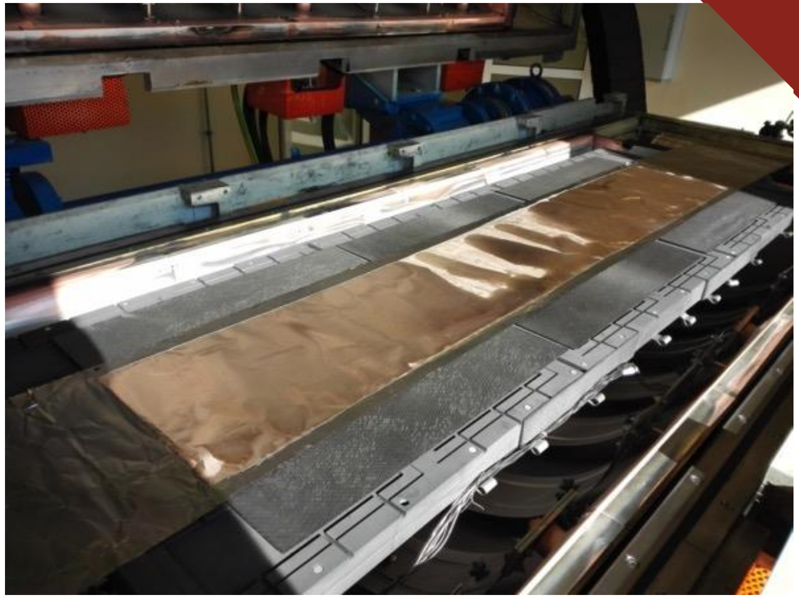

ADVANTAGES AND DISADVANTAGES OF CARBON-BASED MATERIALS IN HYDROGEN STORAGE
FULLERENS
Hydrogen storage above 7 wt. %
High working temperature (about 773K)
High pressure needed (50-120 bar)
Partial decomposition
Hydrogen contamination with volatile hydrocarbons
NANOTUBES
Hydrogen storage up to about 3.5 wt. %
Differences in hydrogen storage capacity due to the problem of repeatable production of nanotubes of a certain diameter
Frequently used high pressure (to about 140 bar) or low temperature (77K)
GRAPHENE
Minor technological manufacturing difficulties, even for spatial structures
Hydrogen storage up to about 3 wt. %
Frequently used high pressure (to about 100 bar) or low temperature (77K)
Highest potential for the intended application
POROUS CARBON
Hydrogen storage above 7 wt. %
Possibility of production with the use of waste - biomass carbonization
Usually needs pressure about 30-50 bar
The need to use low temperature (77K)
Inability to control the size and shape of the pores
Differences in the hydrogen storage capacity due to the diversity of the base material

High-Strength Metallurgical Graphene HSMG®

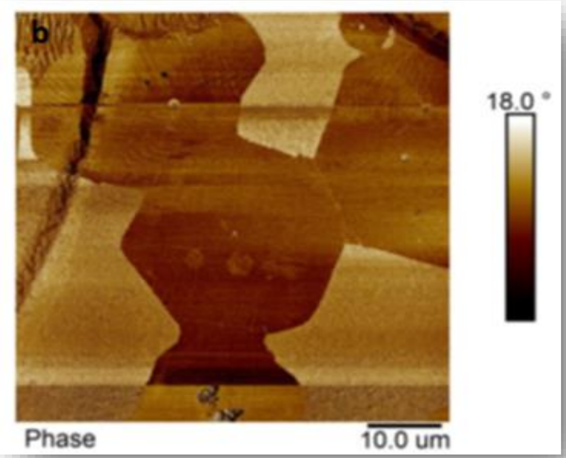
Material obtained via crystallization of monolayer quasi monocrystalline graphene on a liquid copper surface. It was used as a model material for fundamental research on hydrogen sorption and desorption. Secret lies in functionalization of graphene as well as the decoration of it with “spill-over catalysts” towards the creation of nanoporous three-dimensional nanostructures suitable for industrially scaled graphene nanocomposites that reversibly sorb hydrogen

HSMG® Manufacturing

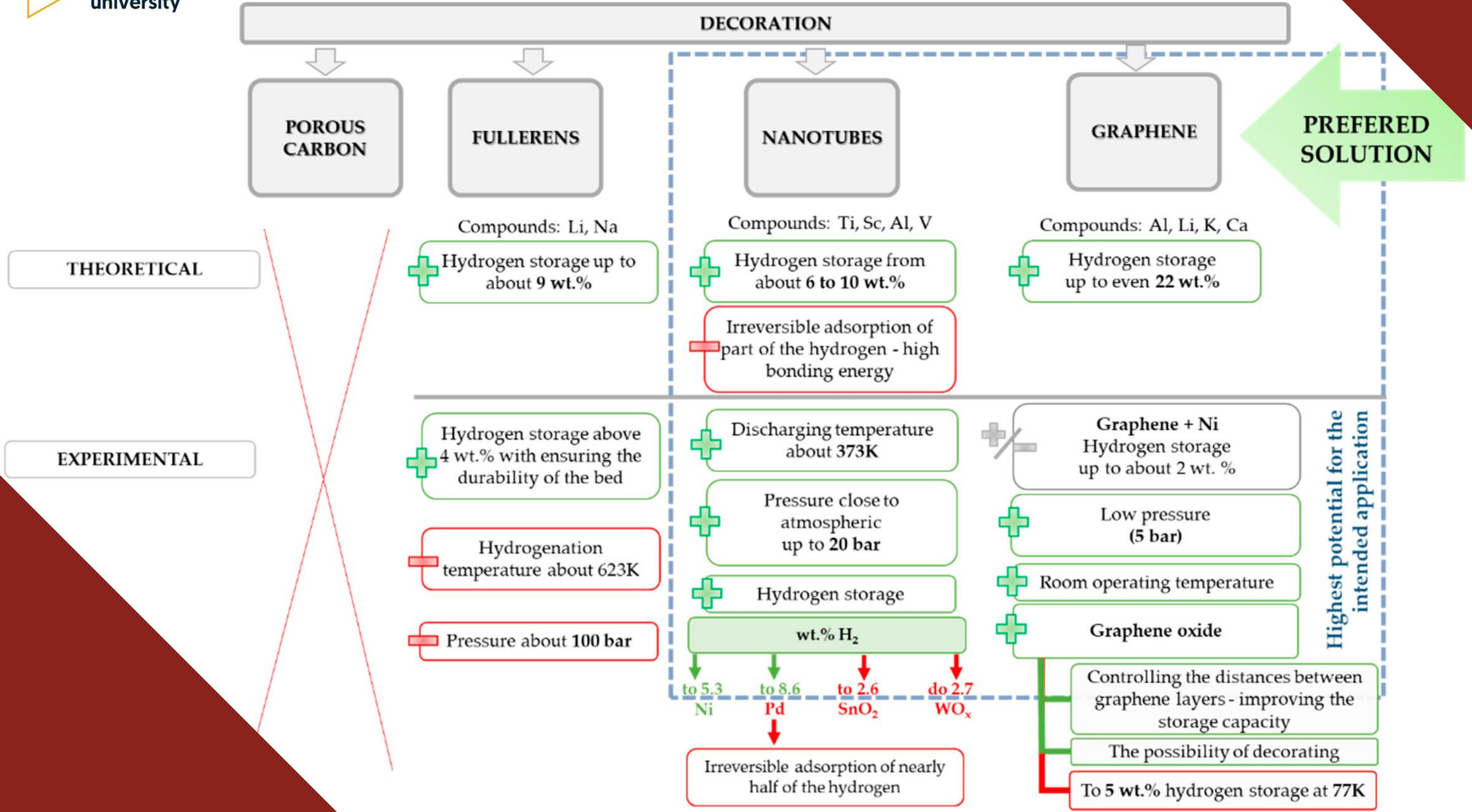




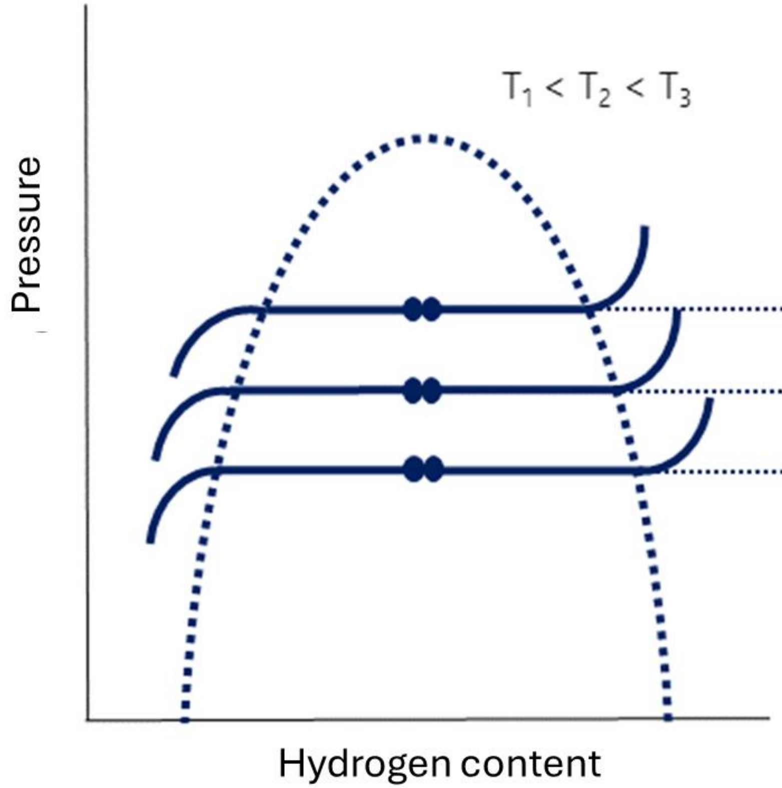
The industrial prototype plant to produce HSMG®



Graphene flakes formed on liquid copper

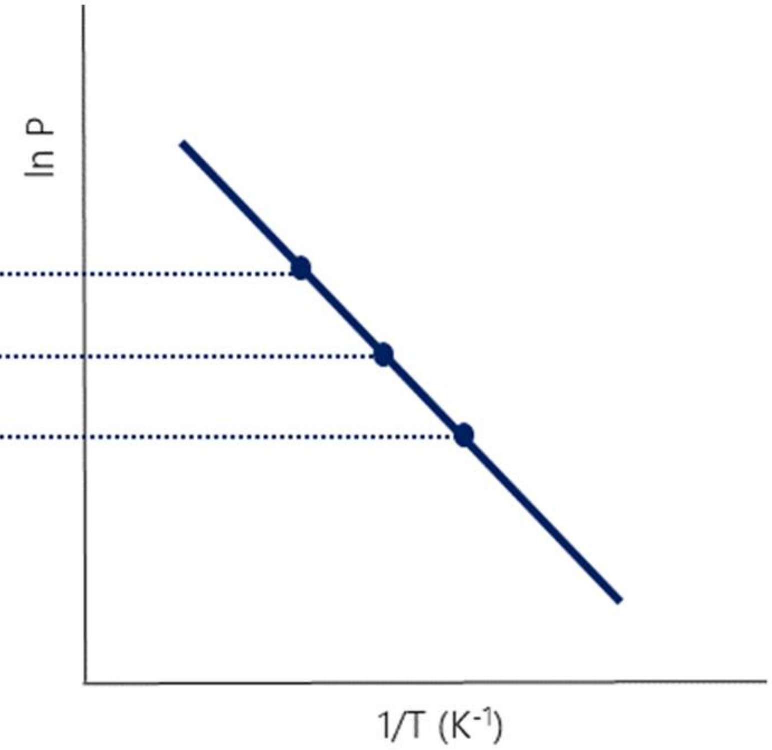

DECORATION
POROUS CARBON
FULLERENS
NANOTUBES
GRAPHENE
PREFERED SOLUTION
THEORETICAL
EXPERIMENTAL
Compounds: Li, Na
Hydrogen storage up to about 9 wt.%
Hydrogen storage above 4 wt.% with ensuring the durability of the bed
Hydrogenation temperature about 623K
Pressure about 100 bar
Compounds: Ti, Sc, Al, V
Hydrogen storage from about 6 to 10 wt.%
Irreversible adsorption of part of the hydrogen - high bonding energy
Discharging temperature about 373K
Pressure close to atmospheric up to 20 bar
Hydrogen storage
wt.% H2
to 5.3 Ni
to 8.6 Pd
to 2.6 SnO2
do 2.7 WOx
Irreversible adsorption of nearly half of the hydrogen
Compounds: Al, Li, K, Ca
Hydrogen storage up to even 22 wt.%
Graphene + Ni Hydrogen storage up to about 2 wt. %
Low pressure (5 bar)
Room operating temperature
Graphene oxide
Controlling the distances between graphene layers - improving the storage capacity
The possibility of decorating
To 5 wt.% hydrogen storage at 77K
Highest potential for the intended application

Safe method of hydrogen storage → Atomic hydrogen is reversibly introduced and released from the bed



Reaction of synthesis/decomposition of metal hydrides

$M + x/2H_2 \leftrightarrow M\,H_x + \Delta\mathcal{H}$



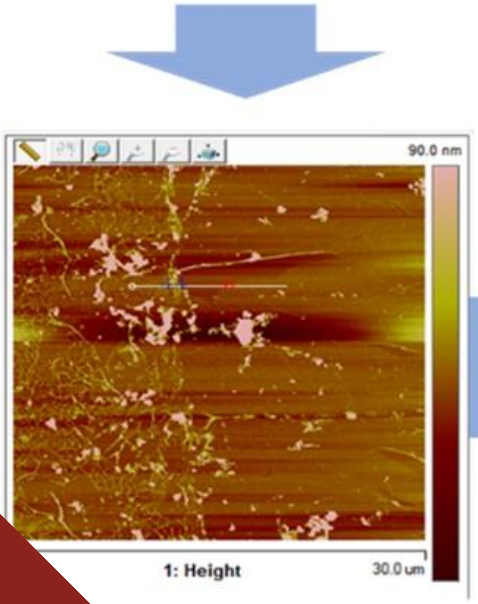
van't Hoff Equation

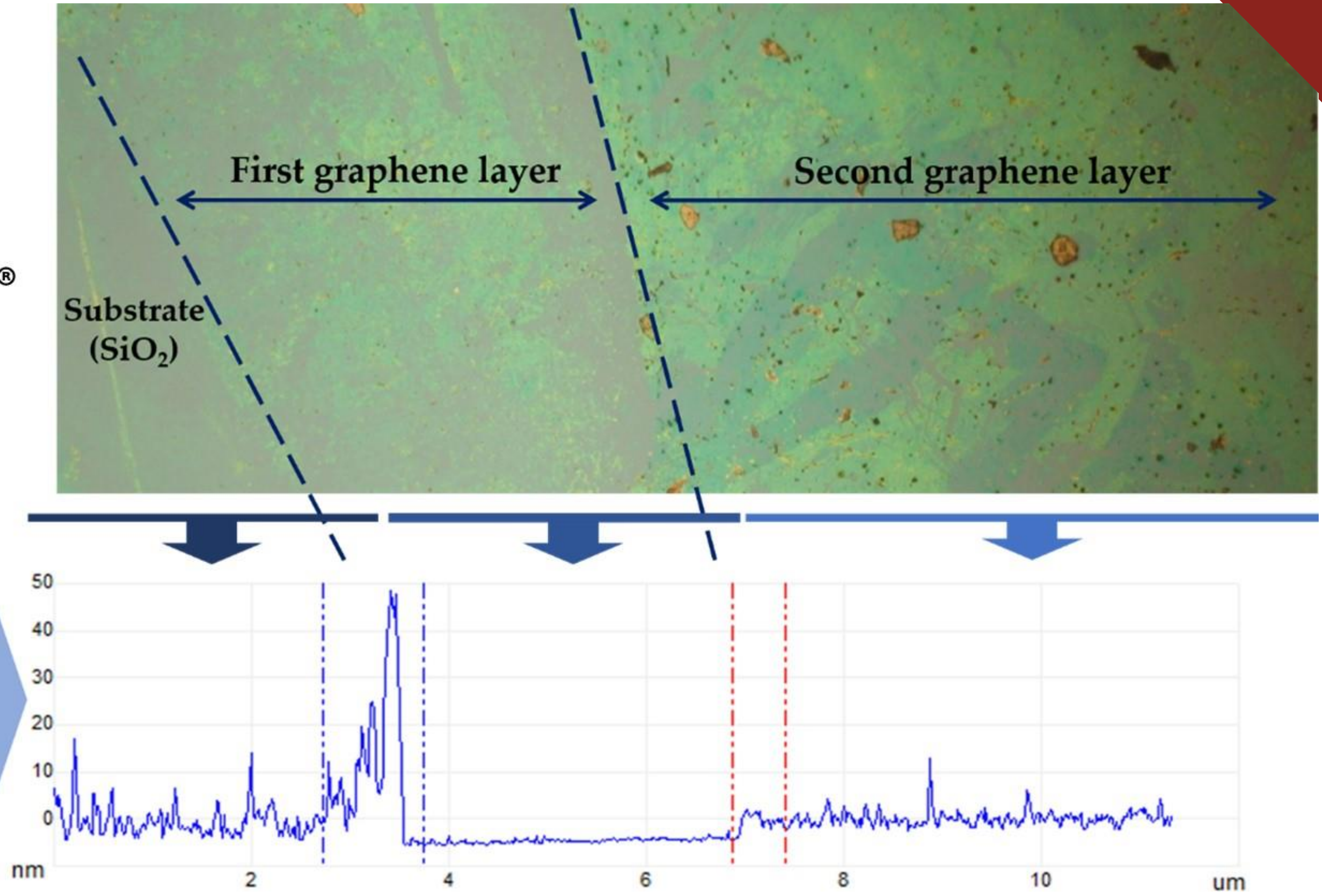
$\ln P = \Delta\mathcal{H}/RT - \Delta S/R$

Structured graphene composite for reversible hydrogen storage

- Raw material - reduced graphene oxide
- Graphene flakes are spatially filamented with oxygen-nitrogen bridges
- Decoration with metallic ‘spill-over’ catalysts for molecular hydrogen dissociation reactions.

Pillared HSMG®





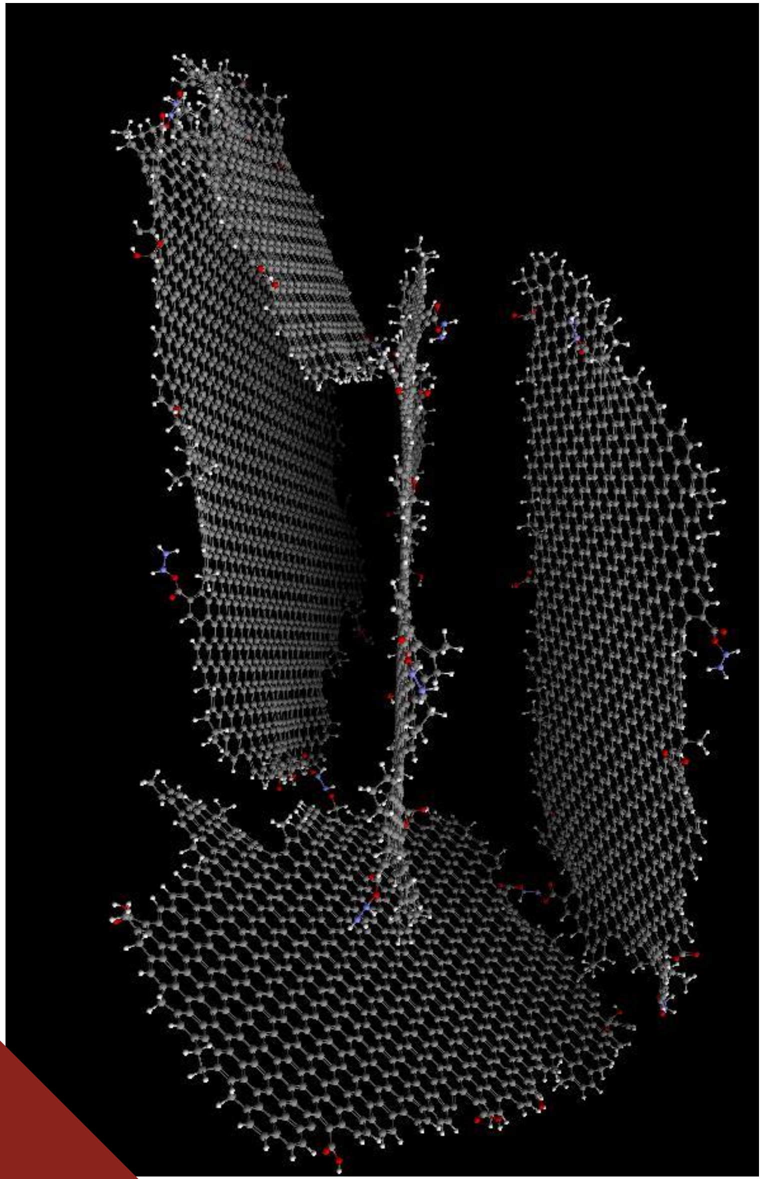
Stages of bed Preparation

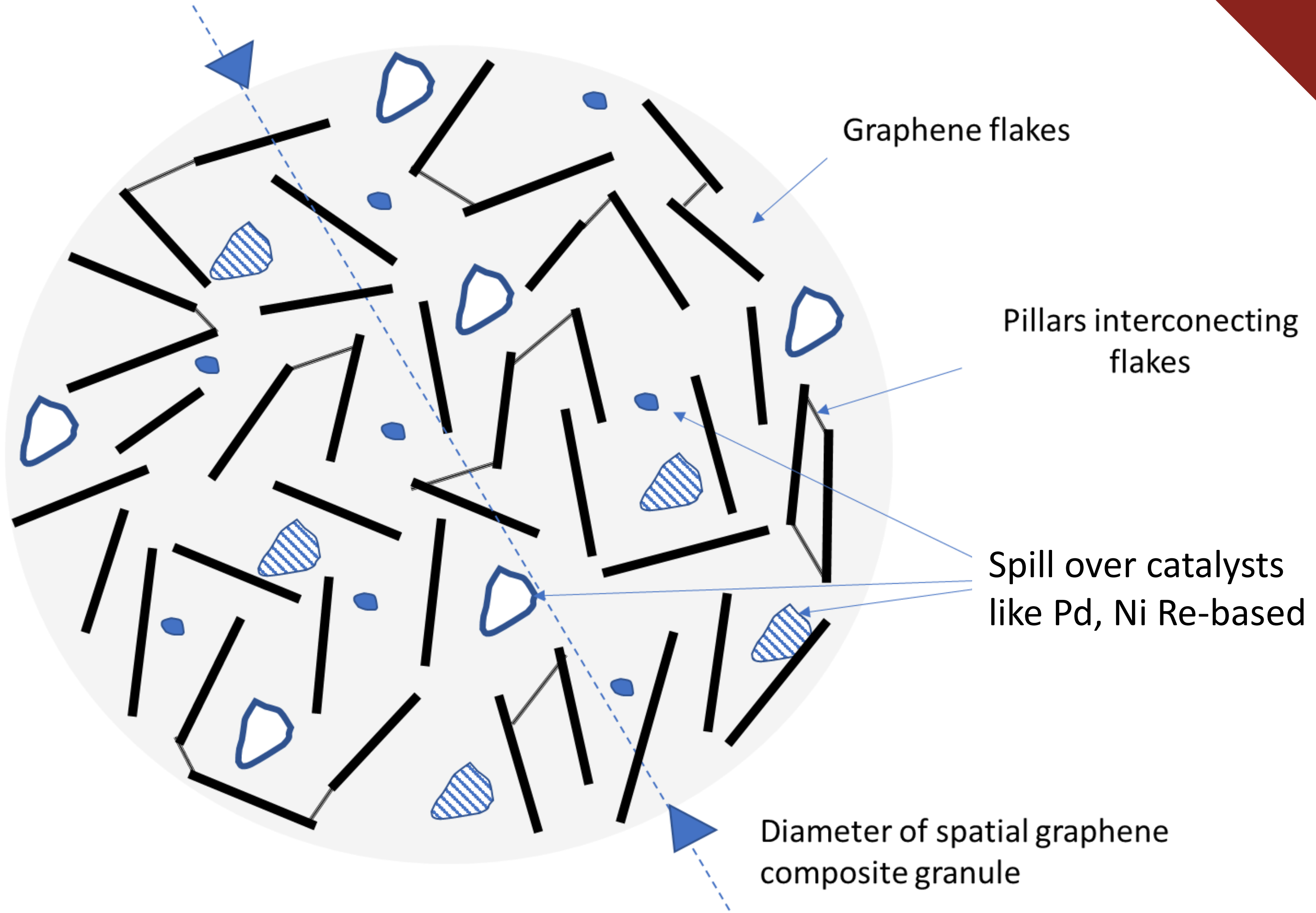
Stage I
Synthesis of GO-3D

Stage II
Expanding of 3D structur

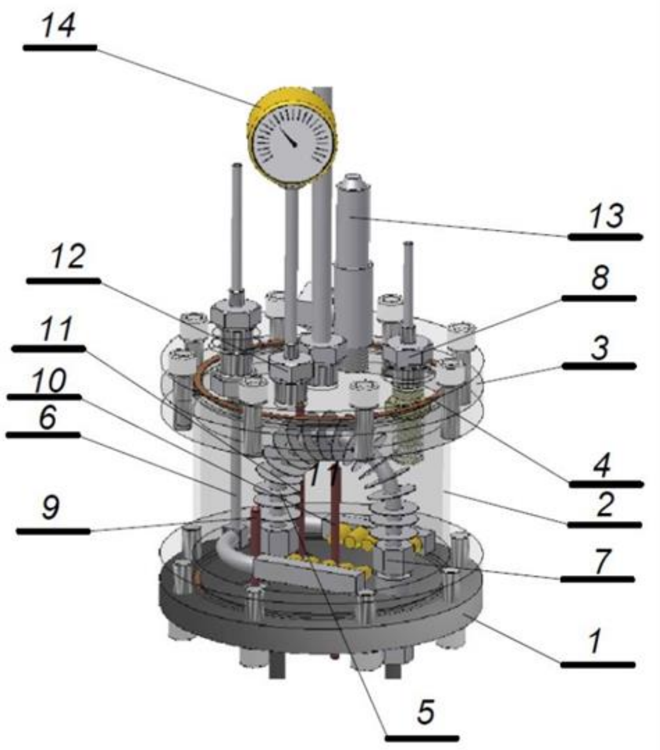
Stage III
Decoration with palladium

Stage IV
Decoration with RE-catalysts



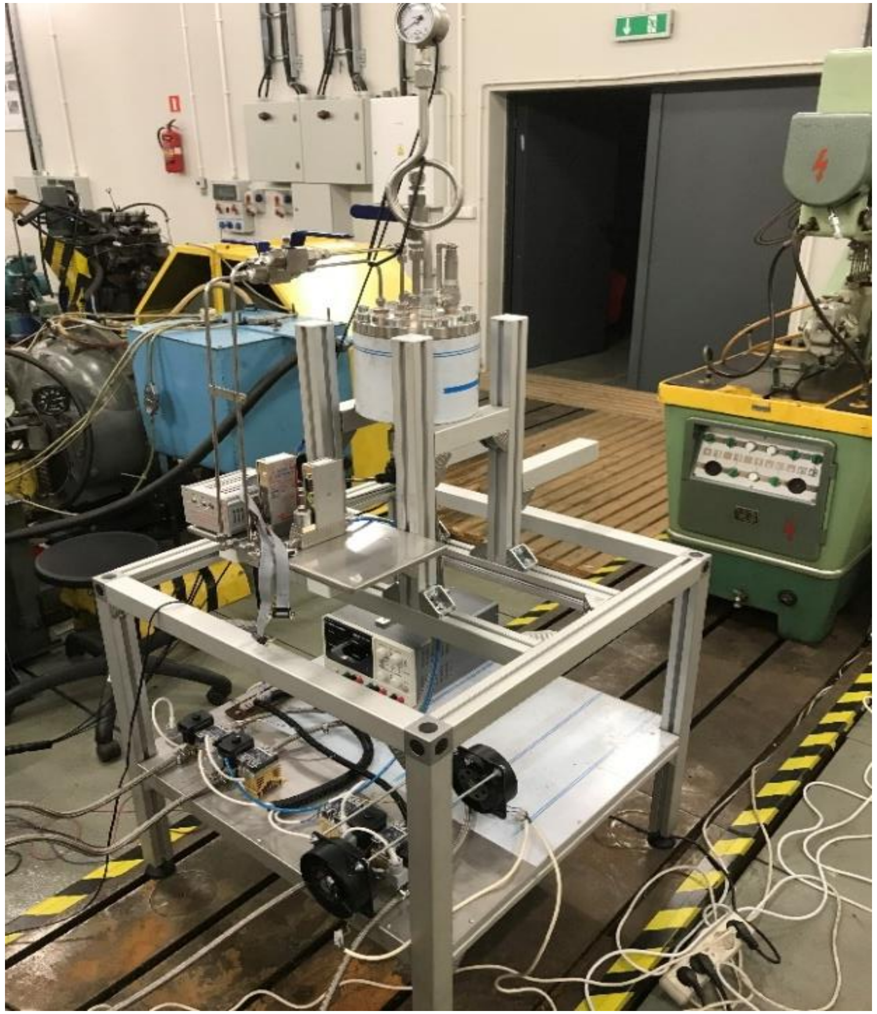

Graphene flakes
Pillars interconecting flakes
Spill over catalysts like Pd, Ni Re-based
Diameter of spatial graphene composite granule

Laboratory experimental model



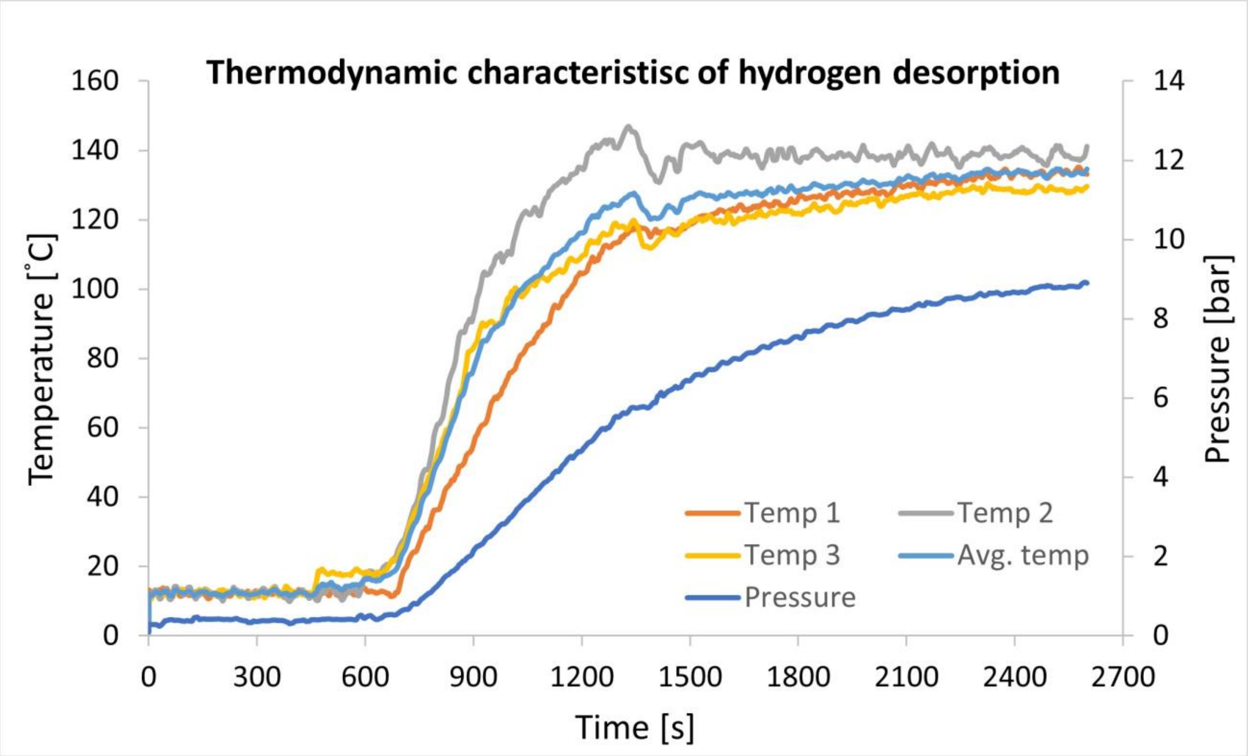
1. Bottom cover
2. Tank cylinder
3. Top cover
4. Copper gasket
5. Ribbed U-pipe
6. Inlet manifold
7. Nut M16
8. Connection
9. Short temperature sensor
10. Medium temperature sensor
11. Long temperature sensor
12. Connection
13. Safety valve
14. Manometer

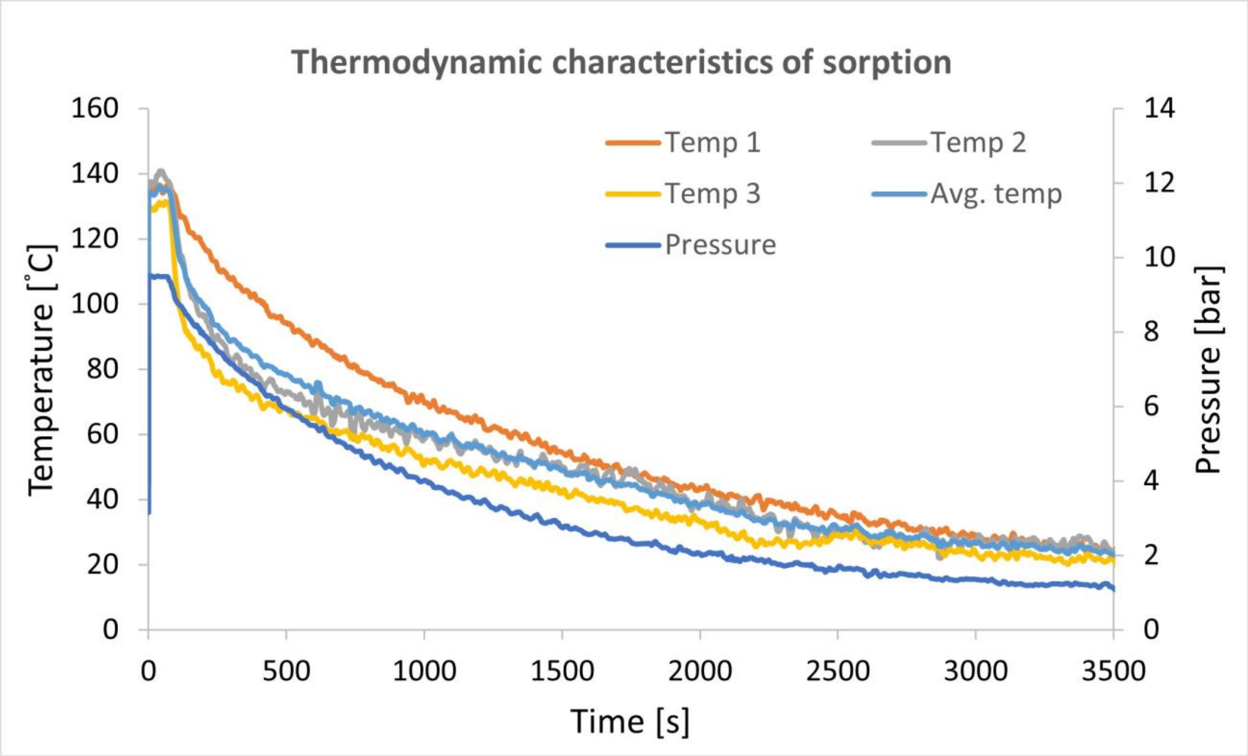
A schematic view of the working bed container with peripheral devices.



Proposed laboratory demonstrator

Laboratory experimental model





Graphene nanocomposite future

The application range of that nanomaterial is hydrogen recycling and hydrogen recovery systems for sake of facilities for low pressure heat treating and thermochemical treating processes. Low-pressure pumpless compressors with nanographene sorbent beds can be used in hydrogen green energy conversion systems or autonomic energy grids as flexible storage of renewable energy. Improving of hydrogen absorption capacity, over the critical threshold of 6,5% by wt., should extend the application range to storage systems in “vehicles of the future”.

Further applications of HSMG®

- Filtering membrane for reverse osmosis;
- Active element in industrial and biological sensors;
- Flexible monolayer semiconductors;
- Reinforcement material for composites
- Etc.

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K. Jastrzebski, M. Clapa, L. Kaczmarek, W. Kaczorowski, A. Sobczyk-Guzenda, H. Szymanowski, P. Zawadzki, P. Kula: „**Spatial Graphene Structures with Potential for Hydrogen Storage**". Energies. 2024, 17(10), Article number 2240.

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