AN ADSORBENT SYSTEM AND AN APPARATUS FOR EFFECTIVE STORING AND FUELLING OF HYDROGEN

Abstract:

The present invention discloses a system to store hydrogen gas in portable containers that can be used in applications such as auto mobiles or other similar devices. The invention comprises cylinders which are either un-insulated or insulated as per the requirement and which contain a purpose-made adsorbent. The adsorbent has a unique morphology, thereby providing high pore volume and high surface area, which under suitable temperature and pressure conditions allows the hydrogen gas to enter the micro, meso, and macro pores of the adsorbent, consequently maximising the hydrogen adsorption. It should be noted that under suitable pressure and temperature parameters, the higher the surface area and the pore volumes of the adsorbent, the higher the storage; this relationship is limited by practical processing limits on the pressure and temperature.

7 OCT 2011

CLAIMS

1. An adsorbent in the form of an activated carbon powder or activated carbon micro-fibers, or a mixture thereof, said adsorbent having a pore volume of between 1 to 11 cc/g and a surface area between 1000 m2/g to 4000 m2/g, said pore volume and said surface area comprising those obtained by micro, meso and macro pore structures.

2. An adsorbent as claimed in claim 1 wherein said powder or said micro-fibers or said mixture is activated by heating it to an initial temperature of 300 °C, preferably to a duration of up to 1 hour, to remove moisture and then further to 400 °C to 600 °C for a prescribed first period, preferably for up to 2 hours.

3. An adsorbent as claimed in claims 1 and 2, wherein said powder when used without said micro-fibers is used in an amount 50% to 100% v/v with respect to the cylinder volume, said micro-fibers when used without said micro-fibers is used in an amount 50% to 100% v/v with respect to the cylinder volume.

4. An adsorbent as claimed in claims 1 to 3, wherein said mixture comprises carbon powder and carbon micro-fibers, said powder being in an amount 24% to 40% v/v with respect to the volume of storage cylinder, and said micro-fibers being in an amount between 20% to 75% v/v with respect to the storage cylinder

E.7 OCT 2011

volume, such that the volume of total mixture is 50% to 100% v/v with respect to the cylinder volume.

5. An adsorbent as claimed in claims 1 to 4 where said powder or said micro-fibers or said mixture are further activated by heating it in the presence of nitrogen at a temperature between 100 to 300 °C, for a prescribed second period, preferably 2 hours.

6. A hydrogen storage apparatus comprising a thermally insulated storage vessel containing an adsorbent, the storage vessel being adapted for pressurization to a first working pressure; inlet and outlet apparatus for filling the storage vessel with gaseous hydrogen and releasing gaseous hydrogen from the storage vessel; and a cooling apparatus for cooling the adsorbent to a first working temperature; characterised in that said adsorbent used is either an adsorbent as claimed in claims 1 or 2, or it is in the form of activated carbon micro-fibres.

7. A hydrogen storage apparatus as claimed in claim 6, further wherein a metal is dispersed in finely divided ionic form on said adsorbent.

8. An apparatus according to claim 7, characterised in that the first working temperature lies in the range from about 36K to about 300K and that the first working pressure lies in the range from about 200 bar to about 455 bar.

E7 OCT 2011

9. An apparatus according to claim 8, characterised in that the storage vessel is adapted for pressurization to a second working pressure up to about 750 bar.

10. An apparatus according to claim 9, characterised in that the cooling apparatus comprises a heat exchanger containing gaseous helium, the heat exchanger being adapted for connection to an external supply of refrigerated gaseous helium.

11. An apparatus according to claim 6, characterised in that the apparatus further comprises a heating apparatus for warming the adsorbent, said heating apparatus being characterised in that it includes an auxiliary tank containing gaseous hydrogen at a second working temperature, said second working temperature is maintained at atmospheric temperature, preferably between 273K to 325K, and maintained higher than the first working temperature, and a warm hydrogen injection apparatus for injecting hydrogen from the auxiliary tank into the storage vessel.

12. A method of storing hydrogen on an adsorbent, comprising the steps of

i) dispersing a metal in finely divided form onto an adsorbent comprising activated carbon micro-fibres;

7 OCT 2011

ii) arranging the adsorbent in a optionally thermally insulated storage vessel adapted for pressurization to a first working pressure, the storage vessel including a heat exchanger; wherein insulated vessel is used in the case where first working temperature is in the range between 36K and 190K,

iii) cooling a supply of hydrogen; and then

iv) introducing the cooled hydrogen into the storage vessel until the storage vessel is pressurized to the first working pressure, and simultaneously

v) circulating a coolant through the heat exchanger to maintain the adsorbent at a first working temperature,

wherein
said first working temperature is in the range from about 36K to about 300K, and said first working pressure is in the range from about 200 bar to about 455 bar.

13. A method according to claim 12, characterised in that the coolant is gaseous helium.

14. A method according to claim 13 characterised by the additional step of

vi) warming the adsorbent as hydrogen is released from the storage vessel.

07 OCT 2011

15. A method according to claim 14, characterised in that step vi) comprises the step of injecting hydrogen at a temperature higher than the first working temperature into the storage vessel.

16. A method according to claim 15, the storage vessel being adapted for pressurization to a second working pressure higher than the first working pressure, characterised by the additional step of reinforcing the storage vessel.

17. A method according to claim 16, wherein after step (v), a further step (vi) is added, said step (vi) being warming the adsorbent to a second working temperature higher than the first working temperature, and storing the hydrogen in the vessel at the second working pressure corresponding to the second working temperature,

wherein said second working pressure lies in the range from about 300 bar to about 750 bar.

Dated This 7th Day Of October 2011

(Tase, Vijay Sharatchandra)
Patent Agent for the Applicant
Registration Number IN/PA 987

To,
The Controller of Patents
The Patent Office, Mumbai Branch

7 OCT 2011

AN ADSORBENT SYSTEM AND AN APPARATUS FOR EFFECTIVE STORING AND FUELLING OF HYDROGEN

Field of the Invention

This invention relates to technologies for the storage of hydrogen by adsorption, such as for use in fuelling motor vehicles. In particular it relates to storage of hydrogen at a range of temperatures between room temperatures (25-40 °C) and low temperatures (such as 36K) and a range of pressures between atmospheric pressure and high pressures such as 200-400Bar.

Background of the Invention

It is known from US 7,036,324 to store hydrogen by adsorption at cryogenic temperatures in the range of about 40K to 80K onto a high surface area adsorbent such as activated carbon in a storage vessel at a pressure of about 10 bar to 30 bar.

DE 10 2005 023 036 A1 teaches the adsorption of hydrogen onto a powdered carbon adsorbent in a pressurized tank cooled by liquid nitrogen to a temperature lying between the respective ebullition temperatures (at normal pressure) of liquid hydrogen and liquid nitrogen. The adsorbent may comprise carbon nanotubes.

US 5,653,951 teaches the adsorption of hydrogen onto an adsorbent comprising a carbon nanostructure, which may be treated with a metal such as Pd, Pt, Ni, Fe,

7 OCT 2011

Ru, Os, Co, Rh, Ir, La, or Mg in an amount from 1wt% - 5 wt% based on the total weight of the nanostructure.

US 6,672,077 B1 discloses a storage system in which hydrogen is adsorbed by physisorption onto a nanostructured storage material cooled by liquid nitrogen.

US 4,716,736 teaches Metal-Assisted Cold Storage of hydrogen by physisorption at cold, but not cryogenic temperatures onto an activated carbon adsorbent having micro crystals of a Group VIII transition metal such as Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, or Os dispersed onto its surface; and references US 3,138,560, which discloses a process for depositing palladium onto a carbon catalyst.

The overall mass and volume of the on-board hydrogen storage system is a key impediment to the development of practical hydrogen fuelled vehicles. Adsorption of hydrogen offers advantages in safety, practicality and efficiency over competing technologies, which include storage in metal hydrides, as a liquid, or as a highly compressed gas. However, maximising the storage density (the overall volume of stored hydrogen at ambient pressure relative to the volume of the adsorbent) remains a key challenge. The object of the present invention is to increase the hydrogen storage density achievable by adsorption.

7 OCT 2011

International application WO 2009/056962 A2 teaches the use of a carbon adsorbent in the form of micro-fibres. Although this showed an improved storage capacity over the then known art, it was felt that it could be improved further.

Brief Description of Figures

Fig. 1 shows a hydrogen refuelling system

Fig. 2 shows a schematic representation of the hydrogen storage apparatus

Figure 3: a graph showing hydrogen storage volume versus pressure and temperature for various pressures

Summary of the Present Invention

The present invention discloses a system to store hydrogen gas in portable containers that can be used in applications such as auto mobiles or other similar devices. The invention comprises cylinders which are either un-insulated or insulated as per the requirement and which contain a purpose-made adsorbent. The adsorbent has a unique morphology that provides it with high pore volume and high surface area and is designed to maximize H2 adsorption. It should be noted that under suitable pressure and temperature parameters, the higher the surface area and the pore volumes of the adsorbent, the higher the storage; this relationship is limited by practical processing limits on the pressure and temperature.

7 OCT 2011

It is also known to a person skilled in the art that charging hydrogen gas in a cylinder without adsorbent limits the storage due to effective lowering of density and compressibility factor.

Room temperature experiments show an increase of hydrogen take up with adsorbent, to a limited extent. However, the Brownian motion prevents hydrogen from entering the micro- and meso-pores in the adsorbent, limiting the hydrogen access to only the macro pores of the adsorbent, thus placing inherent limits on the storage.

Lowering the temperatures increases the gaseous density; this combined with a reduction in the Brownian motion and a tendency of the hydrogen gas under these conditions allows the hydrogen gas to enter the micro and meso pores also. This results in higher storage per liter of cylinder volume. The present invention exploits this phenomenon whereby a higher hydrogen storage density along with a higher energy density is achieved, ultimately reducing the number of cylinders/ cylinder volumes, resulting in weight reduction and cost, for a given range of operation of a vehicle. The amount of hydrogen stored using the present invention is thus significantly higher than the conventional systems or methods for a given storage volume.

7=OCT 2011

Detailed description of the invention

Accordingly in its various aspects the invention provides a system, a method and an apparatus for storing hydrogen.

An illustrative embodiment will now be described, purely by way of example and without limitation to the scope of the claims, and with reference to the accompanying figures, in which:

Referring to the figures, a hydrogen refuelling system comprises a refuelling station 1 for supplying gaseous hydrogen H to a hydrogen storage apparatus 20 in a motor vehicle 10.

The storage apparatus 20 comprises a thermally insulated or uninsulated on-board storage vessel 21 adapted for pressurization to a first working pressure preferably from 1 bar to 400 bar and containing an adsorbent 22. The storage vessel or cylinder 21 may be a carbon composite tank, with stainless steel, titanium or Aluminium liner (of Type 3) l and provided with or without a thermally insulating jacket 23 as known in the art and comprising for example a high quality vacuum and reflective layers. In one embodiment, the jacket 23 comprises multiple layers of aluminized Mylar, arranged in a hard vacuum.

7 OCT 2011

The storage vessel 21 is provided with separate or combined inlet and outlet apparatus 24 comprising releasable couplings and valves as known in the art for filling the storage vessel with gaseous hydrogen H and for releasing gaseous hydrogen H from the storage vessel via a supply line 25 to the demand (for example, the fuel cell or engine that powers the vehicle). While the vehicle is in use, the release of gaseous hydrogen via the supply line 25 cools the adsorbent by the heat of desorption, offsetting the ambient heat load via the insulating jacket 23. A pressure relief valve 26 may be provided to release hydrogen from the vessel 21 when the vehicle is not in use, which relieves excess pressure within the vessel and also cools the adsorbent containing the remaining stored hydrogen by the heat of desorption.

The vessel 21 also includes a cooling apparatus which preferably comprises a heat exchanger 27, which may be a coil, an inner vessel, an outer jacket or any other structure as known in the art and adapted to contain a circulating coolant and thermally connected to the interior of the vessel 21. The heat exchanger 27 contains a coolant, the coolant comprising gaseous helium He for cooling the adsorbent to a first working temperature between about 36K and about 77K. The inlet and outlet apparatus 24 also includes detachable cryogenic couplings and valves as known in the art for connecting the heat exchanger 27 to an external circulating supply of refrigerated gaseous helium He.

7 OCT 2011

Helium is particularly preferred for use in the cooling apparatus since it remains gaseous at very low temperatures, although other suitable gases or cooling technologies (e.g. liquid nitrogen) may be used in alternative embodiments or at other working temperature ranges.

Optionally, a heating apparatus is provided for warming the adsorbent. The heating apparatus may comprise for example a heat exchanger in thermal contact with the adsorbent for carrying a flow of exhaust gas, such as from a fuel cell or engine of the vehicle, or a flow of heated fluid, such as from a cooling system of the vehicle.

In a particularly preferred embodiment, the heating apparatus comprises an auxiliary tank 28 which contains compressed hydrogen gas, which may be supplied via a filling valve 29, either when the vehicle is re-fuelled or, conveniently, from the supply line 25 or pressure relief valve 26. A warm hydrogen injection apparatus 30 is arranged to selectively inject controlled quantities of warm hydrogen gas (which is to say, hydrogen gas at a temperature higher than the first working temperature of the vessel 21) from the auxiliary tank 28 into the storage vessel 21 to warm the adsorbent, offsetting the heat of desorption so as to maintain the rate of hydrogen desorption when the vehicle is in use, particularly when the tank is nearly empty or during periods of high demand, e.g. when the engine of the vehicle is under heavy load. This allows substantially all of the stored hydrogen to be released from the vessel 21 as it empties.

07 OCT 2011

Conveniently, the auxiliary tank 28 contains compressed hydrogen gas at ambient temperature, and does not comprise an adsorbent.

The refuelling station 1 includes a supply of cooled hydrogen H. The hydrogen is drawn from a source 2, which may comprise a hydrogen generator, a cascade of pressurized cylinders, a liquefied hydrogen tank, or any other bulk storage or supply arrangement as known in the art.

The source 2 supplies gaseous hydrogen, if necessary via a compressor 3 which boosts the pressure to the first working pressure of the on-board storage vessel 21, to a thermally insulated intermediate storage vessel 4. The intermediate storage vessel 4 has a heat exchanger 5 which is connected to a circulating supply 6 of gaseous helium He cooled by a cryogenic refrigeration apparatus 7 to a temperature below the first working temperature. For example, the helium gas may be cooled to about 20K. The hydrogen gas H is held within the intermediate storage vessel 4 (which need not contain an adsorbent) at the first working temperature and first working pressure so as to minimize the time required for re-fuelling.

The refuelling station also provides coolant connection apparatus 8 and hydrogen connection apparatus 9, comprising couplings and valves as known in the art, which are adapted for connection to corresponding couplings of the inlet and outlet apparatus 24 of the on-board storage vessel 21 so as to connect respectively

7 OCT 2011

the circulating supply of refrigerated gaseous helium to the on-board heat exchanger 27, and the supply of cooled hydrogen gas H to the on-board storage vessel 21. The helium and hydrogen couplings and valves 8, 9 may be separate, or may be integrated into a combined multiple coupling assembly, which may have separate flexible, thermally insulated hydrogen and helium supply lines or alternatively may have supply lines that are thermally connected, e.g. arranged one inside the other, and insulated by an external jacket so as to minimise the ambient heat load during transfer between the refuelling station and the vehicle.

In use, the couplings of the connection and inlet/outlet apparatus 8, 9, 24 are connected, and the supply of compressed gaseous hydrogen H cooled by the heat exchanger 5 is introduced into the storage vessel 21 until the storage vessel is pressurized to the first working pressure. Gaseous helium He cooled by the refrigeration apparatus 7 is simultaneously circulated through the heat exchanger 27 to offset the heat of adsorption, maintaining the adsorbent 22 at the first working temperature. The combination of pre-cooling of the hydrogen supply at the first working pressure and cooling of the adsorbent by a separate coolant circuit minimises refuelling time.

Preferably, the first working temperature lies in the range from about 36K to about 77K and the first working pressure lies in the range from about 1 bar to about 350 bar, more conveniently from about 1 bar to about 200 bar. In less

7 OCT 2010 E 7 OCT 2011

preferred embodiments, higher or lower temperatures and/or higher pressures may be employed.

The adsorbent is preferably made from carbon and has a high pore volume and high surface area. The high pore volume is provided through pores of different types, that is, micro-, meso-, and macro-pores. In the conventional methods cylinders without the use of adsorbents to store H2 gas at room temperature, an exothermal state and compressibility factor of H2 adversely affects the method of filling the gas and ultimate volume stored is reduced. To avoid the above effects and maximise the storage of gas in a given volume, an adsorbent is used with a morphology for the gas to be provided access to maximum surface area and pores of adsorbent. The inventor found that the best way to do this through increased pore volume, and consequently through greater surface area. This is achieved by activating the adsorbent such that there is a greater pore volume of micro, meso, and macro pores in the adsorbent than the conventional adsorbents.

The conventional carbon adsorbent has a micro and meso pore volume, of 1 to 1.1 cc/g on an average, and the BET surface area of approximately 1000 to1100 m^2/g . This is found by the inventor to be inadequate for practical storage of gases such as hydrogen.

The special method adopted to provide greater pore volume and surface area to the carbon is achieved by activating it by heating the standard adsorbent in

E7 OCT 2011

absence of air, initially at 300 °C, to remove moisture (which itself occupies a 15-20% volume of the adsorbent) and then further to 400 °C to 600 °C to a prescribed period, say 2 Hrs. This process helps remove carbon molecules, and uniformly increases the total surface area and the pore volumes by approx 30% to 50%, to1500 to 2200 m2/gm and 1.3 to 2 cc/gm. In the case where carbon fibers are used along with carbon powder, the pore volume is seen to rise up to 11cc/g (see table 1) with the use of this process.

		BET Method		Mercury Porosimetry		Density		% Per litres of Cyl Vol
		Surface Area m2/g	Pore Vol. cc/g	Surface Area m2/g	Pore Vol cc/g	Bulk density g/cc	Skeletal Density g/cc	
Adsorbant 1	Carbon Powder	1269	1.32	102.1	2.15	0.3	0.852	24% to 100%
Adsorbant 2	Carbon Fiber	1625	1.27	31.08	10.45	0.0851	0.767	20% to 100%

Intermittent testing is done to measure the results, and heating repeated if required to achieve the final result. The present method of testing confirms by BET method the surface area and pore volume of only micro and meso pores. The surface area and pore volumes results reported herein are lower than what the invention actually provided. The actual surface area and pore volumes is higher than that reported herein as the Surface area and pore volumes of macro pores is not detected by BET. The measurements taken using Mercury Porosimetry results would add on to the BET values reported herein.

07 OCT 2011

Prior to filling the cylinder with the adsorbent treated as above, the adsorbent is treated with hot N2 at 100 to 300 °C for two hours. This treatment is seen to enhance the adsorption further. The adsorbent treated thus is now ready for filling into the cylinders in a humidity-free environment using standard filling procedures.

The method of activation disclosed here and the adsorbent resulting from it allows the storage of hydrogen over a large range of temperature and pressure. Hydrogen may be stored at ambient temperatures (Depending on Country and location ranging from 253K to 318K), which makes the filling operations extremely convenient, with a corresponding increase or decrease in storage.

The amount of hydrogen stored depends on the temperature and pressure at which it is filled; the maximum storage obtained towards the lower temperature range and higher pressure range. However, the adsorbent activated for increased pore volume and surface area as disclosed in this application provides a much higher storage capacity at room temperatures and moderate pressure range. This makes it feasible to deploy this technology at the standard filling stations, with certain modifications, without requiring expensive or complicated technology. The moderate pressures and temperatures means the complications of the process are greatly reduced, however compromising on the energy density per litre of storage volume.

07 OCT 2011

The cylinders may require super insulation so as to preserve the cold, at Cryogenic Temperatures, which in turn prevents increases in stored pressure. It is known to a person skilled in the art that in order to store maximum hydrogen in a cylinder stabilizing at room temperature (about 300 K), a charging temperature of -85 deg centigrade (188K), and a pressure of 350 kg/cm2, would not require an insulated cylinder. However, it would require a cylinder that withstands high pressures as over pressurisation is necessary (see Table 2) to compensate the effect of exothermal conditions during rapid charging. Alternatively, a pre-cooled gas can be charged to offset the effect of an exothermic reaction during rapid charging.

As we go lower in temperatures i.e. 100 K, 76K, up to 36k , it would be absolutely necessary to adopt a super insulated design of the cylinder, from the aspect of safety and economy.

It has been observed that under room temperature conditions with adsorbent, the storage offered by the current invention (~35g of hydrogen per litre of container volume under specific filling conditions) is approximately 50% more than that offered by container without the adsorbent (~22g per litre).

It is also observed by the inventor that the using carbon in a powder form rather than in a fibre form is vastly more economical. The carbon adsorbent in a fibrous form is roughly 10 times as expensive as the adsorbent in powder form. Although

07 OCT 2011

carbon fibre is easier to work with, the carbon powder when treated in the way disclosed in this application has become a viable and practical alternative to it.

Carbon fiber has superior pore volumes which can be effectively used if the initial one-off high costs are acceptable. A combination of carbon powder and fiber would be a viable alternative to balance cost/weight equation of the adsorbent per litre of cylinder volume.

As an alternative embodiment, the surface of the particles of the carbon powder may be precipitated with ionic palladium is precipitated in finely divided form as nano-particles or nano-crystals.

Alternatively, the adsorbent 22 comprises activated carbon micro-fibres, on whose surface a metal is dispersed in finely divided, nano-particulate form in an amount of about 1wt% - 5 wt% by weight of the adsorbent. In this specification, a micro-fibre is taken to be a filamentary element having a diameter or transverse dimension in the range from about 1 micron to about 100 microns, and a length of at least 10 times its diameter or transverse dimension.

In alternative embodiments the adsorbent may comprise carbon coated ceramic fibres, nano-structured carbon material, carbon powder, carbon granules, or other high surface area material as known in the art.

7 OCT 2011

However, the applicant has found that carbon nano-structures can be problematic when used as adsorbents due to difficulties in handling in addition to their high cost. It is hypothesised that this may represent a practical limit on the hydrogen storage density achievable using a nano-structured carbon adsorbent.

In an embodiment of the invention, the adsorbent is a carbon wool comprising a randomly oriented mass of activated carbon micro-fibres. The carbon wool may comprise micro-fibres having a diameter of about 8 microns to about 9 microns and a length of about 1mm to about 5 mm, fibres, and is packed into the tank to form a soft, compact but highly permeable mass with a density in the range between 80 to 150g/litre. The carbon wool is so called because it resembles natural wool, having mechanical properties in that it resists compaction, remaining soft and fluffy as the tank is pressurized so that its entire surface area (preferably in the range of at least about 2250 m^2/g or more) and pore volume up to 11cc/g is available for adsorption of the hydrogen gas.

It is known to produce activated carbon micro-fibres from a variety of alternative precursor materials including novoloid (cured phenol-aldehyde), polyacrylonitrile and petroleum pitch. The precursor material may be carbonized and activated by a process or a series of processes as known in the art, such as by pyrolysis followed by oxidation, to produce the adsorbent.

07 OCT 2011

Advantageously, the adsorbent is oxidised by exposure to an atmosphere of CO2 at an elevated temperature, for example, about 800°C, to achieve a surface area of at least 2000m^2/g, preferably at least 3000m^2/g, most preferably at least 4000m^2/g.

The method, equipment, process described above for cryogenic operation range, 76K to 36K, can be extended to the use of Carbon Powder/ Carbon Fiber operating in the Room Temperature to near Cryogenig range of Temperatures, that is between 300K to 77 K.

Experiments and results:

Experiments were carried out to assess the hydrogen storage capacity with and without adsorbent. The carbon powder adsorbent used for the experiments had a surface area of between 1000-1100 m2/g. It was activated by heating in absence of air, initially at 300 °C, to remove moisture (which itself occupies a 15-20% volume of the adsorbent) and then further to 500 to 600 °C a prescribed period, say 2 Hrs. A summary of storage achieved using carbon powder as adsorbent has been provided in Table 2 below:

07 OCT 2011

Table 2:

Hydrogen Storage Comparison Pr v/s Temp			
Pressure and Temperature	**Hydrogen Storage with adsorbent**	**Hydrogen Storage without adsorbent**	**% increase in storage**
Bars and Kelvin	(g/litre)	(g/litre)	
350, 300*	35.71	22.65	58%
300, 300*	33	20	65%
200, 300*	23.65	14	69%
300, 190	42	31.55	33%
135, 140	38.76	21.36	81%
200, 140	42.4	24	77%
200, 76	73.78	50	48%
300, 76	83.25	57	46%
350, 76	87.34	62	41%

Note: * - requires over pressurisation up to 500bar.

It can be seen from the above summary table 2 that the increase in storage obtained varies between 40% and 80%. This has huge implications to the hydrogen storage applications., using an adsorbent without any precious metal, from room temperature of 300K to 77K as compared to storage in cylinders without adsorbent under similar conditions.

Applicant's experiments and calculations indicate that activated carbon in the form of carbon powder can store as much as 87kg hydrogen or more per cubic metre tank volume at a relatively modest pressure of not more than 350 bar, when cooled to a temperature in the range from 300K to 77K. This represents a substantial increase over the storage density hitherto achieved by adsorption. It is

7 OCT 2011

believed that the advantageous effect is due to a combination of adsorption and interstitial storage, on to a high surface area pore volume adsorbent.

The Methodology of H2 Charging of cylinders with adsorbent, can be effective, under two conditions:

a) By Overpressurisation so as to compensate the effect of exothermal conditions (up to 373K), by allowing the cylinder to return to room temp (288 to 300K)

eg To achieve storage of 22.65 g/l at 350 Bar in a cylinder without adsorbent, in 3mins., temperatures rise to 373K. An over-pressurisation at 455 Bar is required, to achieve final stabilisation at 350Bar and 300K.for the same amount of storage. With adsorbent under identical conditions the storage can be higher by 30 % to 40% . This leads to higher power cost and higher cylinder cost.

OR

b) By pre-cooling the H2 gas to 190K to 76K, and reducing the charging pressure, attaining higher storage. This alternative is recommended over (a)

and is supported by isotherms exhibited, which depicts storage increase over 40%.

Fast Charging in 3 minutes, is the refuelling norm of the industry.

However the inventor has resorted to the method (b) of pre-cooling so as to avoid excessive pressures.

07 OCT 2011

Details of the various experiments carried out are disclosed in the following examples.

Example 1

In a first experimental example, a cylindrical stainless steel storage vessel with a coiled tubular internal heat exchanger and an internal capacity (excluding the heat exchanger) of 0.52 litres, and surrounded with cryogenic insulation, was filled with 75g of carbon powders which was packed into the storage vessel to surround the heat exchanger.. The carbon powder prepared by activation described above with improved surface area and pore volume.

The storage vessel was refrigerated by circulating liquid N2 through the heat exchanger, with the temperature of the adsorbent being recorded by a temperature probe arranged inside the storage vessel.

Compressed hydrogen gas was then supplied directly to the storage vessel at room temperature from a cascade of pressurised, uninsulated cylinders, so that the hydrogen gas was cooled by contact with the heat exchanger circulating liquid N2 at 76K, in turn cooling the adsorbent also, as H2 gas flowed into the storage vessel. The supplies of hydrogen gas was turned off once the adsorbent temperature had stabilised and the flow of hydrogen into the storage vessel had stopped, indicating that maximum hydrogen adsorption had been achieved, with

07 OCT 2011

the measured parameters at this time being indicated in Table 1 below as "starting parameters". It should be noted that, although for convenience in the experimental method the hydrogen was supplied at room temperature and cooled within the storage vessel, this is not expected to have any substantial effect on the starting parameters as against the preferred method in which the hydrogen gas is cooled before it is supplied to the storage vessel, although the latter method is expected to greatly reduce the time required for filling the storage vessel.

The hydrogen stored within the storage vessel was then discharged via a discharge valve through a mass flow meter, with the temperature of the adsorbent, the pressure within the storage vessel, and the flow rate of hydrogen gas discharged from the storage vessel being recorded at 1-second intervals. The measured parameters, sampled at 1-second intervals starting from the initiation of hydrogen discharge from the storage vessel, are shown in Table 1 as follows:

Plots incorporated in Figure 3 show the storage against pressure for a range of temperatures. It is evident from these plots that the hydrogen storage capacity of the storage tanks of the present invention provided with adsorbent disclosed herein is substantially higher than the conventional systems of hydrogen storage. Whereas it is possible to increase the capacity of the storage at room temperature by increasing the pressure, it is seem that the storage capacity can be significantly higher at much lower pressures, provided the temperature at which the storage is achieved is sufficiently low. (In case of uninsulated tanks, the temperature when

E7 OCT 2011

allowed to stabilise to ambient temperature, the pressure increases accordingly to achieve corresponding storage at the ambient temperature.) In fact, it is not feasible to achieve such high storage at room temperature within the practicable limits of pressure.

This is further illustrated with the help of some examples:

Example 2.

A total of 21.45 grams of hydrogen gas was discharged from the 0.52 litre storage vessel during a period of 79 seconds, during which time the pressure in the storage vessel dropped by 325 bar and the temperature in the storage vessel fell from 198K to 146K as the hydrogen gas was desorbed from the carbon adsorbent. in 0.52Lt equates to a hydrogen storage density of 41.25 g/l storage vessel volume. This amounts to an increase in storage of 82% as compared to a cylinder without adsorbent at 350 Bar and 300K which would be 22.65 g/l. In this case a higher design pressure capacity cylinder would be required. Results of this experiment have been incorporated in Table 3.

E7 OCT 2011

Table 3:

Recording	Differential Pr in inches	Gauge Pr	Flow Temp.	Cylinder Pr.	
Time in Seconds	of H_2O Column	kg/cm2	°C	Kg/cm2	°C
	Flow Transmitter	during Flow			
13:04:23	25.93	0.27	32.16	317.67	-75.19
13:04:24	45.68	0.03	32.1	315.2	-75.56
13:04:25	27.16	0.02	32.1	312.73	-75.56
13:04:35	86.42	0.15	32.04	281.87	-77.04
13:04:45	233.33	0.43	32.04	233.72	-81.11
13:04:55	464.2	1	32.04	165.82	-86.3
13:05:05	627.16	1.43	32.1	89.28	-93.33
13:05:25	155.56	0.14	31.98	-4.55	-111.11
13:05:35	6.17	-0.02	31.98	-8.25	-114.44
13:05:40	1.24	-0.02	31.98	-8.25	-115.19
13:05:41	1.24	-0.03	32.04	-8.25	-115.19
Average values	294.09	0.61	32.03		

Average Density		0.128045	g/l
Average Flow Rate		15.50554	g/min
Total flow	21.4493g		in 520cc

Notes:29

- H2 Charged at 350 Bar, at 198K Temperature
- The Volume of The Test Cell is 520cc
- Total Volume Stored in one litres of Cyl Volume 41.25g
- Equivalent Storage in a Cylinder without adsorbent 34.3 g/l at 198K
- Increase in Storage approx 20% more at 198K,but compared to room temp 82% more
- By nullifying the effect of exotherm during charging, as 350 bar at RT can store 22.65 g without adsorbent

Results of the above example are graphically illustrated in Figure 3

Example 3

In the experiment of example 2, a total of 1.5 grams of hydrogen gas was discharged from the 0.042 litre storage vessel during an initial period of 17 seconds, during which time the pressure in the storage vessel dropped by 355 bar

~~7 OCT 2011~~ E7 OCT 2011

The total amount of hydrogen stored in the 1.00 litre vessel was thus 35.71grams, equating to a storage density of 35.71 kg/m^3 storage vessel volume at a starting temperature of 300K. This amounts to an increase in storage by 50 to 57%, with adsorbent as compared to cylinder without adsorbent

The experiment of example 1 was carried out at the starting temperature of 300K. The results of this experiment have been provided in Table 4.

Table 4:

Recording Time in Seconds	Diff Pr in Inches of H_2O Column Flow Transmitter	Gauge Pr kg/cm^2 during Flow	Flow Temp. °C	Cylinder Pr. Kg/cm^2
15:14:24	35.8	0.13	27.16	357.92
15:14:25	35.8	0.13	27.35	314.71
15:14:26	54.32	0.13	27.22	278.91
15:14:27	58.03	0.13	27.1	246.81
15:14:28	59.26	0.13	27.1	246.81
15:14:29	59.26	0.13	27.16	215.95
15:14:30	62.96	0.15	27.22	183.85
15:14:31	69.14	0.14	27.16	152.99
15:14:32	70.37	0.14	27.16	152.99
15:14:33	70.37	0.14	27.16	123.36
15:14:34	70.37	0.14	27.28	94.96
15:14:35	70.37	0.14	27.16	69.03
15:14:36	69.14	0.14	27.16	69.03
15:14:37	69.14	0.13	27.22	43.11
15:14:38	69.14	0.13	27.22	18.42
15:14:39	51.85	0.03	27.22	6.07
15:14:40	17.28	0.01	27.04	2.37
Av. values	58.38823529	0.12176 471	27.181765	

7 OCT 2011

Average Density	0.09060774	g/l
Average Flow Rate	5.29745838	g/min
Total flow	1.50094654	g

H2 Charged at 357 Bar, Room Temperature 30 °C igrade
The Volume of The Test Cell is 42cc
Total Volume Stored in one litres of Cyl
Volume 35.71 g with adsorbent
Equivalent Storage in a Cylinder without adsorbent 22.65 g/l
Increase in Storage approx 50 to 57 % more

Results of the above example are graphically illustrated in Figure 1.

Example 4

A third experiment was carried out generally as described above with reference to examples 1 and 2, but having a storage vessel with a volume of 0.042Lt and containing 5.7g of carbon adsorbent. The adsorbent was the same as that used for examples 1 and 2, but the cylinder was directly immersed in a bath of Liquid N2. In actual industrial use pre-cooled H2 to 77K can be charged or closed circuit circulation of He in an internal coil can be effective.

The starting pressure and temperature inside the storage vessel were 350 bar and 76K. Desorption amounted to 3.67 g in 31 seconds, This is equivalent to 87.34 g/l of storage cyl vol. Hence at 350 Bar and 77K, storage is better than Liquid H2 which would be 72 g/l at 20K. This form of storage, with internal cooling coil in the insulated tank with closed circuit cold He, could save a lot of energy as

07 OCT 2011

compared to Liquid H2 storage in which case 40% of the energy in H2 is used to convert it to a liquid state.

The results of this experiment have been provided n Table 5:

Table 5:

	Recording	Diff Pr in Inches	Gauge Pr	Flow Temp.	Cylinder Pr.
	Time in Seconds	of Water Column	kg/cm 2	°C	Kg/cm2
		Flow Transmitter	during Flow		
23/02/2011	15:44:28	16.05	0.24	31.17	286.48
23/02/2011	15:44:29	70.37	0.24	31.17	275.37
23/02/2011	15:45:00	1.24	0.02	31.11	1.3
Average values		75.60939	0.170606	31.13909	
Average Density	0.093322 g/Lt of H2				
Average Flow Rate	6.117913 g/min of H2				
Total flow	3.6707g of	H2 Stored in	42cc		
	Per litres	87.34g at 76 K			

Average Density 0.093322 g/Lt of H2

Average Flow Rate 6.11791 g/min of H2

Total flow 3.6707 g of H2 stored in 42cc
Per litres
87.34 g at 76 K

H2 Charged at 350 Bar, at 76K
Temperature
The Volume of The Test Cell is 42cc. Cooled to

7 OCT 2011

76K
Total Volume Stored in one litres of Cyl Volume 87.34 g with adsorbent at 76K
Equivalent Storage in a Cylinder without adsorbent 62 g/l at 76K
Increase in Storage approx 40 % more

Example 5: 140K

Another experiment was carried out generally as described above with reference to examples 1 and 3, but having a storage vessel of 0.52l capacity and containing 75g of the adsorbent (of same morphology as that used in examples 1 and 2) but the cylinder was cooled from outside using liquid N2. In actual industrial use pre-cooled H2, cooled to 77K is charged or closed circuit circulation of He in an internal coil can be effective.

The starting pressure and temperature inside the storage vessel were 200 Bar and 140K respectively. Desorption amounted to 24.85g in 100 seconds. This is equivalent to 42.4g per litre of storage cylindrical volume. This amounts to an increase by 38%, over a corresponding cylinder without adsorbent.

The results of this experiment have been provided in Table 6.

7 OCT 2011 7 OCT 2011

Table 6:

	Recording	Diff Pr in Inches	Gauge Pr	Flow Temp.	Cylinder Pr.
	Time in Seconds	of Water Column	kg/cm2	°C	Kg/cm 2
		Flow Transmitter	during Flow		
12/29/2010	15:38:15	59.26	0.13	23.02	174.6
12/29/2010	15:38:20	165.43	0.27	23.02	154.85
12/29/2010	15:38:25	190.12	0.32	23.02	140.04
12/29/2010	15:38:30	196.3	0.32	22.96	126.46
12/29/2010	15:38:35	196.3	0.32	22.96	117.81
12/29/2010	15:38:40	193.83	0.32	22.96	106.7
12/29/2010	15:38:45	197.53	0.32	22.96	96.83
12/29/2010	15:38:50	195.06	0.33	22.96	88.19
12/29/2010	15:38:55	196.3	0.33	22.96	78.31
12/29/2010	15:39:00	197.53	0.33	22.96	70.9
12/29/2010	15:39:05	198.77	0.33	22.96	62.26
12/29/2010	15:39:10	200	0.33	22.96	56.09
12/29/2010	15:39:15	200	0.34	22.96	48.68
12/29/2010	15:39:20	200	0.34	22.96	41.27
12/29/2010	15:39:25	200	0.34	22.96	32.63
12/29/2010	15:39:30	200	0.33	22.96	23.99
12/29/2010	15:39:40	182.72	0.28	22.9	5.47
12/29/2010	15:39:50	86.42	0.13	22.9	3
12/29/2010	15:40:00	46.91	0.06	22.9	1.77
12/29/2010	15:40:10	24.69	0.03	22.9	0.53
12/29/2010	15:40:20	13.58	0.01	22.9	0.53
12/29/2010	15:40:30	7.41	0	22.9	-0.7
12/29/2010	15:40:40	4.94	-0.01	22.9	-0.7
12/29/2010	15:40:50	2.47	-0.02	22.9	-0.7
12/29/2010	15:41:00	1.24	-0.02	22.9	-0.7
12/29/2010	15:41:10	1.24	-0.02	22.9	-0.7
Average values		129.15	0.21	22.94	

E7 OCT 2011

Average Density	0.09907127	g/Lt	
Average Flow Rate	8.23859188	g/min	
Total flow	24.8530855	g	in 520cc

Notes:

- H2 Charged at 200 Bar, at 140K Temperature
- The Volume of The Test Cell is 520cc
- Total Volume Stored in one litres of Cyl Volume 42,4 g
- Equivalent Storage in a Cylinder without adsorbent 30.6 g/l at 140K
- Increase in Storage approx 38% more

Example 6: (177K temperature)

Another experiment was carried out generally as described above with reference to examples 1 and 2, but having a storage vessel of 0.52l capacity and containing 75g of the adsorbent (of same morphology as that used in examples 1 and 2) but the cylinder was cooled from outside using liquid N2. In actual industrial use pre-cooled H2, cooled to 77K is charged or closed circuit circulation of He in an internal coil can be effective.

The starting pressure and temperature inside the storage vessel were 200 Bar and 177K respectively. Desorption amounted to 21.35g in 180 seconds. This is equivalent to 41g per litre of storage cylindrical volume. This amounts to an increase by 40%, over a corresponding cylinder without adsorbent.

E 7 OCT 2011

Table 7

	Recording	Diff Pr in Inches	Gauge Pr	Flow Temp.	Cylinder Pr.
	Time in Seconds	of Water Column	kg/cm2	°C	Kg/cm2
		Flow Transmitter	during Flow		
1/12/2010	15:00:50	167.9	0.28	26.36	159.79
1/12/2010	15:01:00	174.07	0.29	26.36	135.1
1/12/2010	15:01:10	175.31	0.29	26.36	115.35
1/12/2010	15:01:20	174.07	0.29	26.36	99.3
1/12/2010	15:01:30	175.31	0.29	26.36	83.25
1/12/2010	15:01:40	174.07	0.28	26.36	68.43
1/12/2010	15:01:50	174.07	0.29	26.36	57.32
1/12/2010	15:02:00	174.07	0.29	26.36	43.74
1/12/2010	15:02:10	174.07	0.29	26.36	31.4
1/12/2010	15:02:20	174.07	0.29	26.36	19.05
1/12/2010	15:02:30	155.56	0.24	26.36	6.7
1/12/2010	15:02:40	48.15	0.06	26.36	1.77
1/12/2010	15:02:50	13.58	0	26.36	0.53
1/12/2010	15:03:00	3.7	-0.02	26.36	-0.7
1/12/2010	15:03:10	1.24	-0.02	26.36	-0.7
1/12/2010	15:03:20	1.24	-0.03	26.36	-0.7
Average Values		125.69	0.20	26.36	

Average Density	0.0973347 2	g/Lt of H2	
Average Flow Rate	8.0558461	g/min of H2	
Total flow	21.3479 g	of H2 stored	in 520cc

Notes:

- H2 Charged at 200 Bar, at 177K Temperature
- The Volume of The Test Cell is 520cc
- Total Volume Stored in one litres of Cyl Volume 41 gm
- Equivalent Storage in a Cylinder without adsorbent at 177 K , 30,6 g/l
- Increase in Storage approx 40 % more

7 OCT 2011 7 OCT 2011

In summary, a preferred embodiment provides a working range from, room temperature to 77K, and room temp to 36K, with pressures up to 350 Bar, storage in a motor vehicle, with lesser number of tanks or lesser volume making an economical solution and lesser weight penalty. The tank may contain a heat exchanger and an adsorbent material comprising of carbon powder/ micro-fibres l with a surface area of about $2250m^2/g$ – $4000m^2/g$, without a metal, dispersed over the surface of the adsorbent. A re-fuelling station comprises a supply of hydrogen at a first working temperature of about 300K–36K and a first working pressure up to about 350 bar, which is supplied to the tank via first releasable couplings, and a supply of refrigerated helium gas at about 20K which is simultaneously circulated via second releasable couplings through the heat exchanger in the tank to offset the heat of adsorption. An auxiliary tank contains compressed hydrogen gas at ambient temperature which is injected in controlled amounts into the storage tank to offset the heat of desorption as the storage tank empties.

In a development, the storage vessel and adsorbent may be cooled and filled with cold hydrogen as described above, at a first temperature of, for example, about 198K and a first pressure of, for example, up to about 350 bar; and then (after disconnection of the filling and cooling lines) warmed to a second working temperature higher than the first working temperature so that the internal pressure rises to a second working pressure higher than the first working pressure, the pressure relief valve then being adapted to vent hydrogen gas at the second

07 OCT 2011

working pressure. The second working temperature may be up to ambient temperature (i.e. up to about 300K), and the second working pressure may be, for example, from about 350 bar up to about 750 bar, the storage vessel being adapted to contain this pressure, e.g. comprising a composite, filament wound structure.

The second pressure may be maintained at not more than, for example, about 750 bar by the heat of desorption as the hydrogen gas is consumed by the fuel cell or engine of the vehicle. The warming may be accomplished in whole or in part by means of a heating apparatus as described above, e.g. by injection of hydrogen at ambient temperature from an auxiliary tank. The adsorbent may also be warmed by the ambient heat load on the storage vessel, and the thermal insulation may be less insulated than the more expensive super-insulation required to maintain the cryogenic storage temperature of the first embodiment. The hydrogen may be stored in the vessel at the second temperature and pressure for an extended period of time.

The invention may find uses in the storage of hydrogen, not only for use in motor vehicles but also in other static or mobile applications.

Although the invention has been described with reference to certain embodiments, the invention is not limited to those embodiments alone. Alterations to the embodiments described are possible without departing from the spirit of the invention. However, the invention described above is intended to be illustrative

07 OCT 2011

only, and the novel characteristics of the invention may be incorporated in other structural forms without departing from the scope of the invention.

It is evident from the foregoing discussion that the present invention is made of the following items.

1. An adsorbent in the form of an activated carbon powder or activated carbon micro-fibers, or a mixture thereof, said adsorbent having a pore volume of between 1 to 11 cc/g and a surface area between 1000 m2/g to 4000 m2/g, said pore volume and said surface area comprising those obtained by micro, meso and macro pore structures.

2. An adsorbent as described in item 1 wherein said powder or said micro-fibers or said mixture is activated by heating it to an initial temperature of 300 °C, preferably to a duration of up to 1 hour, to remove moisture and then further to 400 °C to 600 °C for a prescribed first period, preferably for up to 2 hours.

3. An adsorbent as described in items 1 and 2, wherein said powder when used without said micro-fibers is used in an amount 50% to 100% v/v with respect to the cylinder volume, said micro-fibers when used without said micro-fibers is used in an amount 50% to 100% v/v with respect to the cylinder volume.

7 OCT 2011

4. An adsorbent as described in items 1 to 3, wherein said mixture comprises carbon powder and carbon micro-fibers, said powder being in an amount 24% to 40% v/v with respect to the volume of storage cylinder, and said micro-fibers being in an amount between 20% to 75% v/v with respect to the storage cylinder volume, such that the volume of total mixture is 50% to 100% v/v with respect to the cylinder volume.

5. An adsorbent as described in items 1 to 4 where said powder or said micro-fibers or said mixture are further activated by heating it in the presence of nitrogen at a temperature between 100 to 300 ^{o}C, for a prescribed second period, preferably 2 hours.

6. A hydrogen storage apparatus comprising

a thermally insulated storage vessel containing an adsorbent,

the storage vessel being adapted for pressurization to a first working pressure;

inlet and outlet apparatus for filling the storage vessel with gaseous hydrogen and releasing gaseous hydrogen from the storage vessel;

and a cooling apparatus for cooling the adsorbent to a first working temperature;

27 OCT 2011

characterised in that said adsorbent used is either an adsorbent as described in items 1 or 2, or it is in the form of activated carbon micro-fibres.

7. A hydrogen storage apparatus as described in item 6, further wherein a metal is dispersed in finely divided ionic form on said adsorbent.

8. An apparatus as described in item 7, characterised in that the first working temperature lies in the range from about 36K to about 300K and that the first working pressure lies in the range from about 200 bar to about 455 bar.

9. An apparatus as described in item 8, characterised in that the storage vessel is adapted for pressurization to a second working pressure up to about 750 bar.

10. An apparatus as described in item 9, characterised in that the cooling apparatus comprises a heat exchanger containing gaseous helium, the heat exchanger being adapted for connection to an external supply of refrigerated gaseous helium.

11. An apparatus as described in item 6, characterised in that the apparatus further comprises a heating apparatus for warming the adsorbent, said heating apparatus being characterised in that it includes an auxiliary tank containing gaseous hydrogen at a second working temperature, said second working temperature is

07 OCT 2011

maintained at atmospheric temperature, preferably between 273K to 325K, and maintained higher than the first working temperature, and a warm hydrogen injection apparatus for injecting hydrogen from the auxiliary tank into the storage vessel.

12. A method of storing hydrogen on an adsorbent, comprising the steps of

i) dispersing a metal in finely divided form onto an adsorbent comprising activated carbon micro-fibres;

ii) arranging the adsorbent in a optionally thermally insulated storage vessel adapted for pressurization to a first working pressure, the storage vessel including a heat exchanger; wherein insulated vessel is used in the case where first working temperature is in the range between 36K and 190K,

iii) cooling a supply of hydrogen; and then

iv) introducing the cooled hydrogen into the storage vessel until the storage vessel is pressurized to the first working pressure, and simultaneously

v) circulating a coolant through the heat exchanger to maintain the adsorbent at a first working temperature,

7 OCT 2011

wherein

said first working temperature is in the range from about 36K to about 300K, and said first working pressure is in the range from about 200 bar to about 455 bar.

13. A method as described in item 12, characterised in that the coolant is gaseous helium.

14. A method as described in item 13 characterised by the additional step of

vi) warming the adsorbent as hydrogen is released from the storage vessel.

15. A method as described in item 14, characterised in that step vi) comprises the step of injecting hydrogen at a temperature higher than the first working temperature into the storage vessel.

16. A method as described in item 15, the storage vessel being adapted for pressurization to a second working pressure higher than the first working pressure, characterised by the additional step of reinforcing the storage vessel.

17. A method as described in item 16, wherein after step (v), a further step (vi) is added, said step (vi) being warming the adsorbent to a second working temperature higher than the first working temperature, and storing the hydrogen in

7 OCT 2011

the vessel at the second working pressure corresponding to the second working temperature,

wherein said second working pressure lies in the range from about 300 bar to about 750 bar.

E 7 OCT 2011

CLAIMS

1. An adsorbent in the form of an activated carbon powder or activated carbon micro-fibers, or a mixture thereof, said adsorbent having a pore volume of between 1 to 11 cc/g and a surface area between 1000 m2/g to 4000 m2/g, said pore volume and said surface area comprising those obtained by micro, meso and macro pore structures.

2. An adsorbent as claimed in claim 1 wherein said powder or said micro-fibers or said mixture is activated by heating it to an initial temperature of 300 °C, preferably to a duration of up to 1 hour, to remove moisture and then further to 400 °C to 600 °C for a prescribed first period, preferably for up to 2 hours.

3. An adsorbent as claimed in claims 1 and 2, wherein said powder when used without said micro-fibers is used in an amount 50% to 100% v/v with respect to the cylinder volume, said micro-fibers when used without said micro-fibers is used in an amount 50% to 100% v/v with respect to the cylinder volume.

4. An adsorbent as claimed in claims 1 to 3, wherein said mixture comprises carbon powder and carbon micro-fibers, said powder being in an amount 24% to 40% v/v with respect to the volume of storage cylinder, and said micro-fibers being in an amount between 20% to 75% v/v with respect to the storage cylinder

E.7 OCT 2011

volume, such that the volume of total mixture is 50% to 100% v/v with respect to the cylinder volume.

5. An adsorbent as claimed in claims 1 to 4 where said powder or said micro-fibers or said mixture are further activated by heating it in the presence of nitrogen at a temperature between 100 to 300 °C, for a prescribed second period, preferably 2 hours.

6. A hydrogen storage apparatus comprising a thermally insulated storage vessel containing an adsorbent, the storage vessel being adapted for pressurization to a first working pressure; inlet and outlet apparatus for filling the storage vessel with gaseous hydrogen and releasing gaseous hydrogen from the storage vessel; and a cooling apparatus for cooling the adsorbent to a first working temperature; characterised in that said adsorbent used is either an adsorbent as claimed in claims 1 or 2, or it is in the form of activated carbon micro-fibres.

7. A hydrogen storage apparatus as claimed in claim 6, further wherein a metal is dispersed in finely divided ionic form on said adsorbent.

8. An apparatus according to claim 7, characterised in that the first working temperature lies in the range from about 36K to about 300K and that the first working pressure lies in the range from about 200 bar to about 455 bar.

E7 OCT 2011

9. An apparatus according to claim 8, characterised in that the storage vessel is adapted for pressurization to a second working pressure up to about 750 bar.

10. An apparatus according to claim 9, characterised in that the cooling apparatus comprises a heat exchanger containing gaseous helium, the heat exchanger being adapted for connection to an external supply of refrigerated gaseous helium.

11. An apparatus according to claim 6, characterised in that the apparatus further comprises a heating apparatus for warming the adsorbent, said heating apparatus being characterised in that it includes an auxiliary tank containing gaseous hydrogen at a second working temperature, said second working temperature is maintained at atmospheric temperature, preferably between 273K to 325K, and maintained higher than the first working temperature, and a warm hydrogen injection apparatus for injecting hydrogen from the auxiliary tank into the storage vessel.

12. A method of storing hydrogen on an adsorbent, comprising the steps of

i) dispersing a metal in finely divided form onto an adsorbent comprising activated carbon micro-fibres;

7 OCT 2011

ii) arranging the adsorbent in a optionally thermally insulated storage vessel adapted for pressurization to a first working pressure, the storage vessel including a heat exchanger; wherein insulated vessel is used in the case where first working temperature is in the range between 36K and 190K,

iii) cooling a supply of hydrogen; and then

iv) introducing the cooled hydrogen into the storage vessel until the storage vessel is pressurized to the first working pressure, and simultaneously

v) circulating a coolant through the heat exchanger to maintain the adsorbent at a first working temperature,

wherein
said first working temperature is in the range from about 36K to about 300K, and said first working pressure is in the range from about 200 bar to about 455 bar.

13. A method according to claim 12, characterised in that the coolant is gaseous helium.

14. A method according to claim 13 characterised by the additional step of

vi) warming the adsorbent as hydrogen is released from the storage vessel.

07 OCT 2011

15. A method according to claim 14, characterised in that step vi) comprises the step of injecting hydrogen at a temperature higher than the first working temperature into the storage vessel.

16. A method according to claim 15, the storage vessel being adapted for pressurization to a second working pressure higher than the first working pressure, characterised by the additional step of reinforcing the storage vessel.

17. A method according to claim 16, wherein after step (v), a further step (vi) is added, said step (vi) being warming the adsorbent to a second working temperature higher than the first working temperature, and storing the hydrogen in the vessel at the second working pressure corresponding to the second working temperature,

wherein said second working pressure lies in the range from about 300 bar to about 750 bar.

Dated This 7th Day Of October 2011

(Tase, Vijay Sharatchandra)
Patent Agent for the Applicant
Registration Number IN/PA 987

To,
The Controller of Patents
The Patent Office, Mumbai Branch

7 OCT 2011