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(54) **HOLLOW POROUS-WALL GLASS MICROSPHERES FOR HYDROGEN STORAGE**

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(57) **ABSTRACT**

A hollow glass microsphere is provided having a diameter range of between 1 to 140 microns, a density of between 0.05 to 0.50 gm/cc, a porous-wall structure having wall openings defining an average pore size of between 10 to 1000 angstroms, and which contains therein a hydrogen storage material. The porous-wall structure facilitates the introduction of a hydrogen storage material into the interior of the hollow glass microsphere. Thereafter, a barrier coating may be applied and/or the microspheres are processed to alter or reduce the effective pore size. In this manner, the hollow glass microsphere can provide a membrane for the selective transport of hydrogen through the porous walls of the microsphere, the small pore size preventing gaseous or liquid contaminants from entering the interior of the hollow glass microsphere.

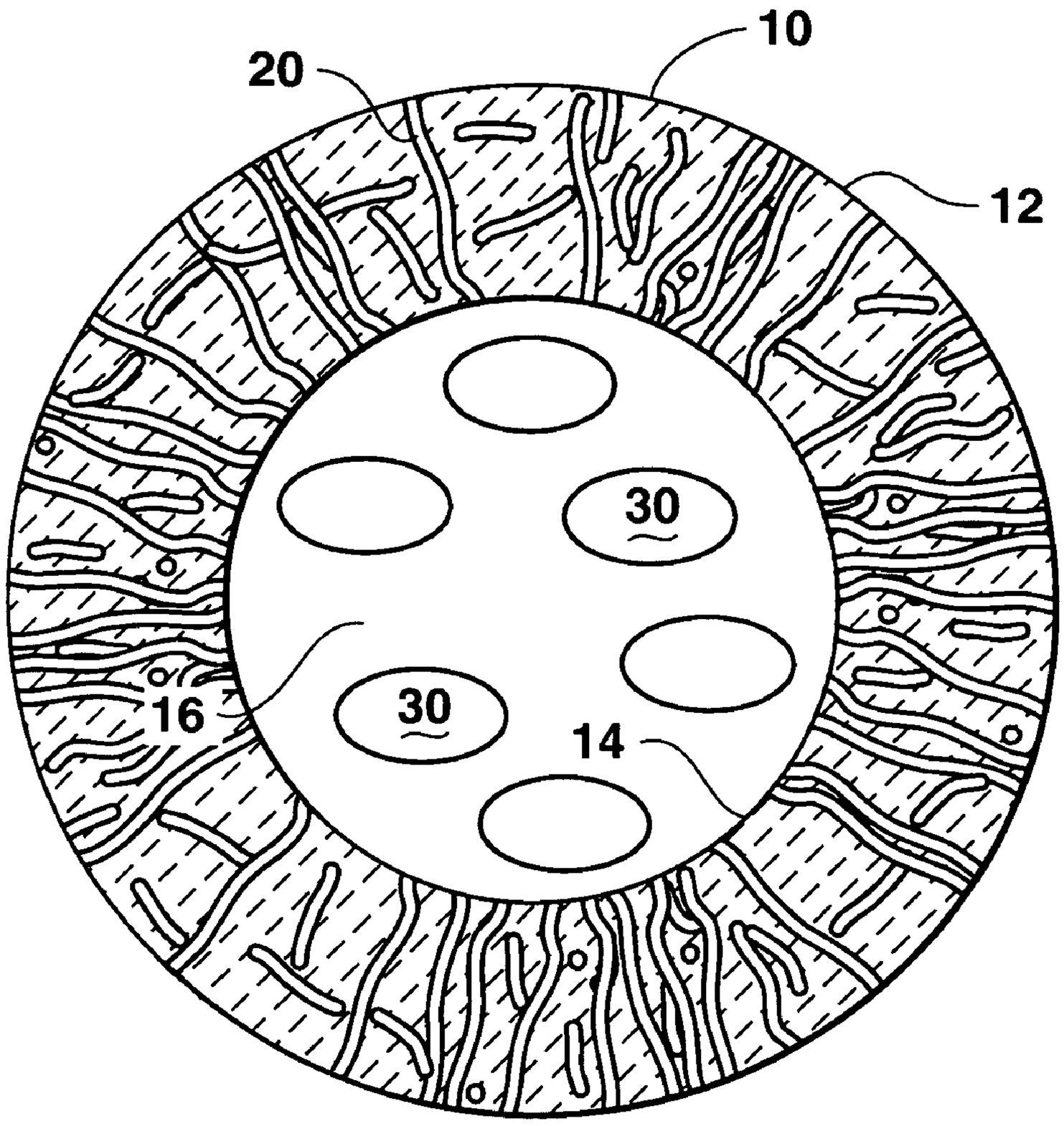

FIG. 1

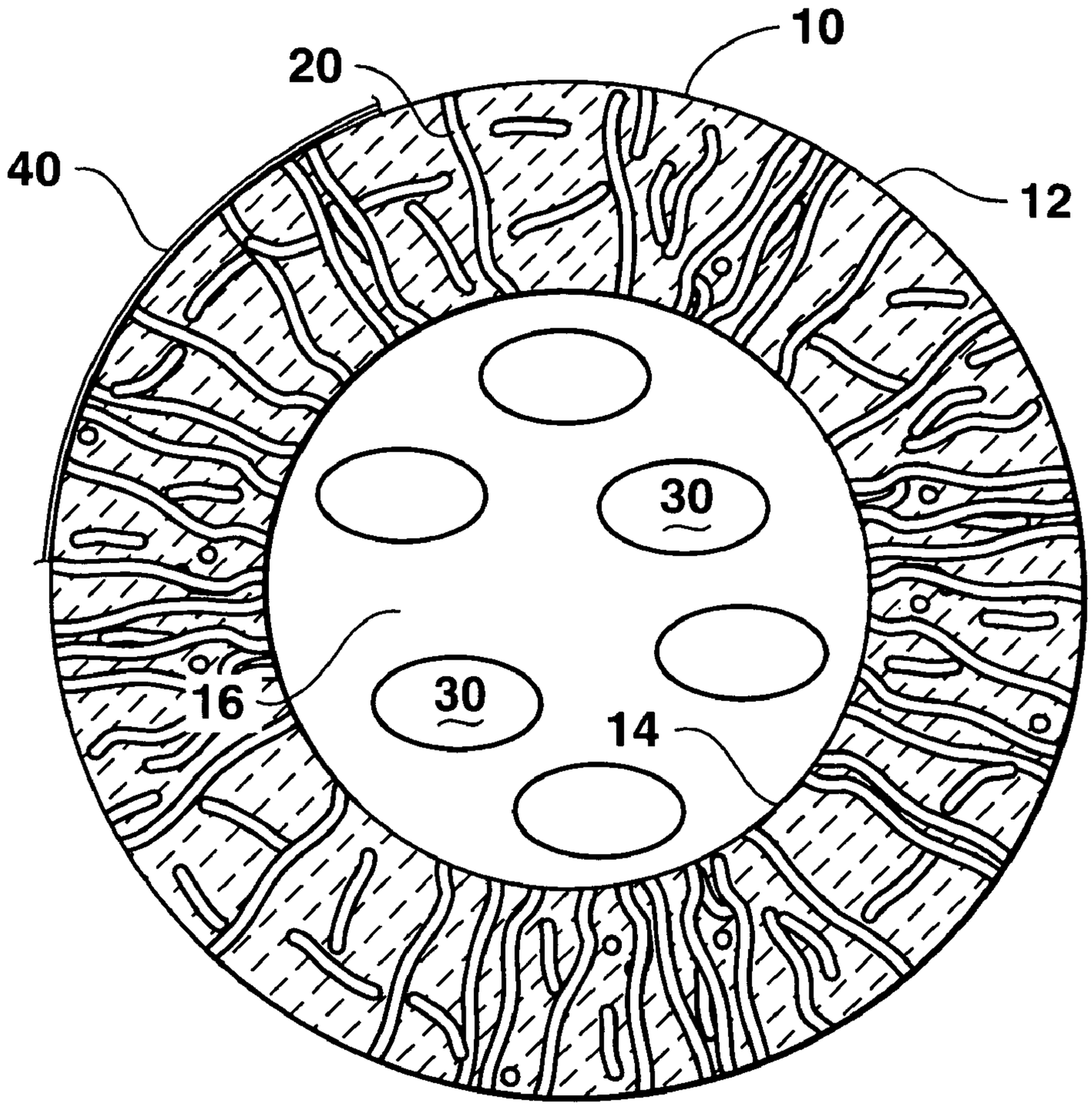

FIG. 2

HOLLOW POROUS-WALL GLASS MICROSPHERES FOR HYDROGEN STORAGE

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

[0001] This invention was made with Government support under Contract No. DE-AC0996-SR18500 awarded by the United States Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

[0002] This invention is directed towards hollow glass microspheres and a process of using the microspheres as part of a hydrogen storage system. The hollow glass microsphere wall defines a series of pores. The pores facilitate the placement of a hydrogen storage material within the interior of the hollow glass microsphere. The porosity of the hollow glass microspheres can thereafter be modified by either altering or reducing the overall pore size or by coating the individual hollow glass microspheres so as to maintain the hydrogen storage material within a sealed interior of the hollow glass microsphere. The coating and/or the controlled pore size enables the selective absorption of hydrogen gas through the walls of the hollow glass microsphere while isolating the hydrogen storage material encapsulated therein from other external gases and fluids.

[0003] The hollow glass microspheres can thereafter be subjected to variations in temperature, pressure, or other release stimulus triggers to bring about the release of hydrogen gas. Once dehydrided, the hollow glass microspheres and hydrogen storage material can be reused so as to once again selectively absorb hydrogen gas.

BACKGROUND OF THE INVENTION

[0004] The formation of hollow glass microspheres (HGMs) is well known in the art. The production of hollow glass microspheres has been described in U.S. Pat. No. 3,365,315 (Beck); U.S. Pat. No. 4,661,137 (Garnier); and U.S. Pat. No. 5,256,180 (Garnier), and which are incorporated herein by reference.

[0005] It is also known in the art to produce large macrospheres having hollow glass walls which provide a semi-permeable liquid separation medium for containing absorbents. The production of macrosphere structures can be seen in reference to U.S. Pat. Nos. 5,397,759 and 5,225,123 to Torobin and which are incorporated herein by reference. The Torobin references disclose hollow glass macrospheres comprising multiple particle glass walls. The reference teaches the use of the macrospheres for gas/liquid separation and for use with absorbents but does not discuss any features or characteristics which would make the microspheres suitable as a hydrogen storage medium.

[0006] U.S. Pat. No. 4,842,620 (PPG Industries) is directed to non-crystalline silica fibers having porous walls which are used in gas separation. The fibers described in this application have different physical characteristics than microspheres and which makes fibers less desirable with respect to hydrogen separation and storage capabilities.

[0007] U.S. Pat. No. 6,358,532 (CaP Biotechnology, Inc.) uses porous-wall hollow glass microspheres for cell clustering and biomedical uses. The porous-wall structures are designed to readily release microsphere contents when present within a biotic system. Alternatively, the microspheres are used to provide a substrate to support cell growth within the porous-wall structure.

[0008] While the above references disclose a variety of glass microspheres and porous-wall structures having various uses in material separation or drug delivery capabilities, there remains room for improvement and variation within the art.

SUMMARY OF THE INVENTION

[0009] It is at least one aspect of at least one embodiment of the present invention to provide for a hollow glass microsphere (HGM) having a diameter range of between about 1.0 micron to about 140 microns, a density of about 0.05 gm/cc to about 0.50 gm/cc, and having a porous-wall structure having wall openings with an average pore size of between about 10 angstroms to about 1000 angstroms, which contains within an interior of the hollow glass microsphere a hydrogen storage material.

[0010] It is another aspect of at least one embodiment of the present invention to provide for a hollow glass microsphere containing therein an effective amount of the hydrogen storage material palladium, the hollow glass microsphere having a pore size which prevents the loss of palladium fines from the interior of the hollow glass microsphere.

[0011] It is at least one aspect of at least one embodiment of the present invention to provide for a hollow glass microsphere (HGM) having a diameter range of between about 1.0 to about 140 microns, a density of about 0.05 gm/cc to about 0.50 gm/cc, and having a porous-wall structure having wall openings with an average pore size which may range from about 10 to about 1000 angstroms, and which contains within an interior of the hollow glass microsphere a hydrogen storage material, the exterior wall of the hollow glass microsphere containing a barrier coating sufficient to prevent gaseous or liquid contaminants from entering an interior of the HGM while permitting the passage of hydrogen gas through the exterior wall.

[0012] These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] A fully enabling disclosure of the present invention, including the best mode thereof to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying drawing.

[0014] **FIG. 1** is a cross sectional view of a hollow glass porous-wall microsphere containing a hydrogen storage material within the interior of the microsphere.

[0015] **FIG. 2** is a cross sectional view similar to **FIG. 1** showing a microsphere having an exterior coating.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] Reference will now be made in detail to the embodiments of the invention, one or more examples of

which are set forth below. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment can be used on another embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. Other objects, features, and aspects of the present invention are disclosed in the following detailed description. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions.

[**0017**] The hollow glass microspheres of the present invention are prepared using a special glass composition which after appropriate heat treatment separates into two continuous glass phases. In the examples provided herein, one of the phases is rich in silica, while the other is an extractable phase. The extractable phase is preferably present in an amount of at least about 30 weight percent of the total glass composition. However, other porous glass compositions may be used.

[**0018**] The extractable phase of the glass composition preferably includes boron-containing materials such as borosilicates or alkali-metal borosilicates. Suitable borosilicates and alkali-metal silicates may be found in reference to the teachings of U.S. Pat. No. 4,842,620 directed to leachable glass fiber compositions and which is incorporated herein by reference.

[**0019**] The extractable and non-extractable glass components are mixed, melted, quenched, and crushed to a fine glass powder consisting of individual glass particles having a particle size of about 5 to 50 microns. The individual glass particles are then reheated using a gas/oxidizer flame. The glass is raised to a temperature where a latent blowing agent within the glass, such as alkali sulfate along with various hydrates, carbonates, and halides, the selection and use of which are well known in the art, causes a single bubble to nucleate within each particle of glass. As the glass particle temperature increases by exposure to the flame, the glass particle reaches a viscosity where the particle transforms to a sphere due to the surface tension forces. As the temperature increases, the pressure within the bubble exceeds the surface tension/viscous forces value and the bubble expands to form a hollow glass microsphere. The hollow glass microsphere is then rapidly quenched to room temperature.

[**0020**] Preferably, the resulting hollow glass microspheres have densities in the range of about 0.05 gm/cc to about 0.5 gm/cc and diameters may range between about 1 to about 140 microns. Once formed, the hollow glass microspheres may be separated on the basis of density so as to select and segregate the hollow glass microspheres according to desired densities. Additionally, it is possible to separate the HGMs according to the microsphere diameter.

[**0021**] The resulting hollow glass microspheres have a glass wall composition in which the glass is essentially homogeneous. The hollow glass microspheres may be heat treated to enhance the glass-in-glass phase separation by mixing the hollow glass microspheres with carbonaceous materials and heating in the absence of oxygen to the desired temperature region. After heat treating the hollow glass microspheres, the homogeneous glass separates into two continuous glass phases: one extractable and the other rich in silica. The extractable phase is readily leachable using strong mineral acids which results in the formation of wall pores within the remaining silica-rich phase. Suitable mineral acids and methods for leaching the glass may be seen in reference to U.S. Pat. No. 4,842,620 which is incorporated herein by reference.

[**0022**] The resulting hollow glass microspheres exhibit a high degree of cell wall porosity. As used herein, the term "porosity" means a series of pores and similar openings which either directly or indirectly define a series of passageways which provide communication between the interior and the exterior of the hollow glass microsphere. An average cell wall porosity of about 10 angstroms to about 1000 angstroms can be achieved using this technology. The cell wall porosity is dependent upon the percentage of extractable components formulated into the special glass composition used in the formation of the HGM and the degree of heat treatment employed. The duration and severity of the extraction process also can have some influence on the characteristics of the resulting cell wall pores including size and density of pores formed.

[**0023**] As seen in reference to **FIG. 1**, a cross section through a hollow glass microsphere **10** is provided. Microsphere **10** comprises a glass wall having an exterior surface **12** and an interior surface **14**. The microsphere **10** further defines a hollow cavity **16** within the interior of the microsphere. As best seen in reference to the figure, a plurality of pores **20** are defined within the glass wall of the microsphere. As illustrated in **FIG. 1**, a number of the pores **20** provide for communication between an exterior of the hollow glass microsphere and the interior cavity **16** of the hollow glass microsphere. Present within the hollow cavity **16** is a hydrogen absorption material **30**. The placement of the hydrogen storage material within the cavity **16** is provided in greater detail below.

[**0024**] Once formed, the porous-wall hollow glass microspheres can be filled with a hydrogen absorbent such as palladium. To successfully introduce palladium into the interior of the HGM, palladium chloride can be forced through the porous glass walls using pressure. Following the introduction of palladium chloride, hydrogen is then introduced under pressure to reduce the palladium chloride to palladium metal. Subsequent heat and vacuum drying may be used to remove any residual hydrochloric acid or water. This process can be repeated through several cycles to increase the amount of palladium ultimately encapsulated within the hollow glass microsphere.

[**0025**] Once a desired amount of palladium is present within the hollow glass microsphere, the porosity of the hollow glass microsphere wall can be altered or reduced by additional heat treatment. Alternatively, the pores can be effectively sealed by applying a coating material **40** such as tetraethyl orthosilicate solution and as illustrated in **FIG. 2**. The coating material can be formulated to permit the diffusion of hydrogen while excluding other gases.

[**0026**] The resulting hollow glass microsphere containing a hydrogen absorbent offers numerous advantages for use

with hydrogen absorbing technologies. For instance, when palladium metal and other metal hydrides are used in a hydrogen absorption/desorption process, the hydrogen storage material tends to fracture into smaller particles or "fines." The resulting fines can clog filters, limiting gas flow through the filtration bed in hydrogen separation devices, and/or blocking gas flow in hydrogen storage devices resulting in an overall loss of efficiency of the hydrogen absorption/desorption system. However, when encapsulated within the hollow glass microsphere, the resulting fines are contained within the hollow glass microsphere and continue to function in an absorption/desorption capacity.

[**0027**] Additionally, it is possible to select HGMs having a sufficiently small pore size such that gaseous poisons which may interfere with the hydrogen absorbing material are physically excluded from entry into the interior of the HGM. As a result, the HGM functions as a selective membrane which permits the flow of hydrogen gas into and out of the hollow glass microsphere while preventing the entry of larger gaseous or liquid molecules.

[**0028**] While it is possible to force hydrogen into and out of solid-walled microspheres, the use of a porous-wall hollow glass microsphere structure allows hydrogen gas to enter and exit the microsphere at much lower pressures and temperatures. Consequently, less strenuous rehydriding/dehydriding conditions can be employed using the porous-wall structure as a conduit to enable the passage of hydrogen gas through the wall of the glass microsphere.

[**0029**] Where the pore size of the resulting hollow glass microsphere is sufficiently large that gaseous poisons or other materials could enter, it is possible to provide barrier coatings to the exterior of the HGM. The various barrier coatings may be selected for special properties so as to provide for selective membrane properties. One such coating material is a sol gel material having a sufficiently defined pore structure that provides for a barrier against gaseous poisons while permitting the flow of hydrogen gas therethrough. One such sol gel material may be found in reference to the commonly assigned U.S. Pat. No. 5,965,482, and which is incorporated herein by reference.

[**0030**] The hollow glass microspheres, containing therein a hydrogen storage material, offer additional advantages within the hydrogen storage technology field. The hollow glass microspheres used in accordance with the present invention may have diameters of between about 1 micron to about 140 microns. Given the size and selectable particle densities, the resulting hollow glass microspheres have fluid-like properties which make the hollow glass microspheres suitable for easier transport and bulk storage. For instance, transportation of large quantities of the filled hollow glass microspheres may be made utilizing existing pipelines used to convey the supplies of petroleum products and/or natural gas.

[**0031**] Though the collective volume of hydrogen storage material may contain enormous quantities of stored hydrogen gas, the transport is much safer in that the hydrogen is stored within a plurality of discrete hollow glass microsphere vessels. As a result, the dangers associated with the storage of a comparable volume of hydrogen gas is greatly lessened since the volume is now distributed within a large number of individual hollow glass microsphere vessels. The individual hollow glass microspheres provide an enhanced level of safety against explosion and fire in that there are no exposed large volumes of hydrogen gas. For example, a leak or release of HGMs containing releasable hydrogen has a much reduced threat of explosion or fire since no free hydrogen is available. Even if released into flame or high temperature conditions, the insulating properties of the hollow glass microspheres are such that the net result is a series of very small releases of hydrogen gas as opposed to a release of a single large volume of hydrogen gas.

[**0032**] While palladium represents one hydrogen storage material which may be incorporated into the interior of the hollow glass microspheres, it should be noted that a variety of other hydrogen storage materials are also suitable for use within the interior of a porous-wall hollow glass microsphere. Such materials include sodium aluminum hydride, lithium aluminum hydride, titanium aluminum hydride, complex hydrides, and various fused or hybrid hydrogen storage materials such as those described in commonly assigned PCT application PCT/US03/34980 which is incorporated herein by reference, and various catalyzed borohydrides as described in commonly owned U.S. provisional application entitled "Catalyzed Borohydrides For Hydrogen Storage having Attorney Docket No. WSR-78-P filed on Aug. 27, 2004, by Express Mail EV504784466US and which is incorporated herein by reference. and combinations of these hydrogen storage materials. Additionally, the hollow glass microspheres can be utilized to provide a "protective environment" for reactive hydrides or other hydrogen storage materials which occupy the hollow interior of the porous hollow glass microsphere.

[**0033**] It is within the scope of the present invention to provide for a number of different hydrogen storage materials which may be contained within the interior of a suitable HGM. Doing so would allow a plurality of different hydrogen storage media to be utilized within a given application. For instance, within a given volume of hollow glass microspheres, there could be two or more different hydrogen storage materials present within discrete populations of microspheres having different hydrogen release properties. In this way, the volume of evolved hydrogen gas may be controlled or regulated by the appropriate environmental conditions or stimuli needed to release the hydrogen.

[**0034**] In addition, the use of the hollow glass microspheres greatly simplifies commercial recharging of the spent hydrogen storage material. For instance, where the hollow glass microspheres containing the hydrogen storage material are used to power a device, the spent HGM may be removed during a refueling operation and subsequently recharged. By allowing a separate recharging or hydrogen absorption process, the HGMs having a hydrogen storage material can be utilized in various environments such as a hydrogen-powered motor vehicle. To the extent the vehicle only needs to provide for a hydrogen release mechanism, the mechanics and operation of the vehicle may be greatly simplified. Upon refueling with a fresh supply of HGMs (containing hydrided hydrogen storage material) the spent HGMs are simply removed for subsequent rehydriding.

[**0035**] It is also envisioned that the formation of a hollow glass microsphere may be simplified by selection of an appropriate hydrogen storage material to serve as the source of the nucleating gas. In other words, a hydrogen storage material which, when heated, may release hydrogen or other

inert gas that may be used as the blowing agent for the resulting microsphere. As a result, it may be possible to use a hydrogen storage or precursor material which evolves a nucleating agent when heated. As a result, it may be possible to form the hollow glass microsphere directly around a hydrogen storage material.

[0036] Although preferred embodiments of the invention have been described using specific terms, devices, and methods, such description is for illustrative purposes only. The words used are words of description rather than of limitation. It is to be understood that changes and variations may be made by those of ordinary skill in the art without departing from the spirit or the scope of the present invention which is set forth in the following claims. In addition, it should be understood that aspects of the various embodiments may be interchanged, both in whole, or in part. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained therein.

That which is claimed:

1. A hydrogen storage apparatus comprising:

a hollow glass microsphere having a porous wall surrounding an internal volume; and,

a hydrogen storage material selected from the group consisting of palladium, alanates, chemical hydrides, and combinations thereof, positioned within said volume of said hollow glass microsphere.

2. The hydrogen storage apparatus according to claim 1 wherein said hollow glass microsphere has a density of between about 0.05 gm/cc to about 0.50 gm/cc.

3. The hydrogen storage apparatus according to claim 1 wherein said hollow glass microsphere has a diameter ranging from about 1.0 micron to about 140 microns.

4. The hydrogen storage apparatus according to claim 1 wherein said porous wall defines a plurality of openings having an average pore diameter of between about 10 angstroms to about 1000 angstroms.

5. The hydrogen storage apparatus according to claim 1 wherein said hollow glass microsphere additionally contains a porous coating on an exterior surface of said microsphere, said porous coating further defining a semipermeable membrane.

6. The process of making a hydrogen storage apparatus comprising the steps of:

forming a hollow glass microsphere having an extractable phase;

removing said extractable phase, thereby providing a porous-wall structure permitting communication between an interior and an exterior of the hollow glass microsphere;

introducing into an interior of said hollow glass microsphere, a hydrogen storage material wherein said hydrogen storage apparatus can reversibly release and store hydrogen.

7. The process according to claim 6 comprising the additional step of providing a selectively permeable coating on an exterior surface of said microsphere.

8. A process of providing a hydrogen storage apparatus comprising:

forming a porous hollow glass microsphere;

introducing through said pores a hydrogen storage material into an interior of said hollow glass microsphere; and,

thereafter treating said hollow glass microsphere so as to alter the pore properties.

9. The process according to claim 8 wherein said step of treating said pores of said hollow glass microspheres comprises a method selected from the group of methods consisting of providing a semi-permeable coating, providing a sol gel coating, heat treating said hollow glass microspheres, and combinations thereof.

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