

METHOD OF REVERSIBLY STORING H_2 AND H_2 -STORAGE SYSTEM BASED ON METAL-DOPED CARBON-BASED MATERIALS

This invention relates to the storage of H_2 in metal-doped carbon-based solid state sorbents, such as carbon nanotubes, carbon nanofibres, activated carbon, graphite and
5 amorphous carbon. Typically the metal-doped carbon-based sorbents can adsorb up to 20 wt% of hydrogen at moderate temperature and 14 wt% at room temperature under ambient pressure.

Hydrogen has been recognized as an ideal energy carrier. However, end-user hydrogen storage is still one of the challenging technical problems attracting increasing
10 research interest [1-5] to make it truly useful. In fact, a substantial number of research groups worldwide have put intensive effort to try to use a hydrogen based fuel cell as power source for automobiles and other devices. These groups have encountered problems associated with high cost and low efficiency of the hydrogen storage systems.

Currently, there are four kinds of H_2 storage systems in use, (a) liquid hydrogen, (b)
15 compressed gas, (c) cryo-adsorption and (d) metal hydride storage systems. A brief description of these existing methods is given below:

(a) The liquid hydrogen storage system is of importance because it offers good solutions in terms of technology and economy, both for mobile storage systems and large-volume storage from volume of from 100 litres to 5000 m^3 . However, in order to store the liquefied
20 hydrogen, the container (dewar) should be made of super-insulating materials, which is very expensive in practice.

(b) The compressed gas storage system is usually applied in underground supply systems, similar to a network of natural gas. This is an economical and simple method, but it is unsafe and not portable.

25 (c) Cryo-adsorbing storage systems show advantage in moderate weight and volume. In this system, hydrogen molecules are bound to the sorbent only by physical adsorption forces, and remain in the gaseous state. The adsorbing temperature is in the range of 60 to 100 K. Normally, activated carbon is used as the sorbent due to its large portion of small

pores serving as arenas for storing H_2 . The efficiency of H_2 uptake is no more than 7 wt%, which is equivalent to about 20 Kg H_2 per cubic meter of activated carbon. The disadvantage of this system relate to the much lower temperature required, which, similar to that of liquid hydrogen systems, makes it necessary to use suitable super-insulated containers, and thus the cost is increased.

(d) Metal hydride storage systems are recognized as a novel concept in hydrogen storage. These store large quantities of H_2 via a chemical reaction of $H + M = M-H$, wherein M is a selected metal for the system. Two major metal systems, i. e. Fe-Ti and Mg-Ni, have been applied as H_2 storage media and have been put into use in automobiles driven by an H_2/O_2 fuel cell. The operating temperature is 40 – 70°C for the Ti-Fe system and 250–350 °C for the Mg-Ni system. The H_2 storage capacity is less than 5 wt% for Ni-Mg and 2 wt% for Fe-Ti, which corresponds to less than 70 Kg H_2 per cubic meter of metals. Furthermore, metal hydride systems normally require 20-40 bar pressure to keep the hydrogen in equilibrium. This renders the container for the metal hydride too heavy and expensive, and limits the systems practical exploitation.

The last two mentioned H_2 storage systems above are chosen only in some special applications due to their relatively low H_2 storage capacity and high cost. The present invention advantageously provides a system which increases H_2 storage capacity relative to prior systems, but also provides for hydrogen storage under practical conditions.

Alkali-metal based materials have been reported as being able to absorb H_2 . For Li-based materials, normally in the case of an Li battery, hydrogen absorption takes place under electro-chemical conditions [1]. LiH can be formed at 300-500°C, but the dissociation requires 700-900°C. For K-based materials, it has been reported that about 160ml hydrogen was absorbed by 1 gram K-intercalated graphite at liquid nitrogen temperature [6].

More recently, several articles have been published [7-8] concerning storing H_2 on carbon materials . A. C.Dollin Et al reported that about 0.01 wt% of H_2 was absorbed by single wall carbon nanotube material (which was estimated as 5 wt% of nanotubes) at 130 K, and A. Chambers et al reported 65 wt% of hydrogen uptake was achieved by using herringbond-like graphite nanofibres under 200 atm pressure.



The present invention advantageously provides a method which increases the hydrogen storage capacity of a solid sorbent. Advantageously, the present invention also provides a method which enables the storage of hydrogen to be reversibly performed under ambient pressure and moderate temperature. Still further, the present invention
5 advantageously provides a means to economically make an efficient sorbent.

The above advantages may be achieved by modifying the nature of a carbon-based material which is to be used as the sorbent in a hydrogen storage system. The modification according to the invention comprises the doping of the carbon-based material with a metal to distinctly change the structural and electronic properties of the carbon-based material.

10 According to one aspect of the invention, there is provided a method of reversibly storing hydrogen comprising exposing a solid sorbent of metal-doped carbon-based material to a hydrogen atmosphere at a temperature of from about 250 K to about 973 K under ambient or higher H₂ pressure.

15 According to another aspect of the invention, there is provided a method of preparing an alkali metal-doped carbon-based material for use in reversibly storing hydrogen comprising mixing a carbon material with an alkali metal salt and calcining the mixture under an atmosphere of inert or reductive gase.

20 There is also provided a hydrogen storage system comprising an alkali metal-doped carbon-based material prepared in accordance with the method described in the immediately preceding paragraph.

Preferably the carbon material of the carbon-based material is selected from carbon nanotubes, activated carbon, carbon powder, amorphous or disordered carbon, carbon fibres, carbon nanofibres and graphite, and the metal is an alkali metal. Preferably carbon nanotubes or nanofibres are used which have been prepared by catalytic disproportionation
25 of CO (nanotube) or decomposition of CH₄ (nanofibres) on a Ni-based catalyst. After purification, more than 90% of the product is advantageously in the form of nanotubes or nanofibres. The structural properties of carbon nanotubes and nanofibres are similar to that of graphite, but with greater interlayer distance: 0.345 nm for nanotubes and nanofibres, compared with 0.335 nm for graphite. The size of nanotubes and nanofibres is in nano-

scale, with average diameter of 5 to 30 nm, for example 15 nm, for nanotubes and 10 to 60 nm, for example 30 nm, for nanofibres. Both nanotubes and nanofibres can reach several microns in length.

Preferably, the metal-doped carbon-based material is an alkali metal-doped carbon-based material. The alkali metal may be, for example, Li, Na, Rb or Cs.

In certain embodiments, the temperature for hydrogen adsorption is in the range of 400-800 K for Li-doped carbon materials, and 250-400 K for Na or K-doped carbon materials. The pressure for the adsorption process is preferably between 1 to 100 atm.

The doping of alkali metals to the carbon materials may be achieved by solid state reaction between the carbon materials and alkali metal salts.

The solid state reaction method preferably involves thoroughly mixing the carbon materials with the alkali metal salt, then subjecting the mixture to high temperature treatment under inert gases, such as He, N₂, Ar, etc. or reductive gases such as H₂, etc.

The said alkali metal salts may include carbonates, nitrates, hydroxides, halogenides, acetates, hydrides, nitrites, or the like. The molar ratio of alkali metal to the carbon materials is preferably from about 1:20 to 1:1.

More particularly, the temperature for the chemical reaction is preferably in the range of from 473 to 1273K according to the alkali metal salts selected (473-1073K for doping Li surrounded by hydrogen or inert gas, and 973-1273K for doping Na and K surrounded by hydrogen).

Embodiments of the present invention will now be discussed in more detail with reference to the accompanying drawings in which:

FIG. 1 is a TGA profile of a reversible H₂ sorption on Li-doped carbon nanotubes. The sample was pretreated at 873K for 1 h, then cooled down to 300K, and heated up again to 873K.

FIG. 2 is a TGA profile of a reversible H₂ sorption on K-doped carbon nanotubes. The sample was pretreated at 873K for 1 h then cooled down to 298K, and kept at 298K for



2 h and was heated to 773K again.

The abnormal capability for reversible H_2 sorption by the alkali metal-doped carbon materials according to embodiments of the invention is derived from the doping of alkali metal into the carbon materials. As previously reported the doping of alkali metal into graphene layers may form a doped compound, C_nM . The electronic structure of the carbon material is changed significantly due to the alkali metal doping, as revealed by our XPS and UPS studies. Alkali metal in the alkali metal-doped carbon-based materials transfers a near unity charge to carbon, resulting in an M^+ state and a significant increase in free electron density in the graphene layers. In the valence band region the alkali metal doping creates an extra density-of-state containing Fermi edge. This alkali metal-derived Fermi-level band shifts the Fermi level closer toward the instrument vacuum level and plays a particularly important role in reducing the activation energy for the dissociative hydrogen chemisorption.

The hydrogen dissociative adsorption on C is a slow activated process, with an activation energy corresponding to an above-zero-energy crossing between the di-H-atoms and H_2 molecular potential curves. Few molecules may have high enough energy to surmount this intrinsic energy barrier, resulting in minimal sticking taking place on carbon at ambient pressure and moderate temperatures without metal-doping. Energetically the key step for this process is the weakening and the final breaking of the H-H bond. The band-structure calculations have indicated that the half-filled Fermi level band created by the alkali metal doping is formed by the hybridization of the alkali metal outermost s orbital with a low-lying bonding C π band. It has primarily a C π character, and is spatially confined near the C planes. This C_nM band can overlap strongly with the hydrogen $(1s^2)^*$ orbital, resulting in the lowering and filling of this antibonding orbital, and hence the reduction of the activation energy for the hydrogen dissociative adsorption. We can therefore observe largely enhanced hydrogen uptake on the alkali metal-doped carbon materials.

The following specific examples are provided to illustrate this invention and the manner in which it may be carried out. It will be understood, however, that the specific details given in each example have been selected for purpose of illustration and are not to be construed as a limitation on the invention. In all these examples, the general conditions under which the experiments were conducted were similar for carbon sorbents doped with

the same alkali metal, except for the selection of carbon materials and H₂ pressure. Example 1 provides more details on the conduction of the experiment.

Example 1

600mg of carbon nano-fibre with average diameter of 30 nm was thoroughly mixed
5 with 30 molar % LiI. The above mixture was heated in a flow of purified helium at ambient
pressure to 700°C and maintained for 1h, and then cooled down to room temperature to
form Li-doped nanofibres. 30 mg of Li-doped carbon nanofibres was put into sample holder
of TG analyzer, and H₂ was introduced as to the purging and holding gas. After maintaining
the sample at room temperature for 60 min and purging by H₂ and maintaining H₂
10 atmosphere at 30 psi in order to drive away the air left in the sample chamber, the
temperature was increased from room temperature to 973K at a rate of 20 K/min, and
maintained at 973K for 1 h to outgas the absorbed water and volatile contaminants. Then,
the sample was cooled down to 623K at a rate of 20 K/min, and maintained for 2 h. A
weight increase of 20 % (saturated) due to hydrogen uptake was achieved after this process.

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Example 2

600 mg of carbon nanotubes was mixed with LiNO₃ (20 molar percentage). The
mixture was heated to 800°C and maintained for half an hour, and then cooled down to
room temperature to form Li-doped carbon nanotubes. Using 20 mg of the prepared Li-
doped carbon nanotubes and putting into the sample holder of TGA, and following the same
20 procedures as example 1, a weight increase of 10 % was achieved.

Example 3

Using graphite as starting material and following the same procedures of example 1,
a weight increase of 12 % was achieved.

Example 4

25 600 mg of activated carbon was mixed with 30 molar % of KOH. The mixture was

calcined at 800°C for half an hour in a flow of purified hydrogen, and then cooled down to room temperature to form K-doped activated carbon. 50 mg of K-doped activated carbon was put in the sample container of the TG analyzer, and purified H₂ was introduced as purge gas to the TG system. The system was heated to 873K to remove absorbed water and volatile
5 contaminants, and then cooled down to 298K and maintain for 2 h. A weight increase of about 14 % was achieved after such process.

Example 5

Using carbon nanofibres as starting material and following the same procedures of example 4, a weight increase of 14 % was obtained.

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Example 6

Using NaOH and activated carbon as starting material and following the same procedures of example 4, a weight increase of about 13 % was achieved.

Example 7

Using Li-doped carbon nanofibres as sorbent, and exposing this to purified H₂ at 200
15 psi, a weight increase of 20 % was achieved within 1 h. This is shorter than the 2 h required for the similar test in example 1.

Example 8

Using Li-doped carbon nanotubes as sorbent, then following the same procedures of example 1, a weight increase of 15 % was achieved.

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To those skilled in the art, it is to be understood that many changes, modifications and variations could be made without departing from the spirit and scope of the present invention. The disclosures and the descriptions herein are purely illustrative and are not intended to limit the scope of claims.

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CLAIMS

1. A method of reversibly storing hydrogen comprising exposing a solid sorbent of metal-doped carbon-based material to a hydrogen atmosphere at a temperature of from about 250 K to about 973 K under ambient or higher H₂ pressure.
- 5 2. A method according to claim 1, wherein said metal-doped carbon-based material is an alkali metal-doped carbon-based material.
3. A method according to claim 2, wherein the alkali metal is selected from Li, Na, K, Rb and Cs.
4. A method according to claim 3, wherein the alkali metal is Li and said
10 solid sorbent is exposed to said hydrogen atmosphere at a temperature of from about 400 to about 800 K.
5. A method according to claim 3, wherein the alkali metal is Na or K and said solid sorbent is exposed to said hydrogen atmosphere at a temperature of from about 250 to about 400 K.
- 15 6. A method according to any one of claims 1 to 5, wherein said solid sorbent is exposed to the hydrogen atmosphere at a pressure of from about 1 to about 100 atm.
7. A method according to any one of claims 1 to 5, wherein said metal-doped carbon-based material is based on a carbon material selected from carbon fibre, carbon nanofibre, activated carbon, carbon nanotubes, graphite and amorphous (disordered) carbon.
- 20 8. A method according to claim 7, wherein said carbon material comprises carbon nanotubes having an average diameter of about 5 to 30 nm.
9. A method according to claim 7, wherein said carbon material comprises carbon nanofibres having an average diameter of about 10 to 60 nm.
10. A method according to claim 2, wherein said alkali metal-doped carbon-
25 based material is prepared by solid state reaction between a carbon material and an alkali metal salt.



11. A method according to claim 10, wherein said chemical reaction comprises mixing said alkali metal salt and said carbon material, and calcining the mixture under an atmosphere of inert or reductive gas.

12. A method according to claim 11, wherein said chemical reaction is carried
5 out under a He, N₂, Ar or H₂ atmosphere.

13. A method according to any one of claims 10 to 12, wherein said alkali metal salt is a nitrate, hydroxide, carbonate, halogenide, acetate, hydride, nitrite or the like.

14. A method according to any one of claims 10 to 13, wherein the molar ratio of alkali metal to the carbon material is from 1:20 to 1:1.

10 15. A method according to any one of claims 10 to 14, wherein the alkali metal salt is an Li salt and said chemical reaction is carried out at a temperature of from about 573 to about 1073 K under a hydrogen or inert gas atmosphere.

16. A method according to any one of claims 10 to 14, wherein the alkali metal salt is an Na or K salt and said chemical reaction is carried out at a temperature of from
15 about 973 to about 1273 K under a hydrogen atmosphere.

17. A method of preparing an alkali metal-doped carbon-based material for use in reversibly storing hydrogen comprising mixing a carbon material with an alkali metal salt and calcining the mixture under an atmosphere of inert or reductive gas.

18. A method according to claim 17, wherein said chemical reaction is carried
20 out under a He, N₂, Ar or H₂ atmosphere.

19. A method according to claim 17 or 18, wherein said alkali metal salt is a nitrate, hydroxide, carbonate, halogenide, acetate hydride, nitrite or the like.

20. A method according to any one of claims 17 to 19, wherein the molar ratio of alkali metal to the carbon material is from 1:20 to 1:1.

25 21. A method according to any one of claims 17 to 20, wherein the alkali metal salt is an Li salt and said chemical reaction is carried out at a temperature of from about 573



to about 1073 K under a hydrogen or inert gas atmosphere.

22. A method according to any one of claims 17 to 20, wherein the alkali metal salt is an Na or K salt and said chemical reaction is carried out at a temperature of from about 973 to about 1273 K under a hydrogen atmosphere.

5 23. A method according to any one of claims 17 to 22, wherein said carbon material is selected from carbon fibre, carbon nanofibre, activated carbon, carbon nanotubes, graphite and amorphous (disordered) carbon.

24. A method according to claim 23, wherein said carbon material comprises carbon nanotubes having an average diameter of about 5 to 30 nm.

10 25. A method according to claim 23, wherein said carbon material comprises carbon nanofibres having an average diameter of about 10 to 60 nm.

26. A hydrogen storage system comprising an alkali metal-doped, carbon-based material prepared in accordance with the method defined in any one of claims 17 to 25.

