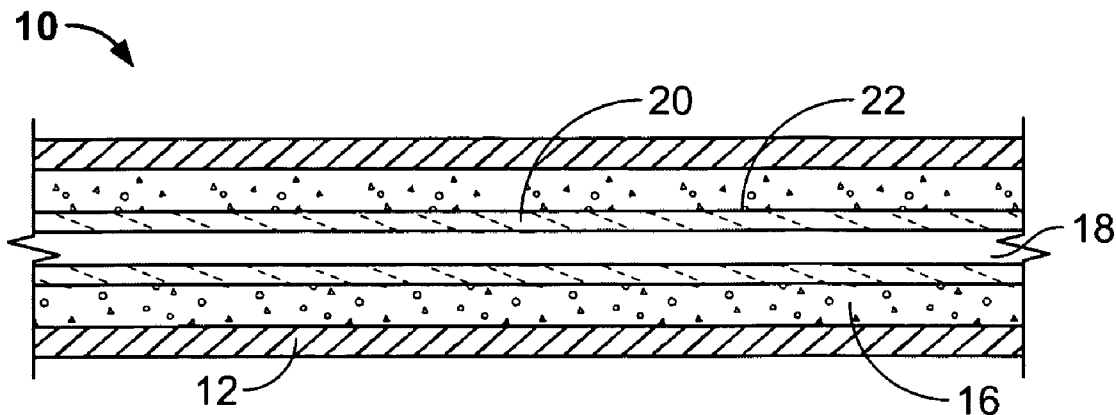




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(19) **United States**(12) **Patent Application Publication**
Golben(10) **Pub. No.: US 2006/0065553 A1**(43) **Pub. Date: Mar. 30, 2006**(54) **FLEXIBLE HYDROGEN DELIVERY
MECHANISM FOR STORAGE AND
RECOVERY OF HYDROGEN**(57) **ABSTRACT**(76) Inventor: **P. Mark Golben**, Florida, NY (US)Correspondence Address:
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CHICAGO, IL 60602 (US)(21) Appl. No.: **10/951,134**(22) Filed: **Sep. 27, 2004****Publication Classification**(51) **Int. Cl.**
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A conduit passage for use in transfer of hydrogen gas within a hydride system, including tubular members semi-permeable to hydrogen gas, permit hydrogen gas to pass through but not oxygen or other gases. The tubular members may comprise a flexible elastic polymeric material, such as polysulfone, polypropylene or polyethylene, including a central conduit passage, for providing hydrogen gas flow, the direction of the hydrogen flow depending on whether hydrogen is being absorbed or desorbed by the metal hydride. Simultaneously, the tube material, acting as a flexible spine, essentially fixes the hydride powder and prevents it from shifting about within the container, as well as being carried away in the hydrogen flow. Sections of the tubular member material may be interspersed throughout the hydride material to provide for peripheral hydrogen dispersion and to accommodate compressive stress forces that may develop as a result of the expansion of the hydride material during hydrogen absorption.



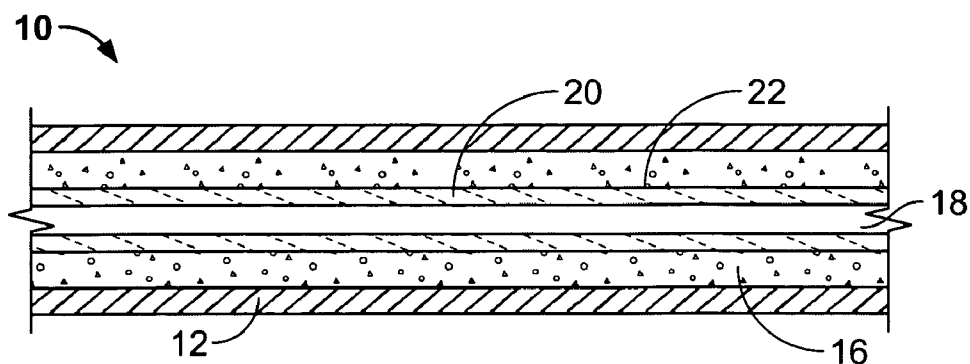


FIG. 1

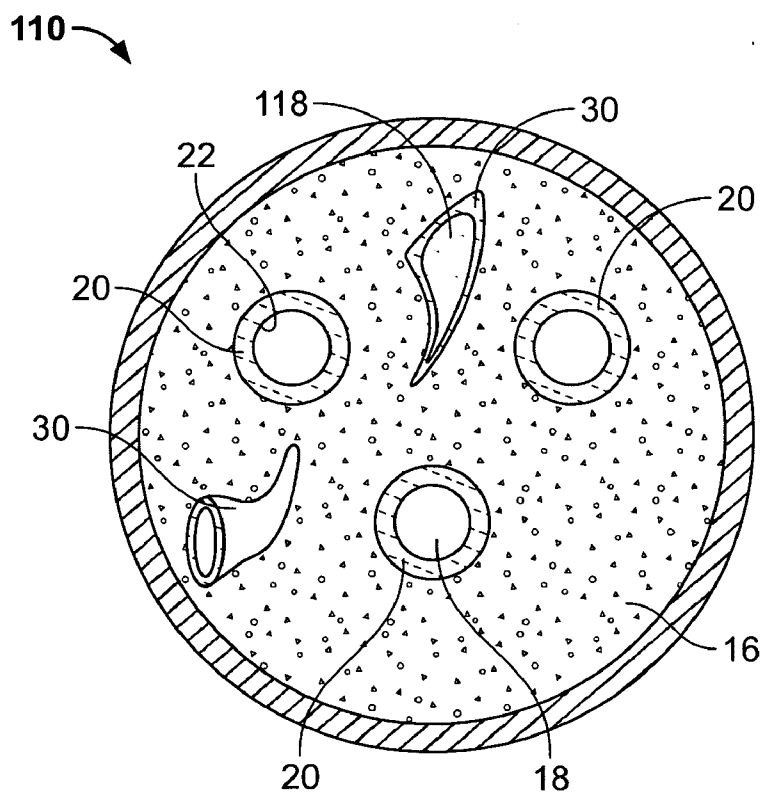


FIG. 2

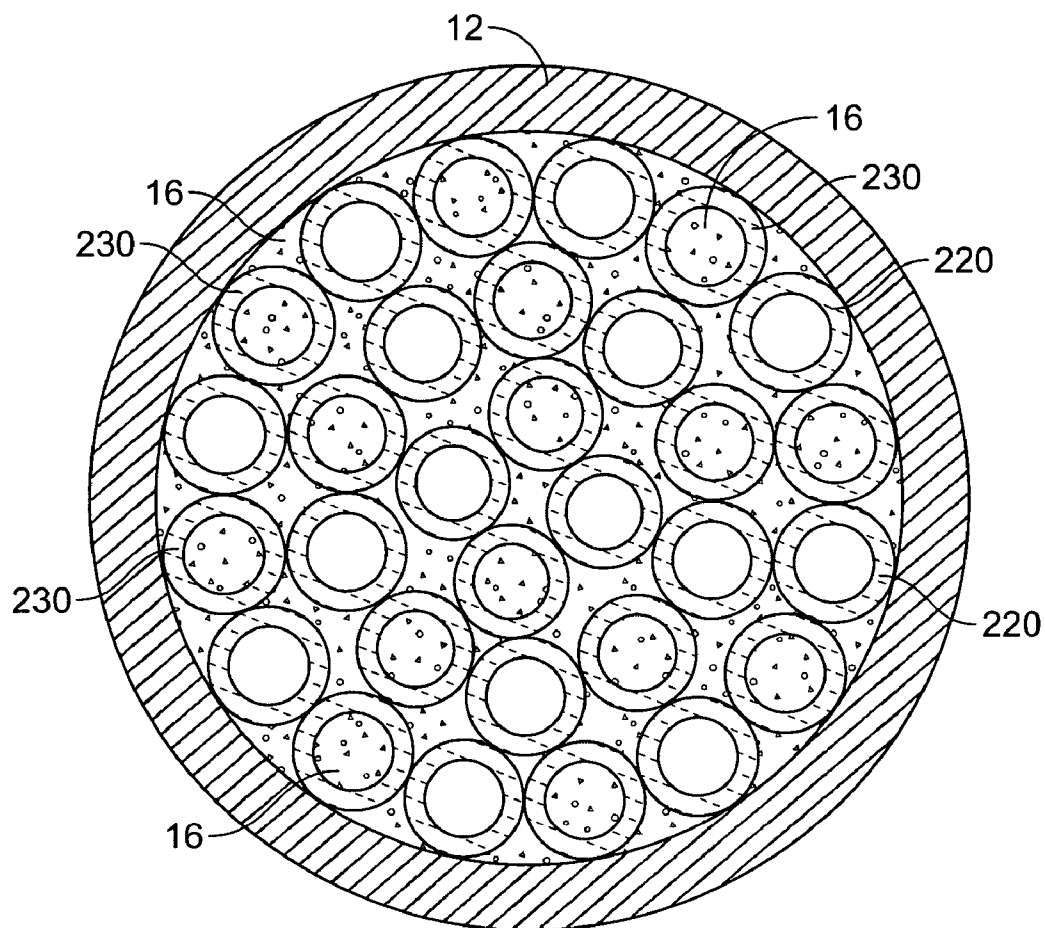


FIG. 3

FLEXIBLE HYDROGEN DELIVERY MECHANISM FOR STORAGE AND RECOVERY OF HYDROGEN

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates generally to an apparatus for transferring, storing and recovering hydrogen from a hydride material and more particularly to such an apparatus used for transferring hydrogen under pressure while simultaneously removing any gaseous impurities from the hydrogen stream before the hydriding step.

[0003] 2. Background Art

[0004] Hydrogen in the combinant form of water has long been employed in many chemical processes. Recent advances have permitted use of elemental hydrogen in gaseous form in physical processes, such as in heat transfer and electrical energy storage. For example, the fuel cell industry, among others, is continually developing new applications for hydrogen, including fuel cells and heat transfer applications. As a result there is a growing need to store hydrogen safely and conveniently in such applications.

[0005] Hydrogen has been stored conventionally as a gas in steel cylinders at high pressures over 2000 psi and at lower pressures as a liquid in insulated containers at very low temperatures. Both methods of storage require comparatively bulky storage containers that are often in need of maintenance. In addition to their unwieldy size, such containers are inconvenient due to the high pressure required for gas storage in cylinders, which can contribute to the possibility of hydrogen gas leakage from the cylinders.

[0006] Storage of hydrogen in metallic compounds and alloys, commonly called hydrides, has been recognized as a solution to the problem of hydrogen volatility and safe storage and delivery. Metal hydrides, in the form of metallic powder, can store large amounts of hydrogen at low pressures in relatively small volumes. Low pressure storage of hydrogen is relatively safe and allows the construction of hydrogen storage and delivery containers having forms significantly different than those presently known. Although the weight of the metal hydride powder is a consideration, there may result a concomitant reduction in the weight of the container, since excessively large pressures will not be encountered, and thick container walls are not as significant.

[0007] Including use in the storage of hydrogen, metal hydrides are also currently being evaluated for a variety of applications, including for gas compression, solar heat storage, heating and refrigeration, hydrogen purification, utility peak-load sharing, deuterium separation, electrodes for electrochemical energy generation, pilotless ignitors and internal combustion engines.

[0008] The processes and equipment used in hydrogen storage is the subject of several commonly assigned U.S. patents, for example, U.S. Pat. Nos. 4,396,114, 5,250,368, 5,532,074 and 5,688,611, the disclosures of which, where appropriate, are incorporated by reference as if fully set forth herein.

[0009] An important consideration, particularly addressed in U.S. Pat. Nos. 4,396,114 and 5,688,611, is the delivery of the hydrogen gas between the metal hydride material in a

container, usually in powder form, and the end use equipment that utilizes the hydrogen gas, for example, a hydride compressor.

[0010] One difficulty that has been investigated is high compressive stress due to the compaction of the powder and expansion thereof during hydride formation. These stress forces are directed against the walls of the storage container and may damage the container itself or the associated internal assemblies unless provision is made to accommodate the impact of the forces. The amount of stress generated by expanding powder has been observed to increase until the yield strength of the container is exceeded, whereupon the container plastically deforms, buckles or bulges and eventually ruptures. Such rupture is to be avoided, since it may become dangerous for fine, often pyrophoric, powder to be expelled by a pressurized, flammable hydrogen gas. Small, experimental cylinders of the aforescribed type have indeed been found to open and/or burst when subjected to repetitive charging-discharging cycles, because of repeated and progressive structural stresses. Additionally, it is undesirable for containers to lose their integrity since any hydrogen stream expelled out of a hydride container may be subject to combustion with possibly catastrophic results.

[0011] While the solution to the problem of hydride powder compaction described in the above-described patents are normally adequate to control excessive bulging and deformity of the container by absorbing the stress of metal hydride particles expanding as hydrogen is absorbed therein, the method has been found to be expensive and static from the ability to otherwise modify the operational efficiency and/or effectiveness of the hydrogen containers. Such solutions also contribute to the weight of the hydride container, reducing the gravimetric hydrogen storage density. What has been found necessary therefore is an inexpensive and lightweight means for accommodating the stress forces resulting from hydrogen absorption/desorption phenomena, while simultaneously filtering from the gaseous hydrogen the gaseous impurities before the absorption process commences at the metal hydride surface.

SUMMARY OF THE INVENTION

[0012] Accordingly, there is provided a hydrogen storage unit comprising an enclosed container including encasement walls and having at least one opening for receiving and discharging gaseous hydrogen, a flexible hydrogen dispersion mechanism including at least one elongated passage for evenly distributing hydrogen essentially throughout the enclosed container, each such elongated passage being defined by at least one tubular structural element comprising an inert semi-permeable membrane, and metal hydride material packed within said enclosed container and between said hydrogen dispersion mechanism and said encasement walls. In a second embodiment, the flexible hydrogen dispersion mechanism further comprises a plurality of elongated tubes having a predetermined thickness capable of providing structural integrity and comprising an elastic flexible material that is selectively permeable to hydrogen and is impermeable to oxygen and other gases. The tubular members may comprise a flexible elastic polymeric material that includes a central passage for delivery of hydrogen gas. The material may be any polymeric material but preferably comprises polysulfone, polypropylene, polyethylene or urethane materials, generally, and may include polytetrafluoroethylene (PTFE).

[0013] The tubular members act as a conduit for hydrogen gas; the direction of the hydrogen flow being a function of whether the hydrogen is being absorbed or desorbed by the metal hydride. Simultaneously, the tube material, acting as a flexible spine for the tube, essentially fixes the hydride powder and prevents it from shifting about within the container. In certain situations, the tube may also accommodate hydride material expansion, for example, when the hydride material becomes supersaturated with hydrogen and the expansion of the hydride material fills up the space within the tube.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **FIG. 1** is a cross-sectional view of one embodiment of the invention.

[0015] **FIG. 2** is cross-sectional view of a second embodiment of the invention shown at a perpendicular orientation to the view of **FIG. 1**.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] Referring now to **FIG. 1**, a generally tubular compartment unit **10** having a tubular wall **12** is shown in cross-section. For a more detailed description of the structure of the unit **10**, including tubular walls **12**, and the hydride material **16** contained by the wall **12**, reference is made to the description found in commonly-owned U.S. Pat. No. 4,396,114, which description is incorporated herein by reference.

[0017] One significant difference from U.S. Pat. No. 4,396,114, providing a marked improvement and important feature of the present invention, is the ability to miniaturize the tubular unit **10**, while simultaneously providing fluid communication within and through the tubular unit **10** so as to evenly distribute the hydrogen gas throughout the hydride material **16**, along the entire length of the tubular unit. It has been suggested to use flexible helically wound springs, axially extending throughout the tubular unit **10**. While the use of such closely wound springs to provide central hydrogen gas passage within the center of the spring, the spring material itself, usually a metal of a specified diameter, takes up a significant volume within the tubular unit **10**, so as to decrease the volumetric space available for the hydride material, and also adds to the weight of the unit. Especially when using a filter sheath, as is described in the aforementioned U.S. Pat. No. 4,396,114, even less space is available. An additional drawback to the prior art devices is that the closely wound springs carry a weight penalty which reduces the gravimetric hydrogen storage capability of the tubular unit.

[0018] Thus, there is proposed herein as a solution to these drawbacks one or more conduit passages **18** for fluid communication that may be defined by elongated tubular members **20**, each comprising a wall **22**. Because the walls **22** of the tubular members **20** are very thin, they do not take up space excessively, so that it may otherwise be available for hydride material **16**. Although necessarily limited by the diameter of the walls **12**, the size of the tubular member **20** may take any diameter consistent with the need to pack as much hydride material as possible within the tubular members **20**. An ideal compromise may be achieved between

maximum hydride packing capacity and the distance from any hydride particle to the nearest wall **22** of the nearest tubular members **20**.

[0019] If that distance is found to be too great, for example, if a large diameter unit **10** is used, then it is possible to use plural separated, preferably randomly oriented, sections **30**, comprised of the same or similar material as the tubular members **20**, to provide passages **118** for optimal hydrogen flow to all areas of the unit **110**, as shown in **FIG. 2**, disposed in parallel

[0020] The material comprising the walls of the tubular members **20** are a permeable, or semi-permeable material that permits essentially only hydrogen gas to flow there-through. The material preferably is flexible to some extent so as to be able to absorb or accommodate for the expected expansion, sometimes as much as 25%, of the metal hydride material **16** as it absorbs hydrogen therein. If necessary, additional filler sections **30** of the material from which tubular members **20** comprised, in which the walls **22** may be oriented parallel or perpendicular to the tubular members **20**, or randomly oriented, may be dispersed throughout the hydride material **16** to accommodate expansion of the hydride material **16**, as shown in **FIG. 2**. These sections **30** also serve the dual purpose of providing both unrestricted delivery of hydrogen to remotely located hydride materials, for example, that which is located adjacent the walls **22**, and also provides flexible filler material that is also capable of accommodating additional stress forces of the expanding hydride material (when hydrogen is being absorbed).

[0021] The material comprising the walls **22** of tubular members **20** may take a number of forms, but must be able to pass hydrogen gas therethrough while keeping out particles of hydride material **16**, some of which may be microscopic in size. That is, materials are most suitable which in thin sheets are permeable to hydrogen gas. Because of the relatively miniscule size of the hydrogen gas molecules, in comparison with, for example, nitrogen or oxygen molecules, some materials will permit hydrogen gas to pass through easily upon only a slight pressure differential across the membrane. Good candidates for materials comprising tubular member walls **22** are considered to be polysulfone, polypropylene, polyethylene or urethane materials, generally, but other such materials may come readily to mind to persons familiar with permeable or semi-permeable membrane materials. Specific materials comprising the tubular member wall **22** that have been found to work well in passing hydrogen gas therethrough include polytetrafluoroethylene (PTFE) or Teflon®, commercially available from E.I. DuPont de Nemours Company of Wilmington, Del.

[0022] As shown in **FIG. 2**, the unit **110** includes multiple tubular members **20** that each may be used to each transfer hydrogen gas longitudinally through the hydride material **16**. In addition thereto, as a separate element interspersed throughout the hydride material **16**, shorter pieces of tubular member walls **22**, randomly oriented relative to the walls **12** of the unit **110**, may provide compressive potential for accommodating the expansion pressures of the hydride material **16** as it expands during the hydrogen charging or absorption part of the hydriding cycle.

[0023] In yet another embodiment, and as shown in **FIG. 3**, a unit **210**, shown in a transverse, cross-sectional view, the enclosing wall **12** has disposed within its inner space a

plurality of tubular members 220 so as to provide a series of compartmentalized conduits and separate passageways for hydrogen dispersal throughout the bed of hydride material 16 disposed within the enclosure 12. Unlike the prior art devices of the aforementioned '114 patent, however, the tubular members 220, 230 do not have a surrounding sheath of material to retain the physical barrier to the transposition or shifting of the hydride material 16 contained within the enclosure 12 of the unit 210. Instead, each of the tubular members 220 has a central passage in the form of a central tubular space. This central tubular space within a majority of the tubular members 230 provides a retainer for hydride material 16, as shown. The remaining tubular members, indicated by reference numeral 220, are free of hydride material 16, but nevertheless extend throughout the length of the longitudinally disposed tubular members 220, for permitting easy and unencumbered fluid communication and hydrogen gas transfer for the hydriding and dehydriding processes.

[0024] The material comprising tubular members 220, 230 may be a flexible material, such as plastic, composite or other appropriate material, suitable to permit easy hydrogen flow therethrough. Preferably, the tubular members 220, 230 are flexible enough to be bent significantly but still to maintain sufficient integrity to retain the desirable filtering properties, as described above. Thus, hydrogen gas can be almost instantaneously transferred along the longitudinal extent of the unit 210 through the tubular members, so as to provide instant pressurization of the hydrogen storage unit 210 and so to provide hydrogen gas to all portions of the hydride bed 16 as needed. Simultaneously, the tubular members 220, 230 also essentially fix the hydride powder 16 between their outer walls and the inner diameter of the walls of enclosure 12 so as to prevent it from shifting about therewithin.

[0025] In addition, and as an optional feature that is shown in FIG. 3, additional hydride material 16 may be dispersed within the tubular members 230, so as to utilize the space within the enclosure 12 efficiently. The tubular members 220, which are intended to provide fluid communication to the hydride bed 16, are disposed in a preselected pattern within the framework of the tubular members 230 so that the space within the diameter of the outer wall 12 is provided with fluid communication at regular intervals and the tubular members 220 are not overly separated from each other. Thus, no portion of the hydride material 16 is disposed at a distance greater than a predetermined dimension, and provides instant access to a fluid stream of hydrogen during hydriding, and conversely, for an escape vehicle for hydrogen during dehydriding.

[0026] The arrangement of unit 210 shown in FIG. 3 permits selective penetration of hydrogen gas through the walls of each of the tubular members 220, 230, which comprise a semi-permeable material, similar to that described above. Thus, fluid communication of impurity gases from the central passage of the tubular members 220, 230 to the hydride material 16 is restricted, and thereby heavier molecules, such as oxygen, nitrogen, carbon dioxide, methane, etc., are retained within the passage of the tubular members 220 and do not come into contact with the hydride material 16, either within the tubular members 230, or between the tubular members 220, 230.

[0027] One advantage of an arrangement such as that illustrated in FIG. 3 is that the hydride material 16 disposed within the central passage of the tubular members 230 is not exposed to any hydrogen gas until after it has been filtered by the walls of each of the tubular members 220, 230, that is, a double filtration results. This feature provides added protection in that impurities not filtered by one wall of the first member 220, are subsequently filtered by the other wall of member 230. Additionally, in the event of a breach of the wall of one or more tubular member 220, unrestricted gas with impurities may affect the hydride material 16 between the tubular members 220, 230 and the wall of enclosure 12, but a reservoir of hydride material 16 will remain in reserve within the tubular members 230 for continued hydrogen storage and transfer operation of the unit 210, for a limited extent and time, at least until the unit 210 can be replaced.

[0028] While the material comprising the inert sheath film 18, 118 or the tubular members 220, 230 is described as comprising polyethylene, polysulfone, polypropylene or other inert material permeable to hydrogen gas, other materials may also be available for these members. For example, membranes may be used that have been treated with catalysts to be semi-permeable to hydrogen. Alternatively, a mole sieve material may be used to render the flexible membrane material reactive to various impurities, i.e., oxygen containing molecules that may be entrained in the hydrogen gas stream, so that the membrane may convert the impurities to non-reactive, inert molecules. For example, a catalyst may convert a CO₂ molecule into oxygen and CH₄, and include an oxidation mechanism that binds to the free oxygen and does not permit the oxygen atoms to penetrate the membrane. Use of a mole sieve material can be designed and preselected to enable the membrane to absorb various impurities during absorption, that may be released back into the hydrogen stream during the subsequent desorption or dehydriding process. The remaining elements of this embodiment may have structures similar to that shown in FIG. 2, and may have other modifications, for example, elements to accommodate hydride expansion, as described above.

[0029] Another possible modification to the structure described above, not shown in the present drawings, is a gas manifold disposed at one or both ends of the longitudinal extent of the unit 210, so that hydrogen gas may be evenly dispersed, without pressure gradients developing between the different the tubular members 220, 230. Thus, at the hydrogen gas intake end, the hydrogen gas may be available at the manifold to equalize the pressure across each of the tubular members 220, 230. Optionally, hydrogen gas back flow can be provided for by a second manifold disposed at the distal end, removed from the hydrogen gas intake, so that the hydrogen gas pressure equalization between the tubular members 220, 230 may take place even if there is some impediment, such as a blockage, in one or more of the tubular members 220.

[0030] This invention is described with reference to the preferred embodiments, but alterations, modifications substitutions and other similar changes would become apparent to a person having ordinary skill in the art after having obtained an understanding of the disclosed invention. Accordingly, the invention is limited only by the following claims and their equivalents.

What is claimed is:

1. A hydrogen storage unit comprising:
 - a) an enclosed container including encasement walls and having at least one opening for receiving and discharging gaseous hydrogen;
 - b) a flexible hydrogen dispersion mechanism including at least one elongated passage for evenly distributing hydrogen essentially throughout the enclosed container, each such elongated passage being defined by at least one tubular structural element comprising an inert semi-permeable membrane; and
 - c) metal hydride material packed within said enclosed container and between said hydrogen dispersion mechanism and said encasement walls.
2. A hydrogen storage unit according to claim 1 wherein said flexible hydrogen dispersion mechanism further comprises an elongated tube having a predetermined thickness capable of providing structural integrity comprising an elastic flexible material that is selectively permeable to hydrogen and is impermeable to oxygen and other gases.
3. A hydrogen storage unit according to claim 1 wherein said flexible hydrogen dispersion mechanism further comprises a plurality of elongated tubes having a predetermined thickness capable of providing structural integrity comprising an elastic flexible material that is selectively permeable to hydrogen and impermeable to oxygen and other gases.
4. A hydrogen storage unit according to claim 1 wherein said flexible hydrogen dispersion mechanism further comprises an ionically treated membrane.
5. A hydrogen storage unit according to claim 2 wherein said elongated tube further comprises an ionically treated membrane.
6. A hydrogen storage unit according to claim 3 wherein each said elongated tube further comprises an ionically treated membrane.
7. A hydrogen storage unit according to claim 1 wherein said flexible hydrogen dispersion mechanism comprise a material taken from the group consisting of polytetrafluoroethylene (PTFE), polysulfone and polypropylene.
8. A hydrogen storage unit according to claim 2 wherein said flexible hydrogen dispersion mechanism comprise a

material taken from the group consisting of polytetrafluoroethylene (PTFE), polysulfone and polypropylene.

9. A hydrogen storage unit according to claim 3 wherein said flexible hydrogen dispersion mechanism comprise a material taken from the group consisting of polytetrafluoroethylene (PTFE), polysulfone and polypropylene.

10. A hydrogen storage unit according to claim 1 wherein said flexible hydrogen dispersion mechanism further comprises polytetrafluoroethylene (PTFE).

11. A hydrogen storage unit according to claim 2 wherein said elongated tube further comprises polytetrafluoroethylene (PTFE).

12. A hydrogen storage unit according to claim 3 wherein each said elongated tube further comprises polytetrafluoroethylene (PTFE).

13. A hydrogen storage unit according to claim 1 wherein said hydrogen storage unit further comprises a plurality of tubular structural sections being randomly dispersed within the hydride material.

14. A hydrogen storage unit according to claim 11 wherein said plurality of tubular structural sections dispersed within the hydride material comprise polytetrafluoroethylene (PTFE).

15. A hydrogen storage unit according to claim 1 wherein said elongated passage further comprises a plurality of tubular structural members dispersed within the hydride material.

16. A hydrogen storage unit according to claim 15 wherein hydride material essentially surrounds each of the plurality of tubular structural members.

17. A hydrogen storage unit according to claim 3 wherein said plurality of tubular structural sections dispersed within the hydride material comprise two groups, a first group of tubular structural members which are free of hydride material from their internal tubular enclosure and a second group of tubular structural members which include a predetermined amount of hydride material within their internal tubular enclosure.

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