

Review Article

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Microporous Materials for Hydrogen Liquefiers and Storage Vessels

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ABSTRACT

Microporous Composite Materials, made of metal oxide ionic fragments inserted in carbonaceous substrates, might be used as intermediates in hydrogen phase transitions, allowing progressive switch between their gas and liquid states. When crossed by an hydrogen flow these composite materials combine adsorbing, magnetic, catalytic and thermal properties efficient in hydrogen devices, liquefiers or storage vessels. Liquefaction and storage are complementary processes in practice, although inverse in principle. Plate-fin devices filled with composite materials can conjugate many thermal functions, heat exchangers, catalytic converters and pressure expanders that are necessary stages in large-scale liquefiers. Break-even storage times permit operation of the liquefaction unit at optimum ortho-para conversion thus yielding minimum practical work to be furnished. A barrage-system of successive porous plugs inserted in Hydrogen vessels would regulate the flow rate by J-T expansions, convert part of the environmental heat in rotational energy and confer stability to the system by damping the fluctuations. Consequently storage vessels of short dormancy period might be manufactured to be of low weight and low cost. After a short review of existing devices, a logical scheme interconnecting physical, economic and technologic challenges suggests that activated carbon materials of cage-like porous structures would promote and accelerate the development of storage vessels in hydrogen transport vehicles and facilitate the liquid hydrogen production by regulating the hydrogen streams in the industrial liquefiers.

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Introduction

Nowadays the climate warming prescribes a fast growth of a new “clean” industry. Hydrogen might become a storable, sustainable, and universal carbonless energy carrier if generated using a renewable energy. Hydrogen based technology can provide the basis for significantly decrease greenhouse gas emissions [1-3].

The storage of hydrogen remains a volumetric problem. For large quantity and long term storage, the dissociation inside metal hydrides would be an adequate solution but it involves technological challenges still unsolved [1]. For continuous use and short term storages the natural forms are the most advantageous; compressed gaseous or liquid bottles are now commercially available [4].

The subject of that letter focus on the relation between the triad: Work consumption, stored energy and storage time represented on the Figure 1, and compares its application in two different and almost opposite industrial contexts: one being the liquefaction of the hydrogen production while the other considers the storage of liquid hydrogen to be used in transport vehicles.

In both applications the concept of a storage time was applied by engineers and scientists to provide a technical answer to an economic question. For the storage of the liquid hydrogen production, a break-even time was defined in terms of a catalytic cost measured in terms of a complexification of the liquefier device and an additional work to be furnished. Such a catalytic cost was then compared to the hydrogen losses by evaporation during the liquid storage time. Consequently the definition of the break-

even time depends on the liquefier apparatus performance, on the financial value of the hydrogen loss and on the economic value of the hydrogen demand [5]. For the storage time of liquid hydrogen to be used in transport vehicles, the concept of a vessel dormancy was introduced and applied in particular by the Livermore and Sandia US National laboratories to measure the performances of various hydrogen vessels [6,7]. Dormancy is defined as the period during which a hydrogen vessel may sustain the heat transfer rate from the environment until the maximal pressure is reached, beyond which the vessel would release hydrogen. In that context the scientific questions of the thermal insulation and mechanical containment performances were measured by the industrial material and manufacture costs of the hydrogen vessels. As before, the cost of storing hydrogen during a period was then compared to the hydrogen losses by evaporation during a storage duration. Consequently the definition of the dormancy time depends on the vessel insulation performance and on the economic and financial values of the hydrogen production and social demands.

In all these present and future applications, it appears quite complex to distinguish and disentangle the scientific challenges from the ideological motivations, past commercial choices and investments. For example, the catalysts operating in the present liquefiers (mainly iron and chromic oxides) have been selected and tested more than 60 years ago. In order to improve the catalytic efficiency, the number of conversion stages and pressure expanders are regularly increased but the evacuation of the heat released in these processes remains costly. In a different sector, the storage models of the H vessels for transport vehicles are still inspired

by traditional fossil fuel reservoirs and conceived as to satisfy individual demands in spite of the increasing need of collective transports.

In the following short letter, it is suggested that microporous carbon materials might offer interesting solutions and alternatives in condensing multiple functions: thermal exchange, pressure expansion and catalytic conversion as intermediates in both directions either starting from the liquid state toward the gaseous one, or inversely. These nano materials would help to re-examine the time-energy triad represented on the Figure 1.

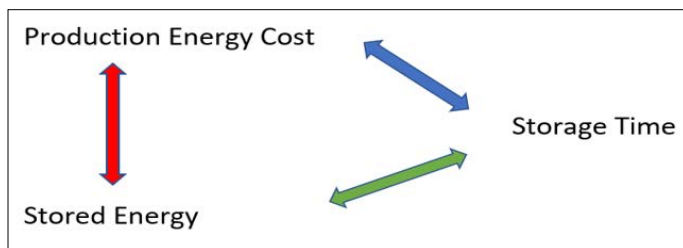


Figure 1: Hydrogen Liquefaction and Storage

The following paragraph follows the cooling path and considers the works to be furnished in the industrial liquefiers. The third section reviews shortly the technological and economic costs to insulate a cold reservoir of liquid hydrogen whereas the fourth one discusses the recently suggested alternative of short term hydrogen storage which uses nano materials to control the hydrogen evaporation, expansion and warming [8].

Liquefaction and Conversion Works

Liquid hydrogen is often considered too costly and energy intensive for widespread applicability. However, a few modellings indicate that liquefaction energy greatly simplifies hydrogen delivery and dispensing, resulting in a total dispensing cost comparable to other approaches. The overall cost reductions for transporting LH₂ might make it the more practical choice for a hydrogen energy net infrastructure especially for large scale commercial fueling stations, predicting future deployment of H₂ fueling stations for different sources of H₂. Regardless of the rate of H₂ vehicle introduction, most fueling stations will be supplied with LH₂ by 2025 which would, in turn, favor cryogenic hydrogen storage [7, 9,10].

Although large industrial liquefiers are typically complex, most are based on the Claude cycle represented on the Figure 2a. Hydrogen is both the product and the working fluid. A few successive heat exchangers, and pressure expanders removing work from the fluid, reduce the stream temperature. Finally, a Joule-Thomson valve brings the fluid into the two-phase regime, and saturated liquid is removed from the cycle [11,12]. Hydrogen catalysis is also an important step of the liquefaction process, because the heat released by conversion in cooling from normal H at 300 K to liquid para at 20 K, is larger than the vaporization heat. Therefore almost all the stored liquid hydrogen has to be converted in order to avoid the boil-off losses.

Hydrogen molecules have the peculiar quantum property of linking the proton nuclear spins to the molecular overall rotation. Consequently each molecule belongs to one of the two possible (spin isomer) varieties: the ortho and para ones whose energies differ by a few hundreds of calories per mole. Hydrogen conversion is usually induced by a magnetic catalyst to establish a thermal

equilibrium between the two varieties together with the solid catalyst [13]. Industrial designs and efficient catalysts (mainly ferric oxides) were first tested and promoted by the NBS in the sixties, soon followed by intensive research programs to improve the conversion process in understanding and efficiency [14-19]. (A detailed account of the experimental and theoretical progresses in between 1930 and 1992, can be found in the review [20]). Most of the theoretical work was devoted to study the magnetic mechanism in trying to identify the energy transfer, underlying path between the hydrogen flow and the solid catalyst [20-24]. More recent reviews investigate a larger class of transfers, but the industrial concern and challenge still remain unchanged, of finding the simplest device to evacuate the “unavoidable” conversion energy [25-27].

Transforming a quantity of hydrogen from a gas at ambient temperature and pressure to a saturated liquid requires work. This work input is used to extract entropy from the low-temperature hydrogen and reject it at ambient temperature. And the ortho-para catalytic conversion requires also an additional work to furnish in the liquefier to increase the nuclear spin order, towards the pure para quantum form. Ideally, hydrogen should be kept at equilibrium concentration throughout the cooling process, so that conversion is always done at the highest-possible temperature. In actual industrial liquefiers, the catalytic conversion is performed by a batchwise procedure, schematically represented on the Figure 2b. The feed hydrogen is partly converted in a first stage, operating at the temperature of liquid nitrogen, and converted in successive stages, operating at lower temperatures. The heat of conversion is usually transferred to the counter-current and released at a higher temperature level.

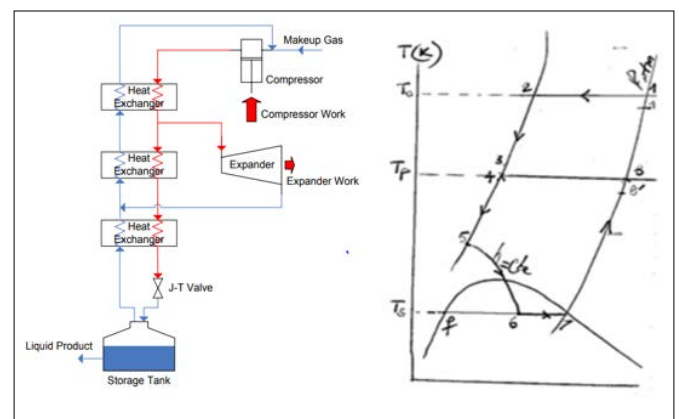


Figure 2: Claude refrigeration process for hydrogen liquefaction
a. Symbolic Diagram, b. T-s Refrigeration Cycle

The theoretical works of liquefaction and conversion, calculated by Baker and Shaner are reported in the Table 1, as corresponding to various strategies of stage wise and reversible processes [5]. For the stagewise processes the energies are transferred from the hydrogen flow to the catalyst (and to the counterflow) at the conversion stage temperatures indicated in the third column of the Table 1, whereas for a reversible process the hydrogen flow is continuously equilibrated by the counterflow. The work required for a multiple stage process is an inverse function of the number of stages until minimum work is obtained with an infinite number of stages. The latter condition can be approximated in a practical way by using continuous converters which need the inclusion of a heat transfer function [17]. It is apparent on the Table 1 that the additional work to be furnished by the liquefier device to convert the initial normal hydrogen flow to an equilibrated liquid form

represents an important part of the total cooling work, for most processes larger than 20%. Hydrogen catalysis is most efficient if done around the liquid nitrogen temperature. Below 50K, gas phase conversion in heat exchangers necessitates extra work. The work associated with a totally reversible catalysis represents about 15% of the total cooling work, but for 3-stage processes overcomes 22%. Converting in the liquid receiver more than triples the conversion work and doubles the 20 K latent heat load.

Theoretical Work for Liquefaction of Hydrogen at 99,8% para					
		Para content	Conversion Stage Temperature K	Conversion Work kJ/g	Total Work kJ/g
1	Reversible	99,8 %	-	2,19	14,28
2	Stagewise + Reversible	99,8 %	110	2,22	14,31
3	Stagewise + Reversible	99,8 %	80	2,33	14,42
4	Stagewise	99,8 %	80 - 65 - 50 - 35 - 20	3,16	15,25
5	Stagewise	99,8 %	80 - 60 - 40 - 20	3,47	15,56
6	Stagewise	99,8 %	80 - 50 - 20	3,65	15,74
7	Stagewise	99,8 %	80 - 20	5,44	17,53
8	Stagewise	99,8 %	20	7,27	19,36
9	No conversion	25%		0	12,09
10	Stagewise	48,54%	80	0,46	12,55

Table 1: Liquefaction and Conversion works

The difficulty of incorporating catalysts into the hydrogen-cooling heat exchangers has led most liquefaction plants to multiply the catalytic stages in order to approximate the continuous limit with staged catalyst beds. Industrial-scale plants such as the Norway SINTEF introduced, in 2019, catalyst-filled plate-fin heat exchangers that incorporate supported ferric (or chromia) oxide catalysts in the feed stream to approach the continuous conversion [28]. The feed stream, in passing through the catalyst-filled plate-fin, is cooled by a counter current stream of refrigerant hydrogen gas and, in the process, the heat of conversion is transferred continuously at temperature levels which are only a few degrees below the equilibrium temperature. In their study, Skaugen et al. compared the performances of two technologies of heat exchangers, employed in large-scale hydrogen liquefiers [28]. The catalyst-filled plate-fin device is compared to the spiral-wound one heat exchanger where several layers of stream flow in pipes wound around an inner mandrel (the refrigerant flows counter-currently at the shell side). They conclude that the plate-fin heat exchanger device is the preferred technology due to higher surface densities. In their large-scale Claude refrigeration process for hydrogen liquefaction with a capacity of 125 tons/day, the heat exchangers duties varied between 1 and 31 MW, the exergy destruction between 3% and 64% while the second law efficiencies varied between 72.3% and 96.6%. However it was also noticed that a significantly improved catalyst would improve the ortho-para conversion exergy destruction.

Such a device would be optimal in order to insert microporous carbon materials in the plate-fin sandwiches. Two opposite research directions should be investigated with either metallic or insulating supports: isothermal or adiabatic conversion. In the first alternative the conversion heat released is evacuated by

thermally conducting plates while in the second one the catalyst must be selected such as to transform the conversion heat into translational velocities alimentering the current stream.

Today's market for liquid hydrogen might be divided in two parts; a main one requires considerable storage time between liquefaction and ultimate usage whereas the other minor one requires little need for long-term storage. For example the large-scale use of liquid hydrogen as fuel for trains or jet aircraft might correspond to an almost continuous operation with liquid hydrogen to be used in less than a day after it was produced. In such cases production locations should be located nearby the departure/arrival stations.

At the opposite long-term storage might be necessary when the delay between production and utilization exceeds say a few days, and in particular nowadays when the number of loading stations remains insufficient necessitating long and heavy truck transportations. For each initial composition a breakeven time exists for which the energy cost for conversion equals the energy cost for the vaporized hydrogen. If the hydrogen is used within the breakeven time limit, partial conversion is advantageous with respect to energy consumption. A breakeven time of 19 hours was noted for normal hydrogen and 36 hours for 48.5 % *para* hydrogen.

Cryo-Compressed and Cryo-Adsorbed Storage Vessels for Transport Vehicles

The sector of transport is responsible for a large part of the atmospheric pollution. Hydrogen powered vehicles use fuel cells to transform the hydrogen energy in electrical form to alimenter the motor. The greatest engineering challenge associated with hydrogen mobility is storing enough hydrogen onboard the vehicle for a reasonable range (500-1000 km). Today's hydrogen-powered

ground vehicles almost exclusively use compressed gas storage, at pressures typically of 350 or 700 bar [4].

Commercial fuel cell vehicles planned for sale or lease in the next couple of years in Europe, Japan and the U.S will use Type IV 700 bar fuel systems that have been rigorously tested to automotive performance standards. Different options exist for hydrogen storage and delivery [9]. Vehicles demand compact, light vessels, and therefore fully wrapped high strength carbon fiber (type III or IV) vessels are typically used [3,10,29,30]. Best advanced methods of cryogenic hydrogen storage recently developed in the cryo-compression and cryo-adsorption storage vessels were studied in the Livermore and Sandia US National laboratories. They reached, in 2009, the 2017 weight and volume targets promoted by the US Department of Energy: a volumetric capacity of 45 gH₂ per liter of vessel and a gravimetric capacity of 7.5 %. A cryo-compressed system operating at a maximum pressure of 345 bar has been demonstrated with a full scale 151 L internal volume, 10.4 kg H₂ vessel installed onboard a type 1 Toyota Prius [6,7,31].

Nearly all LH₂ storage vessels use metallic double-walled containers that are evacuated and contain multiple layers of alternating metallic and thermally insulated polymeric or glass films to reduce heat leaks to the cryogenic fluid via convection, conduction and radiation. They comprise a high-pressure inner vessel with envelopes composed of a carbon-fiber - coated metal, a multilayer vacuum insulation, and a metallic outer jacket. The vacuum space contains numerous sheets of highly reflective metalized plastic. This design leads to the highest performance of thermal insulation available so far [6,9,30]. The two models of cryogenic vessels, the Cryo-compressed and the Cryo-adsorbed ones present an important advance and alternative over the commercial pressurized vessels, which require complex "high-pressureurization" loading stations [31-36].

Recent advances in the materials science and engineering of hydrogen cryo-adsorption materials are based on large surface areas usually much greater than 1000 m² /g and highly porous structures with binding energies of about 2-10 kJ / H₂mol (in the physisorption range). Most attention has been focused on activated nanocarbons, metal organic framework (MOF) compounds, and microporous polymers have been investigated over the past two decades [10,11,30, 35-44]. The comparison of both approaches for cryogenic hydrogen storage focuses on how the respective storage capacities, vessel weight and dormancy vary as a function of temperature, pressure and type of cryo-adsorption material (especially, powder MOF-5 and MIL101). Typical assessments of cryo-compressed and cryo-adsorption hydrogen storage tank systems for automotive applications have been reviewed by Johnson and Benard and Ahn and Purewal [40,41]. The density is an increasing function of the storage pressure for all cases, and this effect increases with decreasing temperature. The largest difference between the sorbent materials and the cryo-compressed case (CCH₂) appears to be around 100 bar and 77 K, where the stored density of MIL-101 and compacted MOF-5 is 50% higher than for CCH₂ (45 versus 30 kg/m³) [7,38]. The relative benefit of the presence of a sorbent material reduces with increasing pressure and decreasing temperature. This detriment arises because the internal skeletal structure of the cryo-adsorption materials takes up space without providing a surface for hydrogen binding, thereby eliminating volume that could otherwise be occupied by dense cold gas. The optimal fill pressure for the CCH₂ vessel is as large as its pressure limit allows and particularly at low temperature of 40 K and pressure larger than 300 bar enables larger H₂ densities while extending storage times before significant fuel venting

occurs. Current LH₂ vessels have evaporation losses from heat leaks between 0.3% and 3% per day [4]. The dormancy period (days), the time or energy for which the system can sustain the heat leak until the maximal system pressure is reached, is calculated by dividing the internal energy change (in Watt-days) by the rate of heat transfer (in Watts). Dormancy depends on the fill level of the vessel, the initial temperature and also the final operating pressure. As the vehicle is parked (not using H₂), heat transfer warms the H₂ increasing the internal energy and with it, both the temperature and pressure. Dormancy ends in this case when the pressure reaches the final operating pressure usually about 6 bar, when H₂ venting or vehicle driving becomes necessary to maintain pressure within the vessel rating. Sorbent based storage system have a greater dormancy than the cryo-compressed system. This is due partly to the isosteric enthalpy of desorption which is endothermic. At 100 bar pressure, the use of adsorption material increases dormancy, since the adsorbed phase can absorb energy and thus increases the energy needed to reach the vessel operating pressure limit.

Unfortunately, present cryo-pressure and cryo-adsorption storage vessels for transportations are heavy, bulky and expensive. They imply excessive mechanical containment and intensive thermal insulation and consequently important investments in their manufacture, production and maintenance costs [45-47]. It has been clearly demonstrated that the engineered embodiments of both the cryo-compressed and cryo-adsorption methods extend the vessel dormancy. But why is it necessary? Or more precisely to what extent? One answer was given in the relation between dormancy and the period of inactivity before the vessel releases H₂ to reduce pressure build-up, which refers to individual and occasional drives when the quantities of hydrogen being stored are themselves small, and the storage time between fills is long. Therefore it is concluded that such individual drives necessitate hydrogen vessels at cryogenic temperatures and at high pressure. However it was argued that with less restrictive constraints weight and cost might be divided at least by a factor 2 [8]. The designing guidelines in future engineering efforts should be directed towards collective transportations with shorter dormancy, hours or days rather weeks, using the relationships found between onboard H₂ capacity and dormancy as a function of the enveloping lining material and type of the catalyst sorbent.

Short Dormancy Double Open Hydrogen Vessels DOV Principles and Structure

Double Open Hydrogen vessels, DOV in the following, present three main structural characteristics to be open, double and including a barrage system [8]. Open in the sense of lack of any interrupting valve. Immediately after the vessel load of liquid hydrogen, the fuel cell is continuously alimented in hydrogen gas until its total transformation in electricity. Consequently the vessel dormancy corresponds to the planed end-use of the stored energy relative to the daily period of each particular transportation. Double means that the DOV storage vessels use metallic double-walled containers between which the hydrogen gas flows, as a counter-current similar in principle to the ones used in the liquefiers and common to most heat exchangers. Finally the DOV storage vessels include a barrage system of successive microporous plugs cumulating three functions shortly detailed in the following (i) gas expansion (ii) adsorption (iii) catalysis. Such a structure can also be complexified and reiterated in multiple channels embedded one another as in industrial thermal exchangers.

The concepts of open DOV, comprising two opposite connected vessels and a barrage system, are based on the cryogenic,

cybernetic, hydrodynamic, and catalytic properties, currently adopted to liquefy hydrogen in the industry. While combining the same thermal functions they operate in opposite direction from the low temperature of the loaded liquid to the room temperature of the ejected gas. On the other side they combine some essential patterns of the Cryo-compressed and Cryo-adsorbed Vessels but at different periods of the discharge, at different temperatures and much lower pressures.

The detailed structure of the DOV compartments, already described in a previous paper is represented schematically in the Figure 3 together with the hydrogen flow path. In the present letter we discuss the inconveniences and advantages resulting from the main DOV patterns. The DOV reservoir has been conceived to be simple to manufacture, through the successive assembly of all its components. The pieces are fixed together sequentially. The torus porous plugs, pipes, and supports are first filed around the inner storage container then inserted, packed and fastened inside the external retroaction container leaving minimum interstitial spaces between the compartments. An overlapping conic top closes the whole reservoir after securing the outlet tube, pasted or fused, and a firm metallic ring is encircled around.

The DOV vessels should be much lighter and less expensive than actual long term hydrogen vessels, because of their much lower internal pressures. Therefore, the DOV linings should not include an inner vacuum, and consequently, their overall thermal conductivity is much larger than the vessels with higher insulation. The linings that envelop each container, external or internal could be manufactured by a multilayer 0.8-1 cm-thick envelope, including multiple layers of composites glass fibers, plastics, mosses, wools, and polyesters such as polyurethane, eventually metalized. Total mass of their walls should not exceed 1.5 kg/L. The use of carbon fibers too expensive should be avoided for these linings.

Thermal Insulation and Hydrogen Warming

The Figure 3 represents the Hydrogen flow path of a typical DOV reservoir. The hydrogen is first loaded in liquid form in an inner storage container. After its evaporation the current effuses through a series of holes or nozzles and then flows out, in opposite direction, diffuses across successive porous plugs, accumulating in the intermediate compartments until being ejected to the Fuel Cell and/or the ignition engine. The double structure of the DOV Reservoirs installs a counterflow that absorbs part of the environmental heat, thereby insulating the storage container and delaying its warming. The temperature increase being also delayed by the successive expansions induced by the barrage system, the maximum internal pressure of the stored hydrogen is maintained moderate, below ~ 150 bar, which allows a lower weight and consequently implies a lower cost.

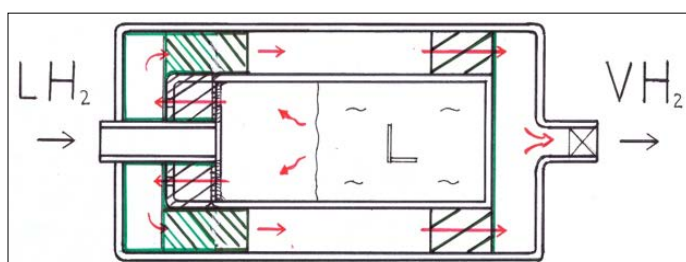


Figure 3: DOV Hydrogen Vessel

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DOV Compartments and Hydrogen Flow Path. Liquid Hydrogen is loaded in the inner compartment. After evaporation it effuses through a series of nozzles, then diffuses across a few microporous catalytic plugs before flowing out toward the Fuel Cell and/or the ignition engine.

The cybernetic device of feedbacks studied by Wiener, Shannon, and Von Neumann was applied in Automatics by Nyquist and Wade Bode to study the stability of loop systems [48,49]. The mechanism applied to the DOV reservoirs combines the principle of feedback control with that of a counter flow cooling currently used in heat exchanger devices and liquefaction procedures. The DOV topology here described, similar to that of Klein's bottle (the top being connected to the bottom), is viewed as a pedagogic illustration of the retroaction effect, although more complex flow paths might be constructed, such as those elaborated in modern heat exchangers or in diffusing through porous plugs along the surface of topological materials [50, 51].

The retroaction container allows the crossing of two flows: heat and matter as illustrated by the retroaction scheme under operation in the DOV reservoirs represented in the Figure 4. Q_i is the incoming heat from the environment into each successive compartment arranged in the direction of the flow: $i \in \mathbb{R}$ and q_i is the outgoing heat from "i" toward the hydrogen container. The environmental heat flowing inside the vessel $Q = \sum Q_i$ is divided into two portions: one part warms the storing hydrogen container H ($q = \sum q_i$), while the other part is evacuated by the counter-flow toward the fuel cell ($Q - q$). The basic functions of the retro-action container to insulate the stored hydrogen and of the microporous plugs to control the flow rate are apparent on the Figure 5 which represents the temporal evolution of the stored hydrogen temperature in function of its entropy. It has the form of a stretched "S" whose graphical branches correspond to successive physical phases (liquid, fluid mixture, and gaseous) following one after the other: (I) Loading and Boil-Off, (II) Pressure Build-Up, (III) Steady Flow and (IV) Back-off.

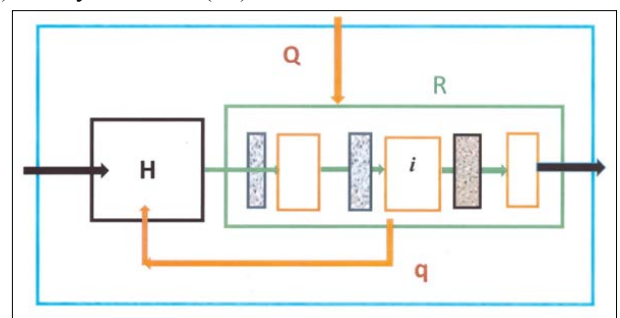


Figure 4: Compartments and Heat Transfers

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Heat Flows: Hydrogen follows a path that effuses out from its storage container H into the retro-action container R through successive compartments i . Each compartment receives the heat Q_i from the environment and transfers a portion of it q_i to the hydrogen container. In total, the retro-action container receives Q and transfers q .

The first phase of a few minutes correspond to the load at a low temperature (20.4 K) and high density (~80 g/L) using a commercially available LH_2 pump. The volume of the H-container is being selected sufficiently large to decrease the hydrogen density

initially to ~ 60 g/L and some vapor evacuation stabilizes the turbulent mixture of liquid and vapor. In the second phase of Pressure Build-Up, the container parameters are selected such that the liquid-gas mixture state crosses the saturation curve and becomes a single fluid phase, close to the critical point around $T_1 = 30$ K, $P_1 = 37$ bar, and $T_1 = 50$ g.L⁻¹. The pressure and the temperature increase first sharply, but progressively the pressure increase becomes limited - by the resulting JT expansions, - by the ortho spinning of the converted molecules, - by the feed dilution due to continuous gas ejection - and by the micro-pore fillings of the nano materials. The system reaches a quasi-steady flow in a third phase when the decrease in hydrogen density due to the gas ejection compensates the increase in the temperature, which in turn limits the hydrogen thermal conductivity of the counter flow and thus increases the reservoir insulation. The Figure 5b enlarges part of the temperature vs entropy function, in a region around a hundred of K where the estimated increasing temperature trajectory of the stored hydrogen, is represented by a black-dotted line that crosses the two iso-density blue curves of 40 and 30 g/L, thereby illustrating the saturation pressure along the 120 isobar of the remaining stored hydrogen. In the last back - off phase, the flow remains sustained by the plugs desorption absorbing a last portion of the incoming heat and delaying the overall warming. The density and the pressure decrease together and the temperature curve concavity turns over, raising slowly towards 300 K.

The DOV model differs from the Cryo-compressed and the Cryo-adsorbed ones in reducing respectively the internal pressure and the quantity of adsorbents by factors in between 2 and 4 [31-36]. However it uses successively both models at their best performing temperature and pressure: first in the initial phases of adsorption around 40-50 K, then after the filling of the micro pores in pressurizing the successive compartments around 100 -120 K and finally, after the pressure relaxation and JT expansions ending around 200K, the carbon materials desorb sustaining the flow in the last warming phase. Therefore the different patterns of pressure and adsorption complement each other in the successive phases of the DOV discharge.

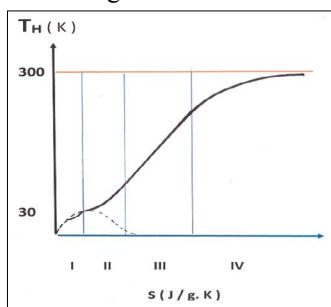


Figure 5a

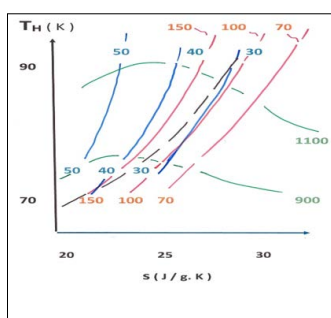


Figure 5b

Figures 5: Hydrogen Temperature vs. Entropy
(a) The temperature $T_H(t)$ increase in the hydrogen container is first

delayed due to hydrogen evaporation and the insulating properties of the retro-action container R until it climbs along a pressure isobar and gradually relaxes to 300 K. (the four temporal phases are indicated in abscissa). (b) The temperature $T_H(t)$ between 70 K and 90 K (dotted black line), crosses successively the iso-density curves of 40 and 30 g/L, and the internal pressure starts to decrease from the 120-130 bar «plateau» in the third phase III. (the isobars are represented in red, iso-densities in blue, and iso-enthalpies in green).

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Flow Regulation by Porous Plugs

The hydrogen flow regulation in a DOV Reservoir is installed by a barrage-system of successive porous plugs of decreasing porosities. These nano materials inserted along the countercurrent path combine four functions: - a variable adsorption-desorption cycle that stores part of the hydrogen diffusing through the plugs, - a mechanical containment that rigidifies the double structure, - successive JT expansions that stabilize the flow and delay the pressure and temperature increases and - a catalytic effect that transforms part of the translational motion in a spin-rotational internal energy.

Absorbent Materials for Porous Plugs

Numerous porous materials exhibit a variety of diffusive patterns through their labyrinthic frames. The cryo-adsorption materials on the model design are to be structured using porous solids, such as activated carbon compounds and zeolites or to be filled with powdered metal-organic frameworks used widely for the separation and purification of gases and even in fuel storage vessels for vehicles [36-39, 41-43, 52-56]. Microporous adsorbents with desorption enthalpies in the range of ~ 5 -15 kJ/mol present a variety of pores, classified as micropores (< 2 nm), mesopores ($\in 2$ -50 nm), and macropores (≥ 50 nm). Chahine and Bose initiated the adsorption studies of hydrogen on different nano-porous activated carbon materials and zeolites, while metal-organic framework structures were further investigated and developed by Rowsell [52-53]. The activated carbon microporous materials AX-21, MOF-5, and MIL-101 have cage-like porous structures, rendering these efficient adsorbents for hydrogen applications in particular for cryo-adsorbed vessels [7,30,41-44]. The adsorbent efficiency correlates with the specific surface area per unit volume of the adsorbent ($\in 0.2$ -1.5 m²/L) defined by the product {specific surfaces ($\in 1.4$ -2.8 m²/kg) x densities ($\in 0.15$ -0.51 kg/L)}.

Hydrogen Pressure Descending Ladder

The flow is basically governed by the pressure gradient between the H container and the outlet condition but modulated by the porous plugs. These "plug-gates" operate successive JT expansions in the counterflow, installing a descending ladder of decreasing pressures in the adjacent compartments and regulating the hydrogen flow at constrained fillings of the micro-and nano-pore conditions. The first plug would have the largest percentage of macropores to facilitate the first discharge. The successive plugs along the current direction, would have an increasing number of meso- and micro-pores with an increasing function of retention. At low temperature (30 - 80 K), diffusion is governed by the transport through wider pore mouths exhibiting also a higher storage capacity with increasing pressures because the associated energy barrier is relatively low. With an increase in temperature the higher kinetic energy leads to an increase in the contribution

of the narrower pore mouths with higher energy barriers [57].

Mechanical Containment

The containers envelopes might be wrapped around with polymer resins and also with an aluminum lining, filled with glass fibers, that strengthens at a low temperature. Each envelope is thin (~1 cm) and light in weight (20 kg/m²). The glass fibers could be composed mainly of the silica SiO₂ of type E, which has a high density with Young's modulus of 73 GPa. The porous plugs inserted in polymer supports in between the containers maintain the interstitial space and strengthen the whole structure increasing its rigidity designed to support the pressure gradients between the hydrogen container (up to 200 bar) and the retroaction container (up to 80 bar) and to sustain the whole reservoir against the environment. Recently, new amorphous states of metal-organic frameworks (MOF) and polymers, have been manufactured to present intrinsic advantages over crystals and powders, in particular a strong mechanical robustness [58]. These amorphous states of metal-organic frameworks (MOFs) and porous coordination polymers, can be produced by various methods among which the pressure-induced amorphization have an advantage of rigidity and a greater ease of processing. A picture of the amorphous metal-organic framework observed recently is reproduced on the Figure 6.

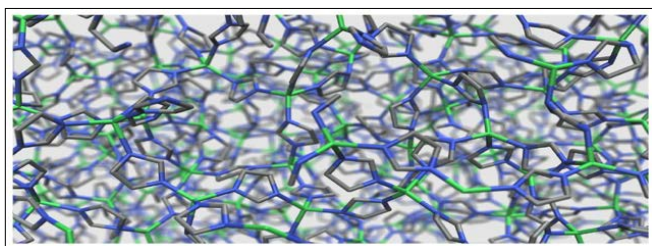


Figure 6: Amorphous MOF

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Typical example of an amorphous state of a metal-organic framework (MOF) which can be produced by pressure-induced amorphization. Topological disorder create alternative properties in cage-like microporous activated carbon materials and porous coordination polymers conjugating a few thermodynamical functions as heat exchangers, catalytic converters and pressure expanders.

Catalytic Porous Plugs

The catalytic function of the successive porous plugs is first to convert the para-hydrogen flow into its ortho variety, absorbing a valuable part of the entering heat (equilibrium o-p mixtures contain rotational energies about to 2/3 of the translational heat) while the last plugs processing at higher temperatures should equilibrate the para variety (higher rotational energies acting as heat pumps). The general properties of the efficient ortho-para converters have been detailed in a few reviews [13,18,25-27]. From early 1958, the National Bureau of Standards in Boulder (USA) promoted iron oxides catalysts as the more efficient ones for multiple reasons: variety of manufacture proceedings, extended surfaces and high surface magnetic momenta [14-17, 59-61]. Even now, such materials are extensively used under different composites in zeolites, graphene oxides or diluted in gel supports, and studied by modern measurements methods: calorific, sound propagation or neutron imaging [62-66]. Nowadays the commercial ortho-para converters usually selected for their efficient performances in the hydrogen conversion comprise the 3d transition metal powdered magnetic oxides (iron, chromium, or nickel) diluted,

impregnated, or dispersed inside the selected porous frameworks and are available as inexpensive commercial standards. They might be processed in the form of self-supported iron or chromium oxides or in multiple-decked sandwiches, or dispersed inside a porous zeolite or attached to a MOF structure [67-69].

Advances in molecular surgery have led to the development of novel techniques for nano particles that open ligands in the MOF or carbon structures [68-69]. The simple activated carbons, pyrolyzed graphites, or even zeolites might be embedded with ionic fragments for immediate applications. Rowsell and Yaghi describe these novel approaches for impregnation with reactive species through coordinative unsaturation [52,53]. This is possible with metal clusters that have additional terminal ligands of attractive secondary building units bound to them in certain MOFs. The solvent molecules coordinated to the metal may be liberated, and the terminal ligand may be removed without detriment to the framework, thereby exposing an open metal site to the void region. Consequently amorphous states of metal-organic frameworks (MOF) and polymers prepared by pressurization and impregnation represent actually the best choice for the micro-porous plugs to be inserted in the DOV vessels for hydrogen transportations.

Energy Temporal Dispensing

The set of "mass and energy" conservation equations, linked to one another, constitutes a chain beginning at initial completion of the loaded hydrogen evaporation, until the evacuation at any time t , with the hydrogen variables related according to the equation of state [8,70]. The temperatures of the hydrogen $T_H(t)$ in the inner container and $T_E(t)$ in the counterflow (averaged over adjacent compartments) are represented as functions of time in the Figure 7.

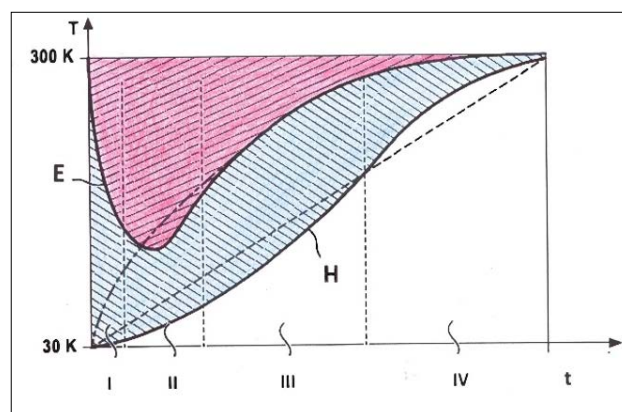


Figure 7: Hydrogen Temperature vs. time

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The hydrogen average temperature $T_E(t)$ in the retro-action container R begins at 300 K, drops due to the cold hydrogen issuing from H and then warms rapidly due to the incoming heat. The hydrogen warming in the hydrogen container $T_H(t)$ is delayed initially due to hydrogen evaporation and the insulating properties of the retro-action container, and later because of the catalytic and expansion effects. The incoming heat Q is represented by the red area, while the transferred heat q by the blue area. (The four temporal phases are indicated in abscissa)

The four temporal phases are indicated in abscissa. The temperature T_H increases gradually during the first "Loading, Boil-Off, and Pressure Build-Up" steps (I) and (II). First T_H

stagnates, evaporation consumes energy and also due to the heat transfer delay. Then the moderate temperature increase of T_H occurs because of the hydrogen depletion (both hydrogen evacuation and plugs filling). The average temperature T_E in the retro-action container R, starts decreasing from the environmental temperature (and a certain amount of remaining hydrogen) until it reaches a minimum value due to the counter-current cooling. This behavior is due to the balance between the contradictory effects of the enthalpy of LH_2 vaporization, the exothermic nature of the adsorption process, the thermal inertia of the sorbent thermal mass, and the pressurization heating. In the third step of “Steady Flow” (III), the hydrogen density in the porous plugs saturates, and the pressure in H reaches a «plateau», while the temperature climbs along the isobar. The concavity of the curve $T_E(t)$ has by now turned over because the temperature in the R container is already high, and the flow rate has reached its highest value. The warming of the H container is delayed slightly as less heat is entering and the curve concavity turns around approximately at the end of the step (III), after almost half of the pre-set period. Finally, in the last step of “Back-off” (IV), involving the final discharge, all curves converge toward their outside and ambient standard values (which are defined by the fuel cell procedures).

The key parameters of a DOV are the energy storage duration τ and the hydrodynamic and thermodynamic resistances. The energy period τ is the pre-set time duration for which the hydrogen is available while feeding the fuel cell. It is, therefore, associated with the energy necessary to drive the vehicle under pre-defined circumstances. On the other hand, the incoming heat in the vessel is a function of the multi-layer composition of the linings. In general, a particular lining that wraps the retro-action container is characterized by a thermal transfer coefficient h expressed in $W.m^{-2}.K^{-1}$. The incoming heat that has entered during the total duration τ , is represented by the slashed red area depicted in Figure 7 (multiplied by the thermal transfer coefficient and the envelope area). Similarly, the heat transferred from the enveloping retro-action container to the H storage container is indicated by the slashed blue area between $h \cdot \tau \cong 18 \theta t$ and $T_H(t)$ multiplied by an almost identical coefficient). Now, considering that it requires approximately 3.5 MJ per kg to transform the hydrogen from a temperature of 30 K to 300 K under standard conditions and that such energy has been provided only through the heat $Q(\tau)$, entered inside the vessel between the initial fueling of mass M of liquid hydrogen and the final time (when all the hydrogen has flown out from the vessel), the period τ of hydrogen energy discharge is related to the container thermal transfer coefficient h by the simple equation :

The above period τ associated to a particular h (in $W.m^{-2}.K^{-1}$) is expressed in hours. The factor θ measures the retro-action effect represented by the proportion of red surface in the Figure 7 (the numerical ratio: total rectangle area: 270 τ divided by the red surface). It reflects the overall vessel geometry and the porosities of the plugs. (The coefficient is chosen for a model of vessel characterized by a ratio: {envelope surface/stored hydrogen mass} = 0.2 m^2/kg). The larger the vessel surface, the larger is the incoming heat and the shorter is the energy period $\tau \cong 13$ h.

It appears clearly on the Figure 7, that the retro-action factor θ represents an amplification that is always larger than 2 and could range between 3 and 5. The thermal heat transfer parameter ‘ h ’ is a function of the envelope wall components. As an important part of the external heat is being continuously evacuated, a thin envelope of glass fibers suffices to limit the heat entry rate in the range of

hundreds of Watts, about 100 times the rate of actual prototypes. If, for example $h = 4 W.m^{-2}.K^{-1}$ and $\theta = 3$, the reservoir would dispense the stored hydrogen during approximately $\tau \cong 13$ h.

Conclusion

Microporous materials should be used as valuable intermediates in the hydrogen phase transition, allowing the progressive switching between gas and liquid hydrogen states. Modern composites can conjugate a few thermodynamical functions as heat exchangers, catalytic converters and pressure expanders. The activated carbon microporous materials of cage-like porous structures, render these efficient adsorbents for hydrogen applications in liquefiers devices or storage vessels. Advances in molecular surgery have led to the development of novel techniques for nano particles that open ligands in the MOF or carbon structures. The simple activated carbons, pyrolyzed graphites, or even zeolites might be embedded with ionic fragments for enhanced catalytic activity. Topological disorder create alternative properties in porous materials [8, 71]. Amorphous metal-organic framework structures prepared by pressurization and impregnation appear ideal porous plugs to be inserted in hydrogen storage vessels and in catalyst-filled plate-fin heat exchangers in large scale industrial hydrogen liquefiers.

In the industrial liquefiers, the flow regulation challenge would be to succeed a continuous conversion of the hydrogen stream while transforming the conversion energy in translational velocity, compensating the adsorption delays and yielding minimum practical work to be furnished.

In the hydrogen vessels for transportations, significant energy saving can be obtained if the catalyzed conversion to para hydrogen is carried out consistent with the expected storage time [8,72]. The DOV vessels would need to reload their forecasted energy for their daily use. Due to the continuous hydrogen ejection, directed to the fuel cell, the pressure vessel of the DOV models remains much lower than in conventional or cryo-compressed models, under 150 bar, and their sorbent mass much less than in cryo-adsorbed models. Requiring less mechanical containment (carbon fibers might be avoided) and less thermal insulation (interstitial vacuum might be avoided) they are simpler to manufacture, lighter and consequently of lower cost. If correlated to the production-distribution network they would ideally satisfy the economic requirements of future collective transportation networks.

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