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General Overview of Cryo-Adsorption for Hydrogen Storage

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Abstract: *Cryo-adsorption is a way to store hydrogen with cold temperatures and adsorbents (porous materials) such as activated carbon or MOFs, achieving a high hydrogen storage density without storing the hydrogen at extreme pressures. It has promise for fuel cell vehicles and ships, mostly due to emerging materials (e.g. COFs) and system configurations. However, it still has challenges moving forward in terms of thermal management and total cost of ownership. This overview provides a summary of recent literature to show the potential of cryo-adsorption for the hydrogen economy.*

Key Words: *Cryo-Adsorption, Hydrogen Storage, Porus materials, Activated Carbon, MOFs, COFs, Fuel cell vehicles, Thermal management, Economic viability, Clean energy.*

I. INTRODUCTION:

Hydrogen is the "cool" element of clean energy as it has high energy density (142 MJ/kg), and when consumed in fuel cells, it only emits water [1]. However, storing hydrogen can be problematic. While it can be compressed at 700 bar, the tanks are heavy, and converting it into a liquid (−253 °C) requires a lot of energy (2,3). Cryo-adsorption can be considered a "Goldilocks" method because it uses low temperatures (60–150 K) combined with tailored sorbents to store hydrogen at "higher" pressures (60–100 bar) (3). It does not use excess heat or electricity since it operates in a relatively low temperature and low-pressure system but is also higher then gas (or ice) storage. In short, its just "right" for applications constrained by space and safety. Multiple arguments support the consideration of hydrogen as one of the key elements in decarbonizing various industry sectors. Hydrogen (1) is a clean fuel that burns without the emission of COx and soot, (2) is abundantly available (3,4) and can be easily produced by electrolysis using electrical energy and water [5] as shown in Fig. 1. This not only makes hydrogen an ideal fuel but also a medium for energy storage. With high-grade heat (adiabatic flame temperature in air of 2400 K at 1 atm) and a lower heating value (LHV) about 2.5 times larger than typical hydrocarbons (120 kJ/g for H2 vs 43 kJ/g, 43.6 kJ/g, and 47.1 kJ/g for Diesel, Jet-A, and natural gas, respectively [6], [7], hydrogen is an excellent zero-emission hydrocarbon replacement for combustion processes.

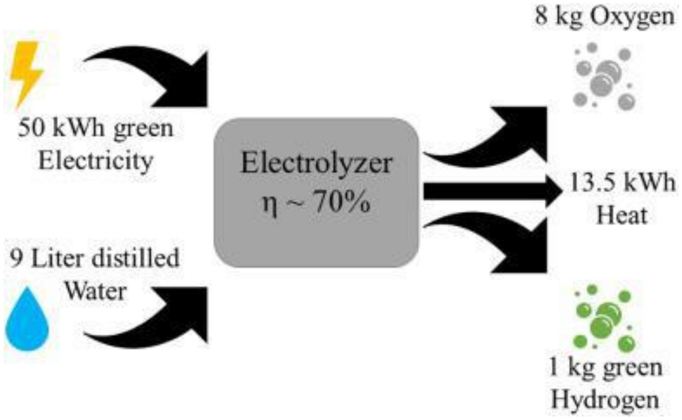

Fig.1 : Electrolysis of water requires 9 l of distilled water and approximately 50 kwh to generate 1 kg of hydrogen using an electrolyzer with 70 % electrical efficiency (8)

Recent research is making cryo-adsorption even more compelling with materials with large surface areas, such as MOFs and COFs that adsorb even more hydrogen (9]:[10]. Machine learning is assisting researchers in exploring what will be the next material, and new fabrication techniques are designing ways around issues related to heat [11,12]. This note highlights how cryo-adsorption works, some exciting new cryo-adsorptive materials, what applications it is being used for, and barriers facing the technology.

2. DEFINITION AND MECHANISM:

Cryo-adsorption pertains to the adsorption of hydrogen gas onto porous materials at cryogenic temperatures (approximately -123 °C to -213 °C or 150 – 60 K) (13). It employs a process known as physisorption to explain adsorption, with hydrogen molecules being held to the material's structure by weak van der Waals forces (3). This differs from chemisorption, which is a stronger force (similar to super-glue) and not easily reversible. The colder it is, the slower the hydrogen molecules move, and therefore the better the hydrogen can be "adsorbed" and packed into the pores of the material (2).

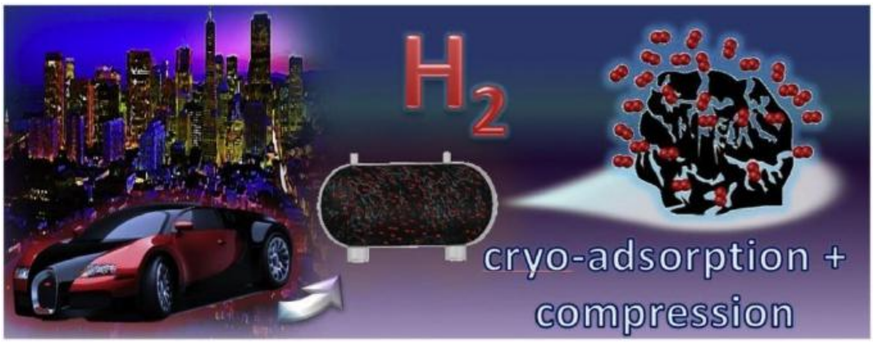

Fig.2: High hydrogen release by cryo-adsorption and compression on porous materials (3)

3. USING AN ANALOGY:

The hydrogen molecules at room temp are like very energetic children at a party; irreplaceable to catch/sustained (can't think of a good way to put this); as soon as you cool all of the molecules to 77 K (-196 °C), we can think about it the little kids are now sitting on the couch and just sticking to the material. You can now store the same amount of hydrogen at 60 bar rather than 750 bar; this would result in much easier handling of the tanks. To release the stored hydrogen, you just have to warm it up or decrease the pressure of the tank (14). The critical point is that the adsorption process will typically produce heat (2–10 kJ/mol for activated carbon). Therefore, when you remove heat energy from the material, just like someone probably took those kids away from the party (3).

Recent research found temperature swings help recover 80% of the hydrogen at ~100 K and 100 bar, so some engineers are still optimizing. This reminiscence of adsorption has many characteristics such as Langmuir and BET adsorption isotherms that explain how much hydrogen is attached to the surface at different pressures and temperatures (14). Engineers are still optimizing material plus temperature and pressure for good process optimization (2).

4. MATERIALS USED FOR CRYO-ADSORPTION

Materials are the stars of cryo-adsorption and need an enormous surface area with small pores to hold hydrogen easily. Here is a brief summary of sorbent materials:

A. Activated Carbon: An old standard, superactivated carbon AX-21, retains ~5.4 wt% hydrogen at 77 K and 60 bar (14). Activated carbon can have a surface area of up to 3000 m^2/g, is relatively inexpensive, but many new materials are taking the spotlight. Research has even been conducted to recycle cigarette butts into oxygen rich carbons with excellent storage capabilities (15).

B. Metal-Organic Frameworks (MOFs): Like molecular Lego, the metal ions are considered the LEGO blocks and the organic linkers are the connectors. MOFs have a high surface area (> 7000 m^2/g) and offer a support for gas storage. An example of this is MOF-177 can adsorb 7.5 wt% H_2 at 77 K/70 bar, while NU-1501-Al can adsorb 14.0 wt% at 77 K and 77 bar (16). As an alternative, there was a study that was published in 2025 obtained via MOF-177, an amazing 14.8 wt% at 20.4 K and 0.1 MPa which outclassed current storage methods for liquid hydrogen, while a NU-1101 was verified with 46.6 g/L (9.1 wt%) at 77 K and 10 MPa. Another technical capability of MOFs is that they can be synthesized with the desired functionalization or custom structure, however they are very costly to produce/modify (9).

C. Covalent Organic Frameworks (COFs): Think of them conceptually like classical MOFs, but they are all organic and covalently bonded with large surface areas (e.g., COF-103 at 4210 m^2/g). For example, COF-105 adsorbs 10.5 wt% H_2 at 77 K (10), and Li-doped COF-108 adsorbs 45.6 mg/g at 233 K and 100 bar (17). Polymer-based composites are also in a good place (21). COFs are also lighter which helps for vehicles (10).

D. Hyper-Crosslinked Polymers (HCPs): These organic polymers with heavy crosslinking have also been showing off in cold environments too, particularly with Friedel-Crafts alkylation (11);12) like the new kid that raises the level of play in the team (11).

E. Other Materials: Zeolites such as H-SSZ-13 can absorb at least 1.28 wt% at 77 K, 0.92 bar (22). Graphene can host 4.65 wt% under ambient conditions but with very high pressures (around 40 atm) (18). Carbon nanotubes (CNTs) can host 8 wt% when cooled to low temperatures, single-walled nanotubes (SWNT) could hold 5-10 wt% at 133 K, 0.04 MPa (19). High-entropy alloys like TiVZrNbHf have been shown to absorb 2.7 wt% at 573 K (20), MXenes have been shown to increase MgH2 after 2 hours at 323 K to 3.5 wt% compared to without MXenes (23). MOFs and COFs are included in this because they are the most important materials, cryo-adsorption can lead to really high storage capacity (9,10).

Machine learning is also a factor in this area because models have been able to achieve 98.7% accuracy in forecasting the amount of hydrogen stored in dibenzyl-toluene as material, which can allow for a much quicker route to the next biggest thing (11).

Table 1: Hydrogen Storage Capacities of Various Adsorbents

Material	Temperature (K)	Pressure (bar)	Capacity (wt%)	Reference
Activated Carbon AX-21	77	60	5.4	(3)
MOF-177	77	70	7.5	(9)
NU-1501-Al	77	77	14.0	(17)
COF-105	77	-	10.5	(10)
HCP (crosslinked >40%)	77	-	High	(12)
SWNT	133	0.04	5–10	(18)
Nb4C3 (MXene)	323	-	3.5	(23)

5. THERMODYNAMICS AND SYSTEM DESIGN

Cryo-adsorption gives off heat (e.g., 2–10 kJ/mol for the case of activated carbon). If not dealt with, this heat will heat things up and reduce how much hydrogen you can store (3). The storage tanks are constructed with vacuum superinsulation and tough carbon fiber composites with high tensile strengths, T700S (2550 MPa), to retain the coldest possible environment available to U.S. researchers (12). Although cooling the systems with liquid N2 is entertaining, it is energy- and power-intensive, and so engineers are working outside the box (3). Engineers have designed new systems that have central and spiral cooling tubes to help with spreading cool evenly in the system during refueling (12). The ultimate goal is to be able to achieve the DOE goals 36 kg-H_2/m^3 and 4.5 wt% for vehicles where cryo-adsorption has made significant progress (1). In a study of compacted MOF-5 at 40 K and 5.6 MPa, it was identified as optimum figure of merit; however, very low temperatures will weigh in on the cold storage component.

Table 2: Comparison of Hydrogen Storage Methods

Method	Volumetric Density (kg/m^3)	Gravimetric Density (wt%)	Operating Conditions	Challenges
Compressed H_2 (700 bar)	40-50	5-6	Room T, 700 bar	High pressure, heavy tanks
Liquid H_2	71	-	20 K, 1 bar	High energy for liquefaction, boil-off
Cryo-adsorption	30-40	5-14	77 K, 60-100 bar	Thermal management, material costs
Metal Hydrides	60-100	2-6	Room T, 1-100 bar	Slow kinetics, material durability

Data from Ahluwalia et al. (2)

6. OBSTACLES AND PROSPECTIVE DIRECTIONS

Cryo-adsorption is not quite there yet. Managing heat is a significant challenge; material, like activated carbon, is an ineffective conductor of heat, and thus keeping everything cold during the actual adsorption is difficult (3). Materials also need to be able to withstand thousands of cycles, and those high-performance materials like MOFs usually cost an arm and a leg (9,17). This study highlighted that going below 77 K drastically increases energy costs, and ultimately leading to a suitable levelized cost of storage (LCOS) is problematic with tank cost and temperature being the two major contributing factors. Researchers are then pursuing new materials with improved heat transfer and developing materials using the latest machine learning tools to accelerate material discovery (11). Comparing cryo-adsorption and cryo-compression will provide more context on the implementation pathway (2).

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