Abstract: The present invention is directed towards boron substituted carbon compounds, methods of storing hydrogen by contacting such compounds with hydrogen to adsorb hydrogen thereon, and fuel cells containing such compounds. The present invention also provides methods for storing hydrogen on B substituted carbon nanotubes.
METHOD FOR STORING HYDROGEN USING NOVEL CARBON-BASED HIGH CAPACITY STORAGE MATERIALS

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/866,196, filed November 16, 2006, the disclosure of which is incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present invention relates generally to carbon-based compounds for the storage of hydrogen, and more particularly to new boratabenzene compounds for this purpose, e.g., to store hydrogen for use in fuel cells.

BACKGROUND OF THE INVENTION

[0003] Increasing concerns about atmospheric pollution, especially regarding global warming due to the greenhouse effect of carbon dioxide emissions, has led to a search for energy sources other than fossil fuels. As the internal combustion engines in motor vehicles are a principal source of carbon dioxide from the burning of gasoline, currently much effort is being devoted to the development of alternative energy sources suitable for use in cars and trucks. Molecular hydrogen (H₂) has been widely proposed as such an energy source because of its potential abundance, high energy content of 142 MJ/kg at least three times larger than that of other chemical fuels (Schlapback et al., Nature 414:353, 2001), and ability to release its energy by combination with oxygen (O₂) to form non-polluting H₂O as the only end product.

[0004] The combination of H₂ with O₂ can be carried out in a fuel cell, which is an electrochemical energy conversion device to produce electricity, differing from a battery in that it is designed for continuous replenishment of the reactants (see, e.g., http://en.wikipedia.org/wiki/Fuel_cell). A fuel cell is preferable to burning the hydrogen in an engine because it is more efficient (about 50% vs 25%), does not produce pollutants as byproducts because of burning in air, and is easier to control. A fuel cell consists of an anode, typically connected to a hydrogen source, and a cathode, typically connected to an oxygen source, separated by an electrolyte through which protons (H⁺) can flow. The anode
and cathode electrodes are connected by an external circuit through which electrons can flow to supply electric power. The electrodes are often in the form of plates and made of a metal such a nickel or carbon nanotubes. The anode is often coated with a catalyst such as platinum or palladium which catalyzes the breakdown of \( \text{H}_2 \) to \( 2\text{H}^+ + 2e^- \). The released \( \text{H}^+ \) travels through the electrolyte, which is often a membrane such as a polymer electrolyte membrane. The electrolyte is impermeable to electrons, which must thus travel through the external circuit from the anode to the cathode, where they combine with the \( \text{H}^+ \) and \( \text{O}_2 \) to produce \( \text{H}_2\text{O} \).

[0005] The fuel cell requires a source of hydrogen, which must therefore be stored. It has been estimated that a fuel-efficient vehicle will require 4 kg hydrogen to drive 400 km (Schlapback et al., Nature 414:353, 2001), which is likely to be the minimum driving range acceptable to the public. At room temperature and atmospheric pressure (about 1 bar), 4 kg hydrogen gas will occupy a volume of 45 m\(^3\), which is not a practical volume for a vehicle. The hydrogen might be reduced to an acceptable volume by compressing it under very high pressure (300 to 600 bar) in special tanks, or by liquefying it at very low temperature (-241°C). However, in addition to the weight and expense such systems would add, hydrogen is a flammable gas and its sudden release from containment in a vehicular accident would be unacceptable.

[0006] Consequently, there has been a great deal of research devoted to an alternative approach to storage of hydrogen: adsorption onto a solid material. In a vehicular accident, the adsorbed hydrogen would not be rapidly released. However, to be useful for fuel cells in vehicles, this method requires that the solid material be able to adsorb a considerable amount of hydrogen. Indeed, the U.S. Department of Energy has set as a goal the development by 2010 of a material with gravimetric capacity for hydrogen (weight of the hydrogen divided by weight of the material plus hydrogen) of 6%, and volumetric capacity of 45 g/L (http://www.eere.energy.gov/hydrogenandfuelcells/storage/tech_status.html). Moreover, the hydrogen must be adsorbed and released (desorbed) at temperatures and pressures consistent with operation in a vehicle, typically 0 to 100 or 150°C and 1 to 10 or 100 bar, and must maintain its integrity over many adsorption cycles. Inexpensive synthesis from common, inexpensive materials and lack of toxicity are also desirable features of such a storage material.
Several classes of materials have been developed in an attempt to meet these criteria. Probably the most exhaustively studied are metal hydrides, in which atomic H binds to a metal or alloy of metals. The binding is generally ionic for alkali and alkaline earth metals (e.g., LiH and MgH2) and interstitial for transition metals. Hydrogen storage capacity can be increased by using a disordered intermetallic material, in which incorporation of selected modifier elements such as transition metals into host elements that form hydrides increases the number of H storage sites (U.S. Patent No. 4,623,597). Some well-known metals whose hydrogen binding properties have been studied are Pd, LaNi5, ZrV2, FeTi, Mg2Ni and TiV2 (Schlapback et al., Nature 414:353, 2001). More generally, intermetallic compounds with formulas AB2, where A is a rare earth mixture and/or titanium and B is nickel, cobalt, manganese, and/or aluminum; or AB2 where A is titanium and/or vanadium and B is zirconium or nickel, modified with chromium, cobalt, iron, and/or manganese have been used (http://en.wikipedia.org/wiki/ Nickel_metal_hydride_battery). However, such materials generally have a hydrogen storage capacity around 2%, which is very adequate for use as the anode in batteries such as nickel metal hydride (NiMH) batteries widely used in consumer electronics, but not in fuel cells for vehicles. Other intermetallic compounds are known that have higher storage capacity, such as Li3Be2H7 with 9% H, but are not reversible within the required range of temperature and pressure (Schlapback et al., Nature 414:353, 2001). Similarly, intermetallic compounds based on Mg, e.g., Mg2Ni, have been intensively studied but lack the desired combination of storage capacity and operating temperature (see, e.g., U.S. Patent No. 5,906,792 and Schlapback et al., Nature 414:353, 2001). Doped sodium alanate (U.S. Patent No. 7,011,768) and scaffolded borazine-lithium (WO 2006/052473) have also been investigated, among others.

An entirely different class of compounds, based on carbon, have also been intensively studied for use in storing hydrogen. Prominent among these are carbon nanotubes, which have been extensively studied and clearly have some storage capacity for H2, although the exact amount is controversial (see Schlapback et al., Nature 414:353, 2001). Similarly, theoretical quantum mechanical (QM) calculations suggest that graphene layers have significant hydrogen binding capacity (Heine et al., Phys. Chem. Chem. Phys. 6:980, 2004 and Patchkovskii et al., Proc. Natl. Acad. Sci. USA 102: 10439, 2005). Similarly, QM calculations predict that boron and beryllium doped carbon fullerenes will bind hydrogen, with, for example, C34Be6 having a room-temperature reversible storage capacity of 1.7 wt%
Nonetheless, no practical hydrogen storage medium based on carbon nanostructures has been developed to date.

Hence, there is a clear need for materials with improved hydrogen storage capacity and properties for use, for example, in fuel cells. The current invention fulfills this and other needs.

**BRIEF SUMMARY OF THE INVENTION**

In one embodiment, the present invention provides a method of storing molecular hydrogen. The first step involves providing a source of molecular hydrogen. The second step involves contacting a compound of Formula I with the molecular hydrogen:

\[ [A]X_{1-4} \]

A of Formula I is a heteroaryl ring system having 5-16 ring members and 1-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least one of said heteroatoms is selected from the group consisting of B and Al, and substituted with 0-6 R\(^1\) groups. Each X of Formula I is a counterion. Each R\(^1\) is independently selected from the group consisting of hydrogen, halogen, Ci-C\(_6\) alkyl, Ci-C\(_6\) haloalkyl, C\(_1\)-C\(_6\) alkoxy, C\(_2\)-C\(_6\) alkenyl, C\(_2\)-C\(_6\) alkynyl, -C(O)R\(^2\), -C(O)OR\(^2\), -OC(O)C\(_1\)-C\(_6\) alkyl, -OR\(^2\), -NR\(^2\)R\(^3\), -C(O)NR\(^2\)R\(^3\), -NR\(^2\)C(O)C\(_1\)-C\(_6\) alkyl, -CN, -NO\(_2\), -SO\(_2\)OR\(^2\), -SO\(_2\)NR\(^2\)R\(^3\), a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R\(^2\) and R\(^3\) of Formula I are each independently a member selected from the group consisting of hydrogen and Ci-C\(_6\) alkyl. In this manner, the molecular hydrogen is adsorbed by the compound of Formula I thereby storing the molecular hydrogen.

In a second embodiment, the present invention provides a fuel cell comprising a compound of Formula I for the storage of molecular hydrogen:

\[ [A]X_{L-4} \]

A of Formula I is a heteroaryl ring system having 5-16 ring members and 1-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least
one of said heteroatoms is selected from the group consisting of B and Al, and substituted with 0-6 \( R^1 \) groups. Each \( X \) of Formula I is a counterion. Each \( R^1 \) is independently selected from the group consisting of hydrogen, halogen, \( \text{C}_1-\text{C}_6 \) alkyl, \( \text{C}_1-\text{C}_6 \) haloalkyl, \( \text{C}_1-\text{C}_6 \) alkoxy, \( \text{C}_2-\text{C}_6 \) alkenyl, \( \text{C}_2-\text{C}_6 \) alkynyl, \(-\text{C}(\text{O})\text{R}^2, -\text{C}(\text{O})\text{OR}^2, -\text{OC}(\text{O})\text{C}_1-\text{C}_6 \) alkyl, \(-\text{OR}^2, -\text{NR}^2\text{R}^3, -\text{C}(\text{O})\text{NR}^2\text{R}^3, -\text{NR}^2\text{C}(\text{O})\text{C}_6 \) alkyl, \(-\text{CN}, -\text{NO}_2, -\text{SO}_2\text{OR}^2, -\text{SO}_2\text{NR}^2\text{R}^3, \) a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And \( R^2 \) and \( R^3 \) of Formula I are each independently a member selected from the group consisting of hydrogen and \( \text{C}_1-\text{C}_6 \) alkyl.

(0012) In a third embodiment, the present invention provides a fuel cell comprising boron-substituted carbon nanotubes complexed with a member selected from the group consisting of Li, Na, K, Mg and Ca.

(0013) In a fourth embodiment, the present invention provides a method of storing molecular hydrogen comprising the step of contacting the hydrogen with B-substituted carbon nanotubes complexed with a member selected from the group consisting of Li, Na, K, Mg and Ca, such that the molecular hydrogen is adsorbed by the B-substituted carbon nanotubes thereby storing the molecular hydrogen.

(0014) In a fifth embodiment, the present invention provides a compound of Formula I:

\[
[A]X_{1-i-d}^1
\]

A of Formula I is a heteroaryl ring system having 5-16 ring members and 2-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least two of said heteroatoms are selected from the group consisting of B and Al, and substituted with 0-6 \( R^1 \) groups. Each \( X \) of Formula I is a counterion. Each \( R^1 \) is independently selected from the group consisting of hydrogen, halogen, \( \text{C}_1-\text{C}_6 \) alkyl, \( \text{C}_1-\text{C}_6 \) haloalkyl, \( \text{C}_1-\text{C}_6 \) alkoxy, \( \text{C}_2-\text{C}_6 \) alkenyl, \( \text{C}_2-\text{C}_6 \) alkynyl, \(-\text{C}(\text{O})\text{R}^2, -\text{C}(\text{O})\text{OR}^2, -\text{OC}(\text{O})\text{C}_1-\text{C}_6 \) alkyl, \(-\text{OR}^2, -\text{NR}^2\text{R}^3, -\text{C}(\text{O})\text{NR}^2\text{R}^3, -\text{NR}^2\text{C}(\text{O})\text{C}_6 \) alkyl, \(-\text{CN}, -\text{NO}_2, -\text{SO}_2\text{OR}^2, -\text{SO}_2\text{NR}^2\text{R}^3, \) a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S.
selected from the group consisting of N, O and S. And R² and R³ of Formula I are each independently a member selected from the group consisting of hydrogen and Ci-C₆ alkyl.

[0015] In a sixth embodiment, the present invention provides a method of storing molecular hydrogen. The first step involves providing a source of molecular hydrogen. The second step involves contacting a compound of Formula II with the molecular hydrogen:

\[ [A]X \quad II \]

A of Formula II is an aromatic cyclic polyene having 5-16 ring members, wherein optionally 1-3 ring members are selected from the group consisting of N, O and S, and substituted with 0-5 R¹ groups. Each X is a counterion. Each R¹ is independently selected from the group consisting of hydrogen, halogen, Ci-C₆ alkyl, Ci-C₆ haloalkyl, Ci-C₆ alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, -C(O)R², -C(O)OR², -OC(O)C-C₆ alkyl, -OR², -NR²R³, -C(O)NR²R³, -NR²C(O)C₁-C₆ alkyl, -CN, -NO₂, -SO₂OR², -SO₂NR²R³, a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R² and R³ of Formula II are each independently a member selected from the group consisting of hydrogen and Ci-C₆ alkyl. In this manner, the molecular hydrogen is adsorbed by the compound of Formula II thereby storing the molecular hydrogen.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Figure 1. A. Structure of (1-H-boratabenzene)Li. B. 3-dimensional model of (1-H-boratabenzene)Li in complex with 3 H₂ molecules. Light grey, carbon; white, hydrogen; dark grey, boron; black, lithium.

[0017] Figure 2. 3-dimensional model of (1,4-H-diboratabenzene)Li₂ in complex with 6 H₂ molecules. Light grey, carbon; white, hydrogen; dark grey, boron; black, lithium.

[0018] Figure 3. A. 3-dimensional model of section of a boron-doped nanotube, where the boron is shown as dark grey and the carbon atoms of the nanotube are shown as light grey. B. 3-dimensional model of section of a boron-doped nanotube complexed with lithium (1 Li per B), with lithium atoms shown in black. C. 3-dimensional model of section of a
boron-doped nanotube complexed with lithium (1 Li per B) and H₂ (3 H₂ per Li), with
hydrogen molecules shown in white.

[0019] Figure 4. A. Schematic drawing of a fragment of the periodic lattice of the
SWCNTs used in the calculations. B. Schematic drawing of section of an "unwound"
SWBC₃Li nanotube. Light grey, carbon; dark grey, boron; black, lithium atoms above the
plane (outside the nanotube); white, lithium atoms under the plane (inside the nanotube).

[0020] Figure 5. H₂ gravimetric storage capacity in SWCNTs at T=300° K as a function of
hydrogen pressure. Points are experimental data from the sources cited. Curves are
calculated for various nanotube diameters d and separations w between the nanotubes.

[0021] Figure 6. A. H₂ gravimetric storage capacity in SWBC₃Li nanotubes at T=300°K
(A) and T=373°K (B) as a function of hydrogen pressure. Curves are calculated for various
nanotube diameters d.

[0022] Figure 7. Schematic of a fuel cell of the present invention, showing hydrogen in a
hydrogen storage container stored via a method of storing hydrogen of the present invention.
The hydrogen travels to the face of anode (A) where the electrons are stripped off the
hydrogen molecule. The remaining protons travel through the anode and electrolyte (B) to
cathode (C). At the cathode, the protons meet up with the electrons which have traveled
through an electric circuit, thereby optionally operating an attached device, and with oxygen
to create water.

[0023] Figure 8. A. 3-dimensional model of tetraphenylmethane (TPM). B. 3-
dimensional model of TPM with two boron substitutions per ring and complexed with two
Li⁺ ions per ring. C. Planar view of polymer of the boron/lithium substituted TPM shown in
Fig. 8B. Light grey, carbon; white, hydrogen; dark grey, boron; black, lithium.

DETAILED DESCRIPTION OF THE INVENTION

1. Definitions

[0024] As used herein, the term "adsorbed" refers to the state of chemical interaction where
a first species accumulates on the surface of a second species and is bound onto the surface of
the second species through surface energy. Typically, it is chemically favorable for the first
species to accumulate on the surface of the second species and become adsorbed thereon.
Adsorption can occur through either chemisorption or physisorption.
As used herein, the term "alkyl" refers to a straight or branched, saturated, aliphatic radical having the number of carbon atoms indicated. For example, C1-C6 alkyl includes, but is not limited to, methyl, ethyl, propyl, butyl, pentyl, hexyl, isopropyl, isobutyl, secbutyl, tertbutyl, etc.

As used herein, the term "alkenyl" refers to either a straight chain or branched alkenyl of 2 to 6 carbon atoms, such as vinyl, propenyl, butenyl, isobutenyl, butadienyl, pentenyl or hexadienyl.

As used herein, the term "alkynyl" refers to either a straight chain or branched alkynyl of 2 to 6 carbon atoms, such as acetylenyl, propynyl or butynyl.

As used herein, the term "aromatic cyclic polyene" refers to a cyclic (monocyclic or fused bicyclic, tricyclic or greater) ring system having from 5 to 16 ring members, and an appropriate number of alkenyl moieties in combination with heteroatoms, anions or cations so as to be aromatic according to Hückel's rule of (4n+2) π electrons, where n is any integer. Exemplary aromatic cyclic polyenes useful in the present invention include, but are not limited to, cyclopentadienyl anion, cycloheptatrienyl cation, cyclononatetraenyl anion, pentalene dianion, acenaphthylene dianion, acepentalene dianion, thiophene, furan and pyridine. One of skill in the art will appreciate that other aromatic cyclic polyenes are useful in the present invention, especially when anionic.

As used herein, the term "aryl" refers to a monocyclic or fused bicyclic, tricyclic or greater, aromatic ring assembly containing 6 to 16 ring carbon atoms. For example, aryl can be phenyl or naphthyl, preferably phenyl. "Arylene" means a divalent radical derived from an aryl group. Aryl groups can be mono-, di- or tri-substituted by one, two or three radicals selected from alkyl, alkoxy, aryl, hydroxy, halogen, cyano, amino, amino-alkyl, trifluoromethyl, alkylenedioxy and oxy-C2-C3-alkylene; all of which are optionally further substituted, for instance as hereinbefore defined; or 1- or 2-naphthyl; or 1- or 2-phenanthrenyl. Alkylenedioxy is a divalent substitute attached to two adjacent carbon atoms of phenyl, e.g. methylenedioxy or ethylenedioxy. Oxy-C2-C3-alkylene is also a divalent substituent attached to two adjacent carbon atoms of phenyl, e.g. oxyethylene or oxypropylene. An example for oxy-C2-C3-alkylene-phenyl is 2,3-dihydrobenzofuran-5-yl.

Preferred as aryl is naphthyl, phenyl or phenyl mono- or disubstituted by alkoxy, phenyl, halogen, alkyl or trifluoromethyl, especially phenyl or phenyl-mono- or disubstituted by alkoxy, halogen or trifluoromethyl, and in particular phenyl.
Examples of substituted phenyl groups as \( R \) are, e.g. 4-chlorophen-1-yl, 3,4-dichlorophen-1-yl, 4-methoxyphen-1-yl, 4-methylphen-1-yl, 4-aminomethylphen-1-yl, 4-methoxyethylaminomethylphen-1-yl, 4-hydroxyethylaminomethylphen-1-yl, 4-hydroxyethyl-(methyl)-aminomethyl]phen-1-yl, 3-aminomethylphen-1-yl, 4-N-acetylaminomethylphen-1-yl, 4-aminophen-1-yl, 3-aminophen-1-yl, 2-aminophen-1-yl, 4-phenyl-phen-1-yl, 4-(imidazol-1-yl)-phenyl, 4-(imidazol-1-ylmethyl)-phen-1-yl, 4-(morpholin-1-yl)-phen-1-yl, 4-(morpholin-1-ylmethyl)-phen-1-yl, 4-(2-methoxyethylaminomethyl)-phen-1-yl and 4-(pyrrolidin-1-ylmethyl)-phen-1-yl, 4-(2-thiophenyl)-phen-1-yl, 4-(3-thiophenyl)-phen-1-yl, 4-(4-methylpiperazin-1-yl)-phen-1-yl, and 4-(piperidinyl)-phenyl and 4-(pyridinyl)-phenyl optionally substituted in the heterocyclic ring.

As used herein, the term "alkoxy" refers to alkyl with the inclusion of an oxygen atom, for example, methoxy, ethoxy, etc. "Haloalkoxy" is as defined for alkoxy where some or all of the hydrogen atoms are substituted with halogen atoms. For example, haloalkoxy includes trifluoromethoxy, etc.

As used herein, the term "carbon nanotube" refers to an allotrope of carbon that takes a form of cylindrical carbon molecules where the ends can be capped with a hemisphere of the buckyball structure. The nanotubes can be single walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs), with diameters of only a few nanometers, and lengths of up to several millimeters, and more typically hundreds of nanometers.

As used herein, the term "contacting" refers to the process of bringing into contact at least two distinct species such that one becomes adsorbed to the other. It should be appreciated that the resulting adsorption product can return to the original starting material through the process of desorption.

As used herein, the term "counterion" refers to singly or multiply positively charged moieties that are metallic or non-metallic, and operate to balance a corresponding negatively charged species. Metal counterions are elements of the periodic table that are metallic and that are positively charged as a result of having fewer electrons in the valence shell than is present for the neutral metallic element. Metals that are useful in the present invention include the alkali metals, alkali earth metals, transition metals and post-transition metals. Alkali metals include Li, Na, K, Rb and Cs. Alkaline earth metals include Be, Mg, Ca, Sr and Ba. Transition metals include Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc,
Ru, Rh, Pd, Ag, Cd, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg and Ac. Post-transition metals include Al, Ga, In, Tl, Ge, Sn, Pb, Sb, Bi, and Po. One of skill in the art will appreciate that the metals described above can each adopt several different oxidation states, all of which are useful in the present invention. In some instances, the most stable oxidation state is formed, but other oxidation states are useful in the present invention. Particularly useful metal ions in the present invention include, but are not limited to, Li(I), Na(I), K(I), Mg(II) and Ca(II). One of skill in the art will appreciate that other metals are useful as counterions in the present invention.

[0036] Non-metallic counterions include ammonium ion that optionally has 1-4 alkyl groups, such as NH$_4^+$ and NMe$_4^+$.  

[0037] As used herein, the term "cycloalkyl" refers to a saturated or partially unsaturated, monocyclic, fused bicyclic or bridged polycyclic ring assembly containing from 3 to 12 ring atoms, or the number of atoms indicated. For example, C$_3$-cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and up to cyclooctyl.

[0038] As used herein, the term "haloalkyl" refers to alkyl as defined above where some or all of the hydrogen atoms are substituted with halogen atoms. Halogen (halo) preferably represents chloro or fluoro, but can also be bromo or iodo. For example, haloalkyl includes trifluoromethyl, fluoromethyl, 1,2,3,4,5-pentafluoro-phenyl, etc. The term "perfluoro" defines a compound or radical which has at least two available hydrogens substituted with fluorine. For example, perfluorophenyl refers to 1,2,3,4,5-pentafluorophenyl, perfluoromethane refers to 1,1,1-trifluoromethyl, and perfluoromethoxy refers to 1,1,1-trifluoromethoxy.

[0039] As used herein, the term "halogen" refers to fluorine, chlorine, bromine and iodine.

[0040] As used herein, the term "heteroaryl" refers to a monocyclic or fused bicyclic or tricyclic aromatic ring assembly containing 5 to 16 ring atoms, where from 1 to 4 of the ring atoms are a heteroatom each B, Al, N, O or S. For example, heteroaryl includes boratabenzene, diboratabenzene, boratanaphthalene, borataanthracene, boratapyrene, diboratapyrene, aluminatabenzene, dialuminatabenzene, pyridyl, indolyl, indazolyl, quinoxalinyi, quinolinyl, isoquinolinyl, benzothienyl, benzofuranyi, furanyi, pyrrolyi, thiazolyl, benzothiazolyl, oxazolyl, isoxazolyl, triazolyl, tetrazolyl, pyrazolyl,imidazolyl, thienyl, or any other radicals substituted, especially mono- or di-substituted, by e.g. alkyl, nitro or halogen. Pyridyl represents 2-, 3- or 4-pyridyl, advantageously 2- or 3-pyridyl.
Thienyl represents 2- or 3-thienyl. Quinolinyl represents preferably 2-, 3- or 4-quinolinyl. Isoquinolinyl represents preferably 1-, 3- or 4 isoquinolinyl. Benzopyranyl, benzothiopyranyl represents preferably 3-benzopyran or 3-benzothiopyran respectively. Thiazolyl represents preferably 2- or 4-thiazolyl, and most preferred, 4-thiazolyl. Triazolyl is preferably 1-, 2- or 5-(1,2,4-triazolyl). Tetrazolyl is preferably 5-tetrazolyl.

[0041] As used herein, the term "heterocycle" refers to a ring system having from 3 ring members to about 20 ring members and from 1 to about 5 heteroatoms such as N, O and S. Additional heteroatoms can also be useful, including, but not limited to, B, Al, Si and P. The heteroatoms can also be oxidized, such as, but not limited to, -S(O)- and -S(O)2-. For example, heterocycle includes, but is not limited to, tetrahydrofuran, tetrahydrothiophenyl, morpholino, pyrrolidinyl, piperazinyl, indolinyl, indolyl, quinuclidinyl and 1,4-dioxo-aza-spiro[4.5]dec-8-yl.

II. Hydrogen Storage Compounds and Materials

[0042] In some embodiments, the invention provides compounds based on carbon heterocycles, especially boron-substituted heterocycles, for the storage of hydrogen.

[0043] In some embodiments, the compounds of the present invention are described by Formula I:

\[ [A]X_{1-4} \]

A of Formula I is a heteroaryl ring system having 5-16 ring members and 1-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least one of said heteroatoms is selected from the group consisting of B and Al, and substituted with 0-6 R1 groups. Each X of Formula I is a counterion. Each R1 is independently selected from the group consisting of hydrogen, halogen, CpC6 alkyl, CpC6 haloalkyl, Ci-C6 alkoxy, C2-C6 alkenyl, C2-C6 alkynyl, -C(O)R2, -C(O)OR2, -OC(O)C1-C6 alkyl, -OR2, -NR2R3, -C(O)NR2R3, -NR2C(O)Ci-C6 alkyl, -CN, -NO2, -SO2OR2, -SO2NR2R3, a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R2 and R3 of Formula I are each independently a member selected from the group consisting of hydrogen and Ci-C6 alkyl.
In another embodiment, the present invention provides a compound of Formula I:

\[ [A]X_{1-4} \]

wherein A is a heteroaryl ring system having 5-16 ring members and 2-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least two of said heteroatoms are selected from the group consisting of B and Al, and substituted with 0-6 R \(^1\) groups. Each X is a counterion. Each R \(^1\) is independently selected from the group consisting of hydrogen, halogen, C-C \(_6\) alkyl, C-C \(_6\) haloalkyl, C \(_2\)-C \(_6\) alkenyl, C \(_2\)-C \(_6\) alkynyl, -C(O)R \(^2\), -C(O)OR \(^2\), -OC(O)C \(_1\)-C \(_6\) alkyl, -OR \(^2\), -NR \(^2\)R \(^3\), -C(O)NR \(^2\)R \(^3\), -NR \(^2\)C(O)C \(_6\) alkyl, -CN, -NO \(_2\), -SO \(_2\)OR \(^2\), -SO \(_2\)NR \(^2\)R \(^3\), a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R \(^2\) and R \(^3\) are each independently a member selected from the group consisting of hydrogen and C-C \(_6\) alkyl.

In a further embodiment, the present invention provides a compound wherein the heteroaryl ring system has 6 ring members and 2 B atoms. In some other embodiments, each X is independently a member selected from the group consisting of Li, Na and K. In another embodiment, all X counterions present are selected from the group consisting of Li, Na and K. In still other embodiments, the compound is selected from the group consisting of (1,2-H-diboratabenzene)Li \(^2\), (1,3-H-diboratabenzene)Li \(^2\) and (1,4-H-diboratabenzene)Li \(^2\). In another embodiment, each X is independently a member selected from the group consisting of Mg and Ca.

One compound of Formula I consists of the 1-H-boratabenzene anion in complex with lithium ((1-H-boratabenzene)Li; see Fig. 1A and compound 2 of Table 1), which has been synthesized as described by Diego et al., J. Am. Chem. Soc. 117:8480, 1995 together with Boese et al., Chem. Ber. 118:1664, 1985; also see U.S Patent No. 6,255,246 at col. 7. Using ab initio QM software as described in greater detail below (Examples), it has been determined that one molecule of this compound can bind 4 H \(_2\) molecules, for a binding capacity of 8.7 wt% (Fig. 1B and Table 1), wherein wt% means the molecular weight of the bound hydrogens divided by the total molecular weight of the compound and the bound hydrogens. Hence, in one embodiment, the invention comprises the use of
(1-H-boratabenzene)Li as a medium to adsorb and store hydrogen. In related embodiments, the invention consists of a hydrogen storage system or a fuel cell containing (1-H-boratabenzene)Li. It will be understood that any other element or chemical group in the +1 charge state can replace the Li, for example sodium (X = Na in Formula 1, compound 3 of Table 1), which provides a hydrogen binding capacity of 9.1 wt% (Table 1) or potassium (X = K in Formula 1). Hence, such compounds can be used to store hydrogen in fuel cells.


[0048] In one method of preparation, an optionally substituted 1,4-diacyetylene, e.g. CH≡C-C≡CH is reacted with a dialkyltinhydride (e.g. (n-C₈H₁₇)₂SnH₂), to form the corresponding dihydrodialkyllstannabenzenes which is reacted with an organoborondibromide, e.g. phenylboron dibromide. To form a substituted species, e.g. the pentafluorophenylboratabenzene, a correspondingly substituted organoborodibromide, e.g. pentfluorophenylboron dibromide is used. Substitution on the boratabenzene ring is achieved by use of a substituted 1,5-diacytylene or, alternatively, by reactions within the skill in the art on a boratabenzene ring or the dihydrodialkyllstannabenzenes. Alternatively, substituted 2,4-pentadienylboranes are used as starting materials in the synthesis disclosed by Herberich, et al.

[0049] In other embodiments, the present invention provides a compound of Formula II:

\[
[A]X U
\]

A of Formula II is an aromatic cyclic polyene having 5-16 ring members, wherein optionally 1-3 ring members are selected from the group consisting of N, O and S, and substituted with 0-5 R₁ groups. Each X is a counterion. Each R₁ is independently selected from the group consisting of hydrogen, halogen, CrC₆ alkyl, C₅-C₆ haloalkyl, Ci-C₆ alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, -C(O)R², -C(O)OR², -OC(O)C₁-C₆ alkyl, -OR², -NR₂R³, -C(O)NR₂R³, -NR₂C(O)C₁-C₆ alkyl, -CN, -NO₂, -SO₂OR², -SO₂NR₂R³, a cycloalkyl ring system having
from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R<sup>2</sup> and R<sup>3</sup> of Formula II are each independently a member selected from the group consisting of hydrogen and C<sub>1</sub>-C<sub>6</sub> alkyl.

[0050] Compounds of Formula II can be prepared by one of skill in the art, such as taught by U.S. Patent Nos. 7,011,768, 6,166,234, 5,057,300 and 4,952,713 (incorporated herein by reference).
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical name</th>
<th>Structural formula</th>
<th>Maximum number of $H_2$ bound</th>
<th>Calculated range of $H_2$ binding energy (kcal/mol)</th>
<th>Weight % of hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>benzene</td>
<td><img src="image" alt="Benzene structure" /></td>
<td>2</td>
<td>1.1</td>
<td>4.9%</td>
</tr>
<tr>
<td>2</td>
<td>(1-H-boratabenzene)Li</td>
<td><img src="image" alt="Boratabenzene structure" /></td>
<td>4</td>
<td>1.0-2.1</td>
<td>8.7%</td>
</tr>
<tr>
<td>3</td>
<td>(1-H-boratabenzene)Na</td>
<td><img src="image" alt="Boratabenzene structure" /></td>
<td>5</td>
<td>1.3-1.6</td>
<td>9.1%</td>
</tr>
<tr>
<td>4</td>
<td>(1-H-aluminatabenzene)Na</td>
<td><img src="image" alt="Aluminatabenzene structure" /></td>
<td>5</td>
<td>1.2-1.4</td>
<td>7.9%</td>
</tr>
<tr>
<td>5</td>
<td>(1-H-aluminatabenzene)Li</td>
<td><img src="image" alt="Aluminatabenzene structure" /></td>
<td>3</td>
<td>1.2-2.0</td>
<td>5.7%</td>
</tr>
<tr>
<td>6</td>
<td>(1,2-H-diboratabenzene)Li$_2$</td>
<td><img src="image" alt="Diboratabenzene structure" /></td>
<td>6</td>
<td>1.1-2.1</td>
<td>11.8%</td>
</tr>
</tbody>
</table>
In another embodiment, the invention consists of a diboratabenzene compound, e.g., 1,2-H-diboratabenzene, 1,3-H-diboratabenzene, 1,4-H-diboratabenzene, for example in complex with lithium. The structures of these compounds are shown in Table 1. According to ab initio QM calculations, each of these compounds can bind 6 H₂ molecules, for an exceptionally high hydrogen storage capacity of 11.8% (Fig. 2 and Table 1). Again, the Li can be replaced by Na, K or other elements or chemical groups in the +1 charge state, with two such atoms in complex with one molecule of the diboratabenzene. Accordingly, (1,4-H-diboratabenzene)Na₂ can bind 8 H₂ molecules (11.6%). Alternatively, since a diboratabenzene ion will typically have a charge of -2, one such ion can complex with one atom or chemical group in the +2 state, e.g., Be, Mg or Ca. Accordingly,

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical name</th>
<th>Structural formula</th>
<th>Maximum number of H₂ bound</th>
<th>Calculated range of H₂ binding energy (kcal/mol)</th>
<th>Wt% of hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>(1,3-H-diboratabenzene)Li₂</td>
<td><img src="image1.png" alt="Structure1" /></td>
<td>6</td>
<td>1.0-2.0</td>
<td>11.8%</td>
</tr>
<tr>
<td>8</td>
<td>(1,4-H-diboratabenzene)Li₂</td>
<td><img src="image2.png" alt="Structure2" /></td>
<td>6</td>
<td>0.9-2.0</td>
<td>11.8%</td>
</tr>
<tr>
<td>9</td>
<td>(1,3,6,8-H-tetraboratapyrene)Li₄</td>
<td><img src="image3.png" alt="Structure3" /></td>
<td>12</td>
<td>1.5-3.0</td>
<td>9.6%</td>
</tr>
<tr>
<td>10</td>
<td>cyclopentadienyl lithium</td>
<td><img src="image4.png" alt="Structure4" /></td>
<td>4</td>
<td>0.9-1.7</td>
<td>10%</td>
</tr>
</tbody>
</table>

[0051]
(1,4-H-diboratabenzene)Mg can bind 4 H2 molecules (7.4%) with binding energies in the range of 0.79-5.98 kcal/mol. Similarly, the invention comprises triboratabenzene compounds, that is compounds in which 3 of the carbons in the ring are replaced with boron, e.g., in complex with Li or Na. Diboratabenzene and triboratabenzene compounds can advantageously be used to store hydrogen, e.g., in fuel cells.

[0052] Other modifications of the boratabenzene, diboratabenzene and triboratabenzene compounds described above are also encompassed in the invention. For example, one or more of the carbon atoms can be substituted by heteroatoms such as N, O or S. In addition or alternatively, any of the H atoms including those bonded to the borons can be replaced by any functional group known to those of skill in the art of chemistry, including halogens (e.g., F, Cl, Br or I), hydrocarbyls, aromatics, amines, amides, carboxylic acids, alcohols, aldehydes, ketones, ethers, esters and so forth. See, e.g., Organic Chemistry by Solomons & Fryhle (8th ed.), John Wiley and Sons, Inc., 2004, for a description of various functional groups. Simple exemplary functional groups include F, Cl, OH, CH3 and NH2. More generally, the invention encompasses the use for hydrogen storage, e.g., as part of a fuel cell, of any compound comprising as part of its molecular structure a boron-substituted, 6-membered carbon ring, preferably anionic and of aromatic character. The present invention also encompasses a method of storing molecular hydrogen, e.g., in a fuel cell, by adsorbing the hydrogen to compound having an anionic, aromatic (e.g., aryl or heteroaryl) ring system in complex with Li, Na, K, Mg or Cu cations. Such compounds will preferably have a hydrogen binding capacity of at least 2 wt%, more preferably of at least 4 or 5 wt%, still more preferably of at least 6 or 7 wt%, and most preferably at least 8 or 10 wt%.

[0053] However, the invention is not limited to boron-substituted 6-member rings, but extends to any boron-substituted carbon ring such as boron-substituted annulenes. Thus, for example, compounds comprising boron-substituted 5-, 7-, 8- or 9-membered carbon rings (e.g., boron-substituted cyclopentadiene, cycloheptatriene, or cyclooctatetraene) are also encompassed, and can be used to store hydrogen, e.g., in a fuel cell, with the same H2 binding capacity as mentioned above. Likewise, compounds comprising two or more fused carbon rings, e.g., 6-membered carbon rings, with at least one ring having a boron substitution are included. Such compounds into which boron can be substituted include polyaromatic hydrocarbons with 2 - 10 rings such as naphthalene, azulene, anthracene, triphenylene, pentacene, coronene, pyrene and ovaline. An exemplary compound with a calculated hydrogen binding capacity of 9.0% is shown as compound 9 in Table 1. Other examples
include, but are not limited to, (1-H-boratanaphthalene)Li and (2-H-boratanaphthalene)Li, each capable of binding $6 \text{H}_2$ molecules per molecule of compound for a hydrogen binding capacity of 8.2 wt%. Preferably, for maximum hydrogen storage capacity, each of the fused rings will contain at least one and possibly 2 or 3 boron atoms. Both the boron-substituted n-membered rings and polycyclic compounds can optionally have additional substitutions with other heteroatoms, e.g., N, O or S; and other functional groups as described above can substitute for any of the hydrogen atoms. Typically, the counterion for such compounds will be Li, Na, K, Mg or Ca. All these compounds will preferably have at least the same $\text{H}_2$ binding capacity as described in the previous paragraph and thus can be used to store hydrogen.

[0054] The invention also encompasses all the compounds described above, but with any element of Group 3 of the Periodic Table, preferably Aluminum (Al), replacing boron (B). Because these elements are in the same group as boron, compounds containing them instead of boron are expected to have similar properties to the boron containing compounds. For example, the compounds 4 and 5 of Table 1, which are specifically encompassed in the invention, correspond respectively to (1-H-boratabenzenes)Na and (1-H-boratabenzenes)Li except with Al replacing B. Both Al compounds have calculated $\text{H}_2$ binding capacity comparable to but slightly less than the respective B compounds (8.7 vs 5.7% for the Li forms and 9.1 vs 7.9% for the Na forms) because of the greater molecular weight of Al compared to B. Hence, such Al compounds will find use in storing hydrogen, e.g., in fuel cells.

[0055] The compounds for hydrogen storage described herein, in particular those comprising as part or all of their structure a 6-membered or other carbon ring singly or doubly substituted with boron and possibly complexed with Li or Na or K, will generally have molecular weight (M.W.) up to 1000 u, but most often less than 500 u and preferably less than 200 u, and most preferably a M.W. between about 75 and about 100 u, where "u" is the unit for atomic mass and 1 u is the inverse of Avogadro's number (6.02x10$^{23}$) in grams.

[0056] In other embodiments of the invention, boron-substituted graphene layers, boron-substituted carbon nanotubes, boron-substituted fullerenes or other carbon nanostructures substituted with boron (e.g., graphitic particles) are provided to store hydrogen, e.g., for use in fuel cells. Typically, 5 - 10% of the carbon atoms will be substituted by boron atoms, but preferably 10 - 15%, and most preferably about or at least
15%. In addition, there can be substitutions with atoms of other elements, e.g., beryllium or nitrogen. In the case of nanotubes, they can be single-walled (SWCNT) or multi-walled (MWCNT) and of any allowed chirality, and in the case of fullerenes, they can have any number of atoms possible for such structures, e.g., C_{20}, C_{36}, C_{50}, preferably C_{60}, C_{70}, C_{76}, C_{84} or even more atoms. Preferably, the boron-substituted carbon nanostructure, e.g., nanotube, will be complexed with atoms of another element, especially Li, Na or K, for storage of hydrogen. A molecular model of such a structure is shown in Fig. 3A,B, and with bound hydrogen in Fig. 3C. Nanotubes are advantageous in that hydrogen molecules can fit inside of them.

(0057) Methods of synthesizing carbon nanotubes are well-known to those of skill and include, for example, arc discharge, laser ablation, and chemical vapor deposition (see, e.g., http://en.wikipedia.org/wiki/Carbon_nanotube). Boron-substituted (boron-doped) nanotubes including SWCNT can be produced from carbon nanotubes, with or without additional nitrogen substitutions, by a chemical substitution reaction employing boron oxide (B_{2}O_{3}) (Han et al., Chem. Phys. Lett. 299:368, 1999; Golberg et al., Chem. Phys. Lett. 308:337, 1999; Golberg et al. Carbon 38:2017, 2000) with as many as 15 at.% of the carbon atoms substituted by boron (Borowiack-Palen et al., Chem. Phys. Lett. 378:516, 2003), or alternatively by pyrolysis of C_{2}H_{2} - B_{2}H_{6} mixtures (Satishkumar et al., Chem. Phys. Lett. 300:473, 1999). Boron-substituted graphene layers can be produced using the same substitution reaction. Li can be inserted into boron-substituted nanotubes electrochemically (Mukhopadhyay et al., 149:A39, 2002). Boron-substituted fullerenes such as C_{59}B and C_{59}B_{6} can also be synthesized (Kim et al., Phys. Rev. Lett. 96:016102, 2006 and Guo et al., J. Phys. Chem. 95:4948, 1991), and the existence of C_{48}B_{2} with a boron content of 20 at.% has also been predicted (Hultman et al., Phys. Rev. Lett. 87:225503, 2001).

(0058) The boron-substituted graphene layers, boron-substituted carbon nanotubes and boron-substituted fullerenes described herein will, when complexed with Li, Na, K or another element or functional group in a +1 charge state, preferably have a hydrogen binding capacity of at least 2 wt%, more preferably of at least 4 or 5 wt%, still more preferably of at least 6 or 7 wt%, and most preferably at least 10 wt%. When used to store hydrogen, H_{2} will be adsorbed to these boron-substituted nanostructures at a pressure of 0 - 100 bar, more preferably 1 - 50 bar, most preferably 1 - 10 bar, and at a temperature preferably between 0°C and 300°C, more preferably between 0°C and 150°C, and most preferably between 20°C and 100°C. The H_{2} will be desorbed by altering the temperature and pressure, for example by
raising the temperature and lowering the external pressure, but within the aforesaid range of values.

III. Methods of Storing Hydrogen

[0059] In some embodiments, the present invention provides a method of storing molecular hydrogen. The first step involves providing a source of molecular hydrogen. The second step involves contacting a compound of Formula I with the molecular hydrogen:

$$[A]X_{1-4} \rightarrow I$$

Where A of Formula I is a heteroaryl ring system having 5-16 ring members and 1-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least one of said heteroatoms is selected from the group consisting of B and Al, and substituted with 0-6 R^1 groups. Each X of Formula I is a counterion. Each R^1 is independently selected from the group consisting of hydrogen, halogen, C_i-C_6 alkyl, C_i-C_6 haloalkyl, C_i-C_6 alkoxy, C_2-C_6 alkenyl, C_2-C_6 alkynyl, -C(O)R^2, -C(O)OR^2, -OC(O)C_1-C_6 alkyl, -OR^2, -NR^2R^3, -C(O)NR^2R^3, -NR^3C(O)C_1-C_6 alkyl, -CN, -NO_2, -SO_2OR^2, -SO_2NR^2R^3, a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R^2 and R^3 of Formula I are each independently a member selected from the group consisting of hydrogen and C_i-C_6 alkyl. In this manner, the molecular hydrogen is adsorbed by the compound of Formula I thereby storing the molecular hydrogen.

[0060] In other embodiments, the present invention provides a method of storing molecular hydrogen using compounds wherein A is a 6-membered heteroaryl with 1 B heteroatom and 1 X counterion. In another embodiment, A is (1-H-boratabenzene). In still another embodiment, X is independently a member selected from the group consisting of Li, Na and K. In yet another embodiment, X is independently a member selected from the group consisting of Li and Na.

[0061] In a further embodiment, the present invention provides a method of storing molecular hydrogen using a compound of Formula I wherein A is (1-H-aluminatabenzene).
In some other embodiments, X is independently a member selected from the group consisting of Li and Na.

[0062] In another embodiment, the present invention provides a method of storing molecular hydrogen using a compound of Formula I wherein A is a heteroaryl ring system having two heteroatoms each independently selected from the group consisting of B and Al. In other embodiments, both heteroatoms are B. In still another embodiment, A is a 6-membered heteroaryl. In yet another embodiment, the compound is selected from the group consisting of (1,2-H-diboratabenzene)X, (1,3-H-diboratabenzene)X, and (1,4-H-diboratabenzene)X, wherein each X is independently a member selected from the group consisting of Li, Na and K. In still yet another embodiment, the compound is selected from the group consisting of (1,2-H-diboratabenzene)X, (1,3-H-diboratabenzene)X, and (1,4-H-diboratabenzene)X, wherein X is selected from the group consisting of Mg and Ca.

[0063] In some embodiments, the present invention provides a method of storing molecular hydrogen using a compound of Formula I wherein each X is a member selected from the group consisting of a metal counterion and an ammonium counterion. In other embodiments, each X is a metal counterion independently selected from the group consisting of alkali metals, alkali earth metals, transition metals and post-transition metals. In still other embodiments, each X is independently an alkali metal selected from the group consisting of Li, Na, K, Rb and Cs. In yet other embodiments, each X is independently a member selected from the group consisting of Li, Na and K. In still yet other embodiments, each X is independently an alkali earth metal selected from the group consisting of Be, Mg, Ca, Sr and Ba. In still other embodiments, each X is independently an alkali earth metal selected from the group consisting of Mg and Ca.

[0064] In a further embodiment, the present invention provides a method of storing molecular hydrogen comprising the step of contacting a compound of Formula I with the molecular hydrogen wherein the compound of Formula I has a molecular weight of less than 500 u, where "u" is the unit for atomic mass and 1 u is the inverse of Avogadro's number (6.02x10^23) in grams. In another embodiment, the compound of Formula I has a molecular weight of less than 200 u. In still another embodiment, the compound of Formula I has a molecular weight of less than 100 u.

[0065] In another embodiment, the present invention provides a method of storing hydrogen wherein at least 5 wt% hydrogen is stored. In still another embodiment, at least 6
wt% hydrogen is stored. In other embodiments, at least 7 wt% hydrogen is stored, or more preferably, at least 8 wt% hydrogen is stored. In another embodiment, at least 9 wt% hydrogen is stored. In yet another embodiment, at least 10 wt% hydrogen is stored. In still other embodiments, at least 11 wt% hydrogen is stored.

[0066] In a further embodiment, the present invention provides a method of storing hydrogen wherein the step of contacting the compound of Formula I with molecular hydrogen is performed at a pressure of from about 1 to about 100 bar and a temperature of from about 0°C to about 150°C. In another embodiment, the temperature is from about 0°C to about 100°C. In other embodiments, the pressure can be up to 500 bar.

[0067] In other embodiments, the present invention provides a method of storing molecular hydrogen. The first step involves providing a source of molecular hydrogen. The second step involves contacting a compound of Formula II with the molecular hydrogen:

\[ [A]X \]

II

A of Formula II is an aromatic cyclic polyene having 5-16 ring members, wherein optionally 1-3 ring members are selected from the group consisting of N, O and S, and substituted with 0-5 R^1 groups. Each X is a counterion. Each R^1 is independently selected from the group consisting of hydrogen, halogen, C_1-C_6 alkyl, Ci-C_6 haloalkyl, Ci-C_6 alkoxy, C_2-C_6 alkenyl, C_2-C_6 alkynyl, -C(O)R^2, -C(O)OR^2, -OC(O)C_1-C_6 alkyl, -OR^2, -NR^2R^3, -C(O)NR^2R^3, -NR^2C(O)C_6 alkyl, -CN, -NO_2, -SO_2OR^2, -SO_2NR^2R^3, a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R^2 and R^3 of Formula II are each independently a member selected from the group consisting of hydrogen and Ci-C_6 alkyl. In this manner, the molecular hydrogen is adsorbed by the compound of Formula II thereby storing the molecular hydrogen. Hence, a compound of Formula II can advantageously be used as part of a fuel cell to store hydrogen.
In some embodiments, the present invention provides a method of storing molecular hydrogen using a compound of Formula II, wherein the compound of Formula II is:

\[
\begin{array}{c}
\text{CpLi} \\
\text{X}
\end{array}
\]

wherein X is a counterion selected from the group consisting of Li, Na and K. When X is Li, this compound, cyclopentadienyl lithium, can be abbreviated CpLi. CpLi can bind up to 4 molecules of hydrogen per CpLi molecule for a hydrogen storage capacity of 10 wt% (compound 10 of Table 1). When X is Na, cyclopentadienyl sodium can bind up to 5 hydrogen molecules for a hydrogen storage capacity of 9.5 wt%.

In a further embodiment, the present invention provides a method of storing molecular hydrogen comprising the step of contacting a compound of Formula II with the molecular hydrogen wherein the compound of Formula II has a molecular weight of less than 500 u, where "u" is the unit for atomic mass and 1 u is the inverse of Avogadro’s number (6.02 x 10^23) in grams. In another embodiment, the compound of Formula II has a molecular weight of less than 200 u. In still another embodiment, the compound of Formula II has a molecular weight of less than 100 u.

In another embodiment, the present invention provides a method of storing hydrogen wherein at least 5 wt% hydrogen is stored. In still another embodiment, at least 6 wt% hydrogen is stored. In other embodiments, at least 7 wt% hydrogen is stored, or more preferably, at least 8 wt% hydrogen is stored. In another embodiment, at least 9 wt% hydrogen is stored. In yet another embodiment, at least 10 wt% hydrogen is stored. In still other embodiments, at least 11 wt% hydrogen is stored.

In a further embodiment, the present invention provides a method of storing hydrogen wherein the step of contacting the compound of Formula II with molecular hydrogen is performed at a pressure of from about 1 to about 100 bar and a temperature of from about 0°C to about 150°C. In another embodiment, the temperature is from about 0°C to about 100°C. In other embodiments, the pressure can be up to 500 bar.

Whatever the structure and form of the compound, H_2 will be adsorbed to it at a pressure of 0 - 100 bar, more preferably 1 - 50 bar, most preferably 1 - 10 bar, and at a temperature preferably between 0°C and 300°C, more preferably between 0°C and 150°C, and most preferably between 20°C and 100°C. The H_2 will be desorbed by altering the
temperature and pressure, for example by raising the temperature and lowering the external pressure, but within the aforesaid range of values. Time can also play a role in the methods of the present invention. Allowing longer times for the contacting of the compounds of the present invention by hydrogen will lead to greater amounts of hydrogen stored, depending on pressure and temperature. One of skill in the art will appreciate that other temperatures and pressures are useful in the methods of the present invention.

[0073] In another embodiment, the present invention provides a method of storing molecular hydrogen wherein the source of molecular hydrogen is a gas mixture comprising at least 1% (v/v) molecular hydrogen. Preferably, the gas mixture is at least 10% (v/v) molecular hydrogen. More preferably, the gas mixture is at least 50% (v/v). In some embodiments, the hydrogen gas mixture comprises other gases, such as nitrogen, helium, neon, argon, oxygen, etc. One of skill in the art will appreciate that other hydrogen gas mixtures are useful in the present invention.

[0074] The molecular hydrogen can be provided by a cylinder of hydrogen, where the cylinder is connected to the hydrogen storage container and hydrogen is allowed to flow into the hydrogen storage container and contact the hydrogen storage compounds of the present invention. In other embodiments, the hydrogen can be manufactured, such as via electrolysis of water, immediately prior to entering the hydrogen storage container and contacting the hydrogen storage compounds of the present invention. One of skill in the art will appreciate that other hydrogen gas mixtures are useful in the present invention. In addition, the hydrogen can be provided by other means and sources known to one of skill in the art.

[0075] The hydrogen storage container according to the present invention is a hydrogen storage container which includes a container and a hydrogen storage material accommodated in the container. The container is not, as far as it can be used under such conditions as low temperatures or high pressures, limited in particular, and various ones such as pressure resistant containers can be used. The container is filled with a hydrogen storage material of the present invention. To store hydrogen, hydrogen is brought into contact with the storage material, e.g., by passing hydrogen gas through the storage material at a certain pressure and temperature, as exemplified above. To release the hydrogen, the conditions are modified, e.g., by lowering the pressure and or increasing the temperature. The hydrogen storage container itself can be made of a variety of materials. Metal containers are preferred, as higher pressures can be obtained. The hydrogen storage container can have a sealable lid
through which the hydrogen storage compound is added to the hydrogen storage container. The hydrogen storage container can also have a valve for hydrogen to enter and exit. In some instances, the hydrogen storage container can have a second valve for purging excess gas, or for allowing hydrogen that is not used by the fuel cell to return to the hydrogen storage container.

[0076] For all the compounds described herein, for example (l-H-boratabenzene)Li, the compound can be in any form to store hydrogen, but preferably as a powder of fine particles (i.e., less than 1 µm in size, preferably less than 100 nm in size, for example approximately 1 nm in size, or 1 to 10 nm in size, or 1 to 100 nm in size) produced for example by mechanical crushing or milling (e.g., ball milling) or other processes well known to those of skill, so that the H₂ can more readily diffuse into the particles. The compound can also be in molten form or dissolved in an organic solvent, or mixed with other substances, for example polymers, e.g., for stabilization. The compound can also itself be polymerized, e.g., a chain of repeating boron-containing carbon rings can be formed by methods well-known to those of skill, and such a polymer used to store hydrogen.

[0077] By way of example, any of the polymeric compounds COF-1 02, COF-1 03, COF 105 and COF-1 08 described in El-Kaderi et al., Science 316:268, 2007, can be used to bind hydrogen when modified by substitution of boron for one or more carbon atoms in one, two, three or preferably all four of the phenyl rings in the component monomers TBPM, TBPS or HHTTP and by conjugation with metallic counterions such as preferably Li or Na, but also K, Mg, Ca, and so forth, preferably so the number of positive ionic charges equals the number of boron substitutions per monomer. Indeed, any of the types of substitutions with B and/or another heteratom described above for ring systems may be made in TBPM, TBPS or HHTTP before synthesis into polymers by self-condensation or co-condensation as described in El-Kaderi et al., Science 316:268, 2007 which is hereby incorporated by reference for all purposes. Such polymers are especially good for storage of hydrogen because they have very low density and large spaces into which the hydrogen molecules can fit. Thus, as another example, the monomer tetrphenylmethane (TPM; tetrahedral carbon with 4 phenyl rings, Fig. 8A) with one or two or three C atoms in each ring substituted by B and conjugated with a corresponding number of Li, Na, K, or other metallic counterions, as shown in Fig. 8B, can be condensed into a diamond-type lattice polymer (Fig. 8C). As yet another example, the monomer tetrabiphenylmethane, similarly substituted and conjugated, can be condensed to form a polymer for binding of hydrogen. Yet other tetrahedral compounds comprising at
least 4 carbon rings, similarly substituted and conjugated, can also be used similarly to form polymers for binding of hydrogen. Initial calculations of the type described in the Examples below indicate that polymers of these types have good ability to bind and release hydrogen at acceptable temperatures and pressures and are therefore suitable for use in, e.g. fuel cells.

[0078] In other embodiments, the present invention provides a method of storing molecular hydrogen comprising adsorbing the hydrogen onto a polymer having monomers having 4 phenyl rings, wherein at least one of the phenyl rings of each monomer is substituted with at least one B atom and is conjugated with at least one metallic counterion. In some other embodiments, each monomer is tetra(4 dihydroxborylphenyl)methane, tetra(4-dihydroxborylphenyl) silane or tetraphenylmethane.

[0079] Hydrogen can be adsorbed on such polymers by contacting the polymers with hydrogen. The contacting of the polymers with the hydrogen can be performed at any pressure. In some embodiments, the contacting is performed at atmospheric pressure. In other embodiments, the contacting is performed at pressures greater than atmospheric pressure.

[0080] In some other embodiments, the present invention provides a method of storing molecular hydrogen comprising the step of contacting the molecular hydrogen with B-substituted carbon nanotubes complexed with a member selected from the group consisting of Li, Na, K, Mg and Ca, such that the molecular hydrogen is adsorbed by the B-substituted carbon nanotubes thereby storing the molecular hydrogen.

IV. Fuel Cell

[0081] A fuel cell is an energy-conversion device that directly converts the energy of a supplied gas into an electric energy. Highly efficient fuel cells employing hydrogen, particularly with their simple combustion product of water, would seem an ideal alternative to current typical power generations means. Researchers have been actively studying such devices to utilize the fuel cell's potential high energy-generation efficiency.

[0082] The base unit of the fuel cell is a cell having a cathode, an anode, and an appropriate electrolyte. Fuel cells have many potential applications such as supplying power for transportation vehicles, replacing steam turbines and power supply applications of all sorts.

[0083] The major components of a typical fuel cell are the anode for hydrogen oxidation and the cathode for oxygen reduction, both being positioned in a cell containing an
Typically, the reactants, such as hydrogen and oxygen, are respectively fed through a porous anode and cathode and brought into surface contact with the electrolytic solution. The particular materials utilized for the cathode and anode are important since they must act as efficient catalysts for the reactions taking place.

[0084] The anode material of the fuel cell of the present invention is such that it is porous, allowing the protons to pass through, and is catalytic such that it splits the molecular hydrogen into atomic hydrogen and strips the electrons from the protons. Suitable anode materials include, but are not limited to, nickel, metals and carbon nanotubes. The anode is also coated with a catalyst such as, but not limited to, platinum, palladium, iron, and other metal catalysts. One of skill in the art will appreciate that other materials are useful as the anode of the fuel cell of the present invention.

[0085] The electrolyte of the fuel cell of the present invention can be prepared from any material that will conduct protons from the anode to the cathode. Exemplary materials include, but are not limited to, aqueous alkaline solutions, polymer-based membranes, solid oxides such as ZrO₂, and molten carbonate.

[0086] The cathode material of the fuel cell of the present invention is such that it is catalytic, capable of taking protons, electrons and molecular oxygen to form water. Suitable cathode materials for the fuel cell of the present invention include, but are not limited to, lanthanum, strontium, iron, manganese, cobalt, chromium, gallium, and combinations of the same. One of skill in the art will appreciate that other metals are useful as the cathode material for the fuel cell of the present invention.

[0087] By using the materials of the present invention for adsorbing hydrogen according to the present invention, it is possible to constitute a hydrogen storage container whose hydrogen storage capacity is large at ordinary temperature. Moreover, by using the hydrogen storage material according to the present invention, it is possible to constitute a hydrogen storage container whose hydrogen storage capacity per unit volume is large.

[0088] The hydrogen storage material, used in the hydrogen storage container according to the present invention, can employ a mode which contains a binder. By containing a binder, it is possible to maintain a uniformly mixed state of the hydrogen storage material. Moreover, in case of forming the hydrogen storage material into a predetermined shape, there is an advantage in that the forming becomes easy. The binder is not such that its types are limited...
in particular. For example, it is possible to use fluorocarbon resins, such as polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE) and polyvinylidene fluoride (PVDF), ethylene-propylene-diene copolymers, styrene-butadiene rubber, carboxy cellulose, and the like.

Moreover, the content proportion of the binder in the hydrogen storage material can desirably be 20% by weight or less. This is because the binder does not have a hydrogen absorb-desorb ability, and accordingly, when the content proportion of the binder exceeds 20% by weight, the hydrogen storage capacity of the hydrogen storage material decreases. It can further desirably be 5% by weight or less. Moreover, in order to effectively exhibit the aforementioned effect obtained by containing the binder, the content proportion can desirably be 0.2% by weight or more.

In some embodiments, the present invention provides a fuel cell comprising a compound of Formula I for the storage of molecular hydrogen:

$$[A]X_{1-4}$$  

I

A of Formula I is a heteroaryl ring system having 5-16 ring members and 1-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least one of said heteroatoms is selected from the group consisting of B and Al, and substituted with 0-6 R¹ groups. Each X of Formula I is a counterion. Each R¹ is independently selected from the group consisting of hydrogen, halogen, Ci-C₆ alkyl, Ci-C₆ haloalkyl, Q-C₆ alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, -C(O)R², -C(O)OR², -OC(O)Ci-C₆ alkyl, -OR², -NR²R³, -C(O)NR²R³, -NR²C(O)Cᵢ-C₆ alkyl, -CN, -NO₂, -SO₂OR², -SO₂NR²R³, a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And R² and R³ of Formula I are each independently a member selected from the group consisting of hydrogen and Ci-C₆ alkyl.

In another embodiment, the present invention provides a fuel cell wherein A is a heteroaryl ring system having 6 ring members and 1 B heteroatom. In still another embodiment, A is a heteroaryl ring system having 6 ring members and 2 B heteroatoms.
In other embodiments, the present invention provides a fuel cell wherein the molecular hydrogen is provided by the desorption of adsorbed hydrogen from a compound of Formula I or Formula II.

In a further embodiment, the present invention provides a fuel cell comprising boron-substituted carbon nanotubes complexed with a member selected from the group consisting of Li, Na, K, Mg and Ca.

In some other embodiments, the present invention provides a fuel cell comprising a compound of Formula II for the storage of molecular hydrogen:

\[
[A]X
\]

A of Formula II is an aromatic cyclic polyene having 5-16 ring members, wherein optionally 1-3 ring members are selected from the group consisting of N, O and S, and substituted with 0-5 \( R^1 \) groups. Each \( X \) is a counterion. Each \( R^1 \) is independently selected from the group consisting of hydrogen, halogen, Ci-C_6 alkyl, Ci-C_6 haloalkyl, CpC_6 alkoxy, C_2-C_6 alkenyl, C_2-C_6 alkynyl, -C(O)R^2, -C(O)OR^2, -OC(O)C_1-C_6 alkyl, -OR^2, -NR^2R^3, -C(O)NR^2R^3, -NR^2C(O)C_1-C_6 alkyl, -CN, -NO_2, -SO_2OR^2, -SO_2NR^2R^3, a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S. And \( R^2 \) and \( R^3 \) of Formula II are each independently a member selected from the group consisting of hydrogen and Ci-C_6 alkyl.

V. Examples

**Example 1: Quantum Mechanical methods used**

The quantum mechanical (QM) calculations were performed at several levels of the theory. The semi-empirical (MNDO, AMI and PM3) energy calculation and unconstrained molecular geometry optimization were carried out using PC GAMESS version of the GAMESS (US) program package (Schmidt et. al., J. Comput. Chem. 14:1347, 1993; Granovskv, http://classic.chem.msu.su/gran/gamess/index.html). The restricted Hartree-Fock (RHF), second-order Moller-Plesset (MP2) and a variant of the RHF based complete active space second-order perturbation theory (CASPT2) calculations (Andersson et al., J. Phys. Chem. 94:5483, 1990, and Andersson et al., J. Chem. Phys. 96:1218, 1992) were performed.
with the Algo-QMT programs developed by the inventors. The Algo-QMT program utilizes the resolution of the identity (RI) method to evaluate the electron-electron interaction integrals as described (Artemyev et al., J. Chem. Phys. 123: 024103, 2005). Two types of molecular basis sets in a Cartesian form were used: (i) Pople's split valence basis set with (6-3 IG**) and without (6-31G) polarization functions (Hariharian et al., Theoret. Chim Acta 28: 213, 1973; Francl et al., J. Chem. Phys. 77:3654, 1982; Rassolov et al., J. Chem. Phys. 109: 1223, 1998); and (ii) Dunning's (augmented) correlation-consistent polarized (aug-)cc-pVXZ (X=D,T,Q,5,6) basis set series (Dunning, Jr., J. Chem. Phys. 90:1007, 1989). These basis sets were taken from Extensible Computational Chemistry Environment Basis Set Database (http://www.emsl.pnl.gov/forms/basisform.html). The RI basis set were used for convergent (with respect to the RI expansion) calculations of every specific quantity, so that the error due to the RI approximation is negligible; see Artemyev et al., J. Chem. Phys. 123: 024103, 2005 for the concept of RI convergent calculations. Alternatively, publicly available RI basis sets such as Turbomole RI basis set (Weigend et al., Chem. Phys. Lett. 294:143, 1998), can be used. The unconstrained and constrained geometry optimization of monomers and intermolecular complexes at the ab initio level of the theory (RI-MP2) were performed with using the Algo-QMT programs. The program utilizes a gradient free local minimization method with both the energy and estimated gradients convergence criteria. The $10^{-6}$ a.u. energy convergence criterion was used in the geometry optimization, and the estimated gradients were at the level of $10^{-4}$ a.u. or below. Alternatively, one can perform similar QM calculations (RHF and MP2) to the above using traditional (non-RI) approaches, e.g. with GAMESS (cited above), GAUSSIAN (e.g., Gaussian 03, Revision C.02 available from Gaussian, Inc., Wallingford, CT) or Jaguar (e.g., Jaguar 5.5 available from Schrodinger, LLC, Portland, OR).

[0096] Valence geometry of the monomers (e.g., of the H$_2$ molecule, (l-H-boratabenzene)Li molecule, etc.) was optimized at the semi-empirical MNDO level as well as at the RI-MP2 (frozen core) level with 6-3 IG and 6-3 IG** molecular basis set without constraints. The latter method provides accuracy (comparable to the available experimental values) of the valence bonds within 0.05 Å and that of the valence angles within 1°. It was established that the distortion of the geometry of the monomers at this level does not charge the H$_2$ interaction energy more than 0.1 kcal/mol. In addition, it was established that for sample monomers (e.g. for benzene, naphthalene, etc, as well as for (l-H-boratabenzene)Li) the MNDO geometry is very close to the MP2 6-3 IG** geometry.
Thus, use of the more readily calculated MNDO geometry for larger systems of that type (e.g., for carbon nanotubes and for BC\textsubscript{3} nanotubes doped with Li ions) was justified. In other cases, however, (e.g., for systems with Na ions) the MNDO geometry was significantly incorrect, and therefore the MP2 6-31G** geometry was used.

5 [0097] For greatest precision, the geometry and the interaction energy of the intermolecular complexes (e.g., one or more H\textsubscript{2} molecules bound to the substrate molecules such as (l-H-boratabenzene)Li described above (see Table 1) were calculated at the MP2 level with the aug-cc-pVTZ molecular basis set (with higher polarization functions dropped, i.e., aug-cc-pVTZ(-hp)), as described above. The basis set superposition error (BSSE) was corrected by using the counterpoise (CP) method. The interaction energy calculated by this method is within 0.2 kcal/mol of the MP2 basis set limit, as was verified by calculations with full aug-cc-pVTZ, aug-cc-pVQZ and aug-cc-pV5Z basis sets for selected cases. Further validation for these methods is provided by the excellent agreement between the result for the interaction energy (in the optimal geometry) of the H\textsubscript{2} molecule with the benzene molecule of 1.0 kcal/mol compared with values of 0.94 to 1.17 kcal/mol obtained by means of different methods (Hubner et al., J.Phys.Chem A 108: 3019, 2004).

10 [0098] However, it has also been established that the MP2 6-31G** intermolecular geometry and energy (without the CP correction for BSSE) are within 0.3 kcal/mol of the MP2 aug-cc-pVTZ(-hp) values in most cases of the H\textsubscript{2} molecule bonding. This is due to compensation of the BSSE error and the error of the relatively short basis set 6-31G**. Thus, in many cases, the intermolecular geometry optimization was performed at the MP2 6-3 IG** (no CP) level and calculated the interaction energy in the optimal geometry at the MP2 aug-cc-pVTZ(-hp) level. If the energies in the two basis sets differed by more than 0.5 kcal/mol, then the geometry of the complex was reoptimized at the more time-consuming MP2 aug-cc-pVTZ(-hp) level. Also, in certain experiments, binding of one H\textsubscript{2} molecule to the substrates were studied using unconstrained and rigid monomers optimization. The interaction energy was the same within 0.1 kcal/mol. Thus, binding of several H\textsubscript{2} molecules to the substrates were studied using the rigid monomers optimization.

20 (0099) In addition, CASPT2 calculations were performed for selected cases (e.g., for (l-H-boratabenzene)Li + H\textsubscript{2} complex, for (l-H-boratabenzene)Na complex + H\textsubscript{2}, etc.) to study the influence of the higher order (post MP2) electronic correlations on the H\textsubscript{2} binding energy. The results suggest that the higher-order electronic correlations can decrease the MP2
binding energy of the hydrogen molecule by at most 0.2-0.3 kcal/mol. This estimate is close to the results of the coupled clusters calculations of the interaction of benzene molecule with $H_2$ (Hiibner et al., J.Phys.Chem A 108: 3019, 2004), and is not enough to effect the conclusions drawn from the calculations.

For thermodynamic calculations, force field methods were used. A force field was fitted to the calculated interaction energies of the $H_2$ molecules with the substrates. The hydrogen molecule was treated as a single force center, and the interaction energy was approximated by the sum of pair-wise interaction functions of the hydrogen molecule with the $i$-th atom of type $X$ of the substrate

$$V_{ia}(r) = \sum_{X'} V_{iX'}(r - \vec{r}_X)$$

The interaction functions (the force field components) $V_{iX'}(r)$ for the relevant atom types were expanded into linear combination of basis functions of two types: $n^{-\alpha}e^{-\beta r}$ and

$$\left(1 - \frac{e^{-\gamma r}}{r}\right)^\alpha$$.

The expansion coefficients as well as the nonlinear parameters of the basis functions were determined in the course of the fitting procedure. In the case of the interaction function of the $H_2$ molecules with aromatic carbon atoms (those graphene, nanotubes, benzene, boratabenzene, etc.), the $V_{ic}(r)$ function was compared with that from Patchkovsii et al., Proc. Natl. Acad. Sci. USA 102: 10439, 2005, and the functions were very similar.


Example 2: Validation of the methods

To validate the methods, the gravimetric $H_2$ storage capacity of single walled carbon nanotubes (SWCNTs) as described above was calculated and compared the results with available experimental data (Panella et al., Carbon 43: 2209, 2005; Lawrence et al., Appl. Phys. Lett. 84: 918, 2004; Hass et. al., J. Materials. Res. 20: 3214, 2005; and Liu et al.,
J. Phys. D: Appl. Phys. 38:R23 1, 2005). The geometry parameters of the SWCNTs were taken from the semi-empirical MNDO calculations. The nanotubes were aligned parallel to each other and located so as to form a periodic lattice as shown in Fig. 4A, with periodic conditions imposed in all 3 dimensions. The armchair-type (n,n) SWCNTs were considered with \( n = 8, 10, 12, \) and \( 14; \) the nanotube diameters were, respectively, \( d = 10.8 \, \text{Å} \), \( 13.5 \, \text{Å} \), \( 16.1 \, \text{Å}\) and \( 18.8 \, \text{Å} \). The separation \( w \) between the nanotubes was taken as either \( w = 3.4 \, \text{Å} \) (close contact between the nanotubes) or \( w = 6.2 \, \text{Å} \).

[0104] Fig. 5 compares the calculated room temperature \((T = 300^\circ \text{K})\) gravimetric \( \text{H}_2 \) storage capacity of SWCNTs with the experimental results; the average diameter of the experimental nanotubes is denoted on the figure when the information is available from the publication. Measurements of the hydrogen storage capacity in nanotubes are known to be subject to several technical problems: purity of the nanotubes (i.e. the lack of foreign adsorbed particles); the ratio of the closed end and the open end nanotubes; poorly reproducible (and generally unknown) distributions of the diameter, length and packing of the nanotubes across the samples; etc. This means that agreement between experimental and computed quantities cannot be expected to be precise. In view of these limitations, one concludes that the agreement of the calculated results and the experimental data is reasonable, with the experimental results falling near or between the curves calculated using various diameter and separation parameters. In addition, strong sensitivity of the storage capacity on the separation between the nanotubes is apparent, what can partially explain the diversity of the experimental values.

**Example 3: Hydrogen storage capacities of various materials**

[0105] For various compounds, the maximal number of \( \text{H}_2 \) molecules that one molecule of the compound can bind with binding energy at least \( 1 \, \text{kcal/mol} \), the corresponding \( \text{wt}\% \) of hydrogen, and the range of binding energies of the \( \text{H}_2 \) molecules were calculated using the described methods with aug-cc-pVTZ (-hp) basis set at MP2 level with the CP correction, are shown in Table 1.

**Example 4: Hydrogen storage capacities of boron-doped nanotubes**

[0106] After validation as described above, the methods were used to calculate of the gravimetric storage capacity of single walled \( \text{BC}_3\text{Li} \) nanotubes (SWBC3LiNTs, i.e., having one atom of boron per three atoms of carbon) as a function of pressure at various temperatures. The structure of a representative SWBC3UNT is shown schematically in Fig.
4B. The geometry parameters of the SWBC3LiNTs were taken from the semi-empirical MNDO calculations. For the calculations, the nanotubes were aligned parallel to each other to form a periodic lattice, analogously to Fig. 4A. The armchair-type SWBC3LiNTs with diameter $d = 17.4$ A, 20.3 A or 23.2 A were considered. The separation $w$ between the nanotubes was taken as $w = 8$ A, which is close to the distance at which the interaction potential energy between H$_2$ and the two nanotubes at the half distance is maximum.

Fig. 6 shows the calculated gravimetric hydrogen storage capacity of the SWBC3LiNTs at $T = 300^\circ$K (room temperature) and at $373^\circ$K (approximately 100°C). At 300°C, the storage capacity is quite high (5-6 wt% at 50-100 bar), essentially independently of the tube diameter $d$. However at 373°C and 1 bar, the gravimetric storage capacity is only 0.5-0.6%. Therefore, 5-6 wt% hydrogen can be adsorbed at very reasonable temperature and pressure, and then almost all the stored hydrogen released by raising the temperature and/or lowering the pressure to other reasonable values. Moreover, at $T = 77^\circ$K (liquid nitrogen temperature), the gravimetric storage capacity is calculated to be as high as 11 wt% at $P = 100$ bar, so the hydrogen storage capacity can be further increased if desired by lowering the temperature. Analogous results were calculated for SWBC5LiNTs and even SWBC7LiNTs, which have substantial but somewhat lower hydrogen storage capacity than SWBC3LiNTs.

**Example 5: Preparation of (l-H-boratabenzene)Li**


**Example 6: Procedure for the Storage of Molecular Hydrogen**

The hydrogen storage compounds prepared and described above can be accommodated in a hydrogen storage container that has a lid sufficient to allow the hydrogen storage container to be filled with the hydrogen storage compounds of the invention and
where the lid can be sealed. The hydrogen storage container has at least one valve to allow
entrance of hydrogen gas. In addition, the hydrogen storage container is made of a material
(typically metal) to withstand pressures greater than atmospheric pressure, and greater than
100 bar if desired. The dimensions of the hydrogen storage container are appropriate to hold
a sufficient amount of compound that will be useful in a fuel cell device. Hydrogen gas can
be provided via a pressurized cylinder available from Air Products.

[0110] The compounds are placed in a suitable hydrogen storage container, and the sealable
lid is closed and sealed. A hydrogen source, such as a hydrogen cylinder is attached to the
valve of the hydrogen storage container, the valve is opened and hydrogen is allowed to enter
the hydrogen storage container until a set pressure is achieved. The hydrogen storage
container can also be heated or cooled as required. Following a set interval, the hydrogen
storage container valve is closed, and the hydrogen cylinder is removed from the hydrogen
storage container. The hydrogen storage container can then be returned to atmospheric
pressure or can remain at elevated pressure.

Example 7: Fuel Cell

[0111] Figure 7 provides a schematic of one embodiment of the fuel cell of the present
invention. The hydrogen storage container is made of a suitable container that contains
hydrogen stored on the compounds of the present invention using the methods described
above for the storage of hydrogen. The hydrogen can be released from the hydrogen storage
container at a suitable rate and pressure to contact the anode (A). After breaking apart the
molecular hydrogen and stripping the electrons away, the remaining protons travel through
the anode and electrolyte (B) to cathode (C). After being stripped off of the hydrogen, the
electrons which have traveled through an electric circuit, thereby optionally operating an
attached device, and continue to the cathode. At the cathode, the electron and protons
combine with oxygen provided at the cathode to form water. The oxygen is provided through
external means and the water that is produced is removed from the fuel cell.

Example 8: Preparation of CpLi and related compounds

[0112] CpLi is a commercially available compound and can be obtained from Acros
Organics (catalog # 31658 0050; http://www.acros.com). In addition, CpLi, and related
compounds, can be prepared as is taught in U.S. Patent Nos. 7,011,768, 6,166,234, 5,057,300
and 4,952,713 (incorporated herein by reference).
Although the invention has been described with reference to the presently preferred embodiments, it should be understood that various modifications can be made without departing from the invention.

All publications, web pages, patents and patent applications cited are herein incorporated by reference in their entirety for all purposes to the same extent as if each individual publication, web page, patent and patent application was specifically and individually indicated to be incorporated by reference in its entirety for all purposes.
WHAT IS CLAIMED IS:

1. A method of storing molecular hydrogen, comprising the steps of:
   (a) providing a source of molecular hydrogen; and
   (b) contacting a compound of Formula 1 with the molecular hydrogen:

   \[ \text{[A]}X_{1-4} \]

   wherein

   - A is a heteroaryl ring system having 5-16 ring members and 1-4 heteroatoms
   - each independently selected from the group consisting of B, Al, N, O and S, wherein at least
   - one of said heteroatoms is selected from the group consisting of B and Al, and substituted
   - with 0-6 R^1 groups;

   - each X is a counterion;

   - each R^1 is independently selected from the group consisting of hydrogen,
     halogen, Ci-C_6 alkyl, Ci-C_6 haloalkyl, C_1-C_6 alkoxy, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C(O)R^2,
     C(O)OR^2, -OC(O)C_i-C_6 alkyl, -OR^2, -NR^2R^3, -C(O)NR^2R^3, -NR^2C(O)C_i-C_6 alkyl, -CN,
     NO_2, -SO_2OR^2, -SO_3NR^2R^3, a cycloalkyl ring system having from 3 to 8 ring members, a
     heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each
     independently selected from the group consisting of N, O and S, an aryl ring system having
     from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members
     and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O
     and S; and

   - R^2 and R^3 are each independently a member selected from the group
     consisting of hydrogen and C_1-C_6 alkyl, such that the molecular hydrogen is adsorbed by the
     compound of Formula 1 thereby storing the molecular hydrogen.

2. The method of claim 1, wherein A is a 6-membered heteroaryl with 1
   B heteroatom and 1 X counterion.

3. The method of claim 2, wherein A is (1-H-boratabenzene).

4. The method of claim 3, wherein X is independently a member selected
   from the group consisting of Li, Na and K.

5. The method of claim 4, wherein X is independently a member selected
   from the group consisting of Li and Na.
6. The method of claim 2, wherein A is (1-H-aluminatabenzene).

7. The method of claim 6, wherein X is independently a member selected from the group consisting of Li and Na.

8. The method of claim 1, wherein A is a heteroaryl ring system having two heteroatoms each independently selected from the group consisting of B and Al.

9. The method of claim 8, wherein A is a 6-membered heteroaryl.

10. The method of claim 9, wherein said compound is selected from the group consisting of \((1,2\text{-H-diboratabenzene})X_2\), \((1,3\text{-H-diboratabenzene})X_2\) and \((1,4\text{-H-diboratabenzene})X_2\), wherein each X is independently a member selected from the group consisting of Li, Na and K.

11. The method of claim 9, wherein said compound is selected from the group consisting of \((1,2\text{-H-diboratabenzene})X\), \((1,3\text{-H-diboratabenzene})X\) and \((1,4\text{-H-diboratabenzene})X\), wherein X is selected from the group consisting of Mg and Ca.

12. The method of claim 1, wherein each X is a member selected from the group consisting of a metal counterion and an ammonium counterion.

13. The method of claim 12, wherein each X is a metal counterion independently selected from the group consisting of alkali metals, alkali earth metals, transition metals and post-transition metals.

14. The method of claim 13, wherein each X is independently an alkali metal selected from the group consisting of Li, Na, K, Rb and Cs.

15. The method of claim 14, wherein each X is independently a member selected from the group consisting of Li, Na and K.

16. The method of claim 13, wherein each X is independently an alkali earth metal selected from the group consisting of Be, Mg, Ca, Sr and Ba.

17. The method of claim 16, wherein each X is independently an alkali earth metal selected from the group consisting of Mg and Ca.
18. The method of claim 1, wherein the compound of Formula I has a molecular weight of less than 500 u.

19. The method of claim 18, wherein the compound of Formula I has a molecular weight of less than 200 u.

20. The method of claim 1, wherein at least 5 wt% hydrogen is stored.

21. The method of claim 1, wherein at least 6 wt% hydrogen is stored.

22. The method of claim 1, wherein at least 10 wt% hydrogen is stored.

23. The method of claim 1, wherein the step of contacting is performed at a pressure of from about 1 to about 100 bar and a temperature of from about 0°C to about 150°C.

24. The method of claim 1, wherein the step of contacting is performed at a temperature of from about 0°C to about 150°C.

25. The method of claim 1, wherein the source of molecular hydrogen provides a gas mixture comprising at least 1% (v/v) molecular hydrogen.

26. A fuel cell comprising a compound of Formula I for the storage of molecular hydrogen:

\[ [A]X_{1+} \]

wherein

A is a heteroaryl ring system having 5-16 ring members and 1-4 heteroatoms each independently selected from the group consisting of B, Al, N, O and S, wherein at least one of said heteroatoms is selected from the group consisting of B and Al, and substituted with 0-6 R\(^1\) groups;

each X is a counterion;

each R\(^1\) is independently selected from the group consisting of hydrogen, halogen, C\(_1\)-C\(_6\) alkyl, C\(_1\)-C\(_6\) haloalkyl, C\(_7\)-C\(_8\) alkoxy, C\(_2\)-C\(_6\) alkenyl, C\(_2\)-C\(_6\) alkynyl, -C(O)R\(^2\), -C(O)OR\(^2\), -OC(O)C\(_6\) alkyl, -OR\(^2\), -NR\(^2\)R\(^3\), -C(O)NR\(^2\)R\(^3\), -NR\(^2\)C(O)C\(_1\)-C\(_6\) alkyl, -CN, -NO\(_2\), -SO\(_2\)OR\(^2\), -SO\(_2\)NR\(^2\)R\(^3\), a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each.
independently selected from the group consisting of N, O and S, an aryl ring system having
from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members
and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O
and S; and

R² and R³ are each independently a member selected from the group
consisting of hydrogen and C₁-C₆ alkyl.

27. The fuel cell of claim 26, wherein
A is a heteroaryl ring system having 6 ring members and 1 B heteroatom.

28. The fuel cell of claim 26, wherein
A is a heteroaryl ring system having 6 ring members and 2 B heteroatoms.

29. The fuel cell of claim 26, wherein the molecular hydrogen is provided
by the desorption of adsorbed hydrogen from a compound of Formula 1.

30. A fuel cell comprising boron-substituted carbon nanotubes complexed
with a member selected from the group consisting of Li, Na, K, Mg and Ca.

31. A method of storing molecular hydrogen comprising the step of
contacting the molecular hydrogen with B-substituted carbon nanotubes complexed with a
member selected from the group consisting of Li, Na, K, Mg and Ca, such that the molecular
hydrogen is adsorbed by the B-substituted carbon nanotubes thereby storing the molecular
hydrogen.

32. A compound of Formula 1:

\[[A]X_i^{-1}\]

wherein
A is a heteroaryl ring system having 5-16 ring members and 2-4 heteroatoms
each independently selected from the group consisting of B, Al, N, O and S, wherein at least
two of said heteroatoms are selected from the group consisting of B and Al, and substituted
with 0-6 R¹ groups;
each X is a counterion;
each R¹ is independently selected from the group consisting of hydrogen,
halogen, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₂-C₆ alkenyl, C₂-C₆ alkynyl, -C(O)R²,
-C(O)OR², -OC(O)C₁-C₆ alkyl, -OR², -NR²R³, -C(O)NR²R³, -NR²C(O)C₁-C₆ alkyl, -CN,
-\text{NO}_2, -\text{SO}_2\text{OR}^2, -\text{SO}_2\text{NR}_2\text{R}^3$, a cycloalkyl ring system having from 3 to 8 ring members, a heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S, an aryl ring system having from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O and S; and

$\text{R}^2$ and $\text{R}^3$ are each independently a member selected from the group consisting of hydrogen and $\text{CpC}_6$ alkyl.

33. The compound of claim 32, wherein said heteroaryl ring system has 6 ring members and 2 B atoms.

34. The compound of claim 32, wherein each X is independently a member selected from the group consisting of Li, Na and K.

35. The compound of claim 32, wherein said compound is selected from the group consisting of $(1,2\text{-H-diboratabenzene})\text{Li}_2$, $(1,3\text{-H-diboratabenzene})\text{Li}_2$ and $(1,4\text{-H-diboratabenzene})\text{Li}_2$.

36. The compound of claim 32, wherein each X is independently a member selected from the group consisting of Mg and Ca.

37. A method of storing molecular hydrogen, comprising the steps of:

(a) providing a source of molecular hydrogen; and

(b) contacting a compound of Formula I

$$[\text{A}]X \quad \text{II}$$

wherein A is an aromatic cyclic polyene having 5-16 ring members, wherein optionally 1-3 ring members are selected from the group consisting of N, O and S, and substituted with 0-5 $\text{R}^1$ groups;

$\text{X}$ is a counterion;

each $\text{R}^1$ is independently selected from the group consisting of hydrogen, halogen, C-C$_6$ alkyl, C$_1$C$_6$ haloalkyl, C-C$_6$ alkoxy, C$_2$C$_6$ alkenyl, C$_2$C$_6$ alkynyl, -C(O)R$^2$, -C(O)OR$^2$, -OC(O)C$_1$C$_6$ alkyl, -OR$^2$, -NR$^2$R$^3$, -C(O)NR$^2$R$^3$, -NRC(O)C$_1$C$_6$ alkyl, -CN,

-\text{NO}_2, -\text{SO}_2\text{OR}^2, -\text{SO}_2\text{NR}_2\text{R}^3$, a cycloalkyl ring system having from 3 to 8 ring members, a
heterocyclic ring system having from 5 to 10 ring members and from 1 to 3 heteroatoms each
independently selected from the group consisting of N, O and S, an aryl ring system having
from 6 to 10 ring members and a heteroaryl ring system having from 5 to 10 ring members
and from 1 to 3 heteroatoms each independently selected from the group consisting of N, O
and S; and

R² and R³ are each independently a member selected from the group
consisting of hydrogen and C₁-C₆ alkyl, such that the molecular hydrogen is adsorbed by the
compound of Formula II thereby storing the molecular hydrogen.

38. The method of claim 37, wherein the compound of Formula II is:

\[
\begin{array}{c}
\text{\includegraphics[width=0.1\textwidth]{furan.png}} \\
X
\end{array}
\]

wherein X is a counterion selected from the group consisting of Li, Na and K.

39. A method of storing molecular hydrogen comprising adsorbing the
hydrogen onto a polymer comprising monomers comprising 4 phenyl rings, wherein at least
one of the phenyl rings of each monomer is substituted with at least one B atom and is
conjugated with at least one metallic counterion.

40. The method of claim 39, wherein said each monomer is independently
a member selected from the group consisting of /e/ra(4-dihydroxoborylphenyl)methane,
/e/ra(4-dihydroxoborylphenyl)silane and tetraphenylmethane.
Figure 5

exp., d=10A, Haas, et.al., 2005
exp. Lawrence, et.al., 2004
exp., d=17A, Panella, et.al, 2005

(8,8), d=10.8A, w=3.4A
(10,10), d=13.5A, w=3.4 A
(12,12), d=16.1A, w=3.4A
(14,14), d=18.8A, w=3.4A
(10,10), d=13.5, w=6.2A

wt% vs P, bar
Figure 6A

A

\[ \text{wt. %} \]

\[ P, \text{ bar} \]

- \( d=17.4\text{A}, w=8\text{A} \)
- \( d=20.3\text{A}, w=8\text{A} \)
- \( d=23.2\text{A}, w=8\text{A} \)
Figure 6B

B

![Graph showing wt% vs. P, bar with lines for different d and w values.]

- d=17.4A, w=8A
- d=20.3A, w=8A
- d=23.2A, w=8A