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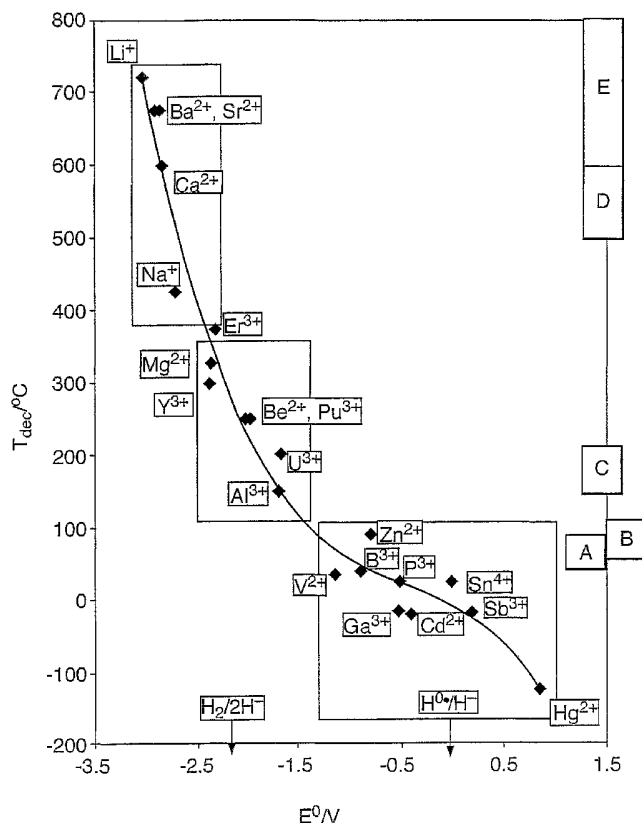
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[Continued on next page]

(54) Title: METAL HYDRIDE SYNTHESIS AND A FUEL CELL USING METAL HYBRIDES FOR HYDROGEN STORAGE



(57) Abstract: There is provided a process for
producing a metal hydride, which process com-
prises mechanically grinding or milling a com-
pound of a first metal with a hydride of a sec-
ond metal in order to produce an intimate mix-
ture of said first metal compound and said sec-
ond metal hydride, such that *in situ* generation
of the hydride of the first metal occurs. There
is also provided an electrical energy generating
system comprising: (i) a hydrogen fuel cell hav-
ing an inlet for hydrogen gas; and (ii) a storage
vessel containing a solid metal hydride material,
said solid metal hydride material being substan-
tially free from solvent, said storage vessel be-
ing connected to the inlet of the hydrogen fuel
cell; wherein the solid metal hydride material
thermally decomposes to release hydrogen gas
at a temperature within the operating range of
the hydrogen fuel cell. The metal hydride pro-
duced in the first aspect of the invention may be
used in this electrical energy generating system.



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METAL HYDRIDE SYNTHESIS AND A FUEL CELL USING METAL HYDRIDES FOR HYDROGEN STORAGE

Field of the Invention

The present invention relates, in one aspect, to a process for producing a metal hydride, and in a second aspect to a hydrogen-fuelled energy generating system comprising a solid state hydrogen storage medium connected to a fuel cell.

Background of the Invention

As world-wide concern for environment pollution increases and as legislation on pollutant emissions tightens, alternative fuel sources to replace traditional fossil fuels are increasingly sought. Hydrogen is particularly attractive since the only by-product of its combustion is (non-polluting) water. Several types of electricity-generating fuel cells using hydrogen as a fuel source have been developed. The hydrogen can be produced immediately prior to use, from, for example, petrol, methanol or methane. This approach requires the necessary on-board chemical reformers to produce hydrogen at a sufficient rate, which is inconvenient for mobile applications (e.g. electric vehicles) where weight is an important consideration. Alternatively the hydrogen can be pre-produced and stored for future use either as a compressed gas or (more usually) as a liquid. Due to the relatively low density of compressed or liquid hydrogen this requires large storage containers. In addition, there are serious safety concerns over the use of such large quantities of a highly flammable gas.

There is thus a pressing need for an alternative approach to hydrogen storage: the key requirements are that the storage medium stores sufficient hydrogen (by weight and volume) to be useful and that the hydrogen can be released controllably from the storage medium under relatively moderate operating conditions.

Thus, a first object of the present invention is to provide a hydrogen-fuelled energy generating system which obviates or mitigates at least one disadvantage of the known systems.

Metal hydrides and borohydrides are compounds having a wide range of uses. Their synthesis is usually carried out in non-aqueous (organic-based) solution and involves environmentally damaging organic solvents and is relatively expensive. As a result, bulk

production of metal hydrides is limited to only a few compounds, namely LiAlH_4 , NaH , LiBH_4 and NaBH_4 . Thus, there is need for a more cost effective, less environmentally damaging method for synthesising metal hydrides.

Thus, a second object of the present invention is to provide an improved method of making metal hydrides.

Summary of the Invention

According to a first aspect of the present invention there is provided a process for producing a metal hydride, which process comprises mechanically grinding or milling a compound of a first metal with a hydride of a second metal to produce an intimate mixture of said first metal compound and said second metal hydride, such that in situ generation (impact synthesis) of the hydride of the first metal occurs.

According to a second aspect of the present invention, there is provided an electrical energy generating system comprising:

- (i) a hydrogen fuel cell having an inlet for hydrogen gas; and
- (ii) a storage vessel containing a solid metal hydride material, said solid metal hydride being substantially free from solvent, said storage vessel being connected to the inlet of the hydrogen fuel cell;

wherein the solid metal hydride material thermally decomposes to release hydrogen gas at a temperature within the operating range of the hydrogen fuel cell.

Brief Description of the Figure

The Figure shows the relationship between T_{dec} (the temperature at which binary chemical hydrides decompose to their constituent elements and hydrogen) and E^0 (the standard redox potential for the M^{n+}/M^0 redox pair in acidic aqueous solutions) for a number of binary metal hydrides, and also indicates the operating temperatures of various types of hydrogen fuel cells.

Detailed Description of the Invention

According to the first aspect of the present invention there is provided a solid state process for producing a metal hydride, as defined above. The process occurs in the solid state. The process comprises mechanically grinding or milling a compound of a first metal with a hydride of a second metal. Preferably, the mechanical grinding or milling is conducted so that substantially all reacting particles have a maximum size of 50 nm. Preferably at least 95 % of all reacting particles have a maximum size of 50 nm. Preferably the mechanical grinding or milling is effected by a ball-milling process, more preferably by high-energy (i.e. high-speed) ball milling. It will be understood that each particle comprises a number of much smaller grains or domains. These grains or domains are preferably on a nanoscale level, more preferably being about 1 to 65 nm in size. The intimate mixture of the nanoscale particles, which have a high surface area and high surface energy, allows the targeted mechanochemical synthesis of the desired hydride to take place.

The particles may also be a composite structure of the desired metal hydride and a catalytic phase.

The introduction of partial disorder and/or intergrowth structures at the nanoscale also affects the kinetics and/or thermodynamics of the products in fundamental and beneficial ways. Thus, the thermodynamics of the system are strongly affected by the high surface energy of the particles, while the kinetics of the system benefit from the very high surface area of reacting, nanoscale particles. This type of approach allows for the blending of structures at the nanometre level. For example, the repeated fracture and reconstitution of the particles at the nanoscale permits the continual creation of highly reactive interfaces between the constituents of the system, enabling the rapid interdiffusion of reacting elements of the target material.

It will be understood that the expression "metal hydride" as used herein is intended to include simple binary compounds exemplified by NaH as well as ternary (and other) compounds exemplified by LiAlH_4 and NaBH_4 .

The process of the first aspect of the invention is preferably carried out at ambient temperature, i.e. without the separate provision of heat from an external source. It will of course be appreciated that the process itself may generate heat, whereby individual particles absorb mechanical energy from the mechanical grinding or milling.

The compound of the first metal is preferably an oxide or a halide, with exemplary halides being fluoride and chloride. Most preferably the compound of the first metal is an oxide.

The first metal and the nature of the hydride are chosen according to the particular end-use required of the first metal hydride which is the target of the process. In the case where the first metal hydride is to be used as a source of hydrogen in a polymeric-electrolyte-membrane cell or an alkaline fuel cell, the first metal hydride preferably thermally decomposes to release hydrogen at a temperature of less than about 125 °C, and more preferably from about 60 °C to about 90 °C. The first metal is preferably Zn.

The second metal hydride is preferably selected from cheap, readily-available hydride materials. Exemplary second metal hydrides include NaH, NaBH₄ and LiAlH₄.

In a highly preferred embodiment of the invention, the first metal compound is either ZnO or ZnCl₂, most preferably ZnO, and the second metal hydride is NaBH₄, the product of the mechanochemical process being Zn(BH₄)₂.

The quantities of the first metal compound and the second metal hydride used in the process are preferably approximately stoichiometric with regard to the anticipated mechanochemical reaction. For example in said highly preferred embodiment, the compounds are used in a 2:1 molar ratio of NaBH₄ to ZnO.

It will be understood that the characteristics of the product will vary according to the process conditions which may be adjusted as follows:

- (i) ball/powder ratio from about 10:1 to 25:1,
- (ii) diameter of milling balls from about 8 to 20 mm,
- (iii) use of process control agents (e.g. methanol or ethanol)
- (iv) nature of milling media (e.g. hardened steel or WC+Co)
- (v) atmosphere (e.g. H₂ or Ar)

Depending on the conditions used, the particle size is between 5 and 40 mm with the typical grain size within the particles being from about 1 to 65 nm. About 70 to 90 % conversion to product is achieved.

The resulting material can be tested for hydrogen evolution without further purification. Hydrogen content/desorption characteristics of the product can be determined using known techniques. For example:

- (1) Thermogravimetric analysis (using an Intelligent Gravimetric analyser (IGA), a computerised thermogravimetric analyser) allows pressure-composition-temperature curves to be constructed for hydrogen storage materials, enabling the wt% hydrogen in the product to be accurately determined.
- (2) Thermopiezic analysis monitors pressure changes within a fixed volume as a function of temperature, primarily used to determine hydrogen sorption kinetics, it can also be used to rapidly estimate the hydrogen content of materials.
- (3) High pressure Differential Thermal Analysis (DTA), can be used under vacuum to study desorption spectra of hydrided materials.

The reaction to yield hydrogen is irreversible, the other products being compounds of Zn, B and Na₂O.

Other examples of hydride materials which decompose between about 60 °C and 120 °C include ZnH₂ (which can be synthesised according to the claimed process from ZnO and NaH), U(BH₄)₄ (which can be synthesised from UF₄ and NaBH₄) and CuH (which can be synthesised from Cu₂O and NaH).

The invention also provides a metal hydride obtainable in accordance with a process of the invention as defined above.

In accordance with the second aspect of the present invention, there is provided an electrical energy generating system as defined above. It will be understood that solid metal hydride provides a low temperature source of hydrogen and thus serves, in use, as a solid fuel powering the fuel cell.

Preferably, the active hydrogen content of the solid hydride material is at least 6.5 wt%.

Preferably, the solid metal hydride is synthesised by the method of the first aspect of the present invention.

Preferably the hydrogen fuel cell is a polymeric-electrolyte-membrane cell or an alkaline fuel cell. Such cells generally operate between about 60 and 120 °C. The preferred metal hydride material is Zn(BH₄)₂, which thermally decomposes to release hydrogen gas at about 85 °C.

The preferred metal borohydride, $\text{Zn}(\text{BH}_4)_2$, is also attractive in that its active hydrogen content, at stoichiometric chemical compositions, can be as high as 8.4wt%. In addition, $\text{Zn}(\text{BH}_4)_2$ generated by traditional methods, for example from metathetic reactions involving (freshly fused) ZnCl_2 , and either LiBH_4 , NaBH_4 or KBH_4 in ultra-dry tetrahydrofuran or ether, results in $\text{Zn}(\text{BH}_4)_2$ solutions. Attempts to remove the solvent result in crystals having large volumes of solvent occluded therein. Such crystals have a dramatically reduced active hydrogen content, which may be below 6.5 wt%, the desirable minimum hydrogen content. It is difficult to remove the solvent from the crystals without decomposition of the $\text{Zn}(\text{BH}_4)_2$ and loss of active hydrogen.

Several solid hydride materials having a relatively high hydrogen content are available at a sufficiently low cost to make them viable as a hydrogen storage medium for a fuel cell. These materials include NaH , LiAlH_4 and NaBH_4 . Unfortunately, these materials decompose to release hydrogen gas at relatively high temperatures (about 400 °C for NaBH_4 , about 125 °C for LiAlH_4 , and about 420 °C for NaH), which rule them out as practical hydrogen sources in current fuel cells. Solid hydrides have not been considered as viable hydrogen sources in fuel cell applications, since the cost of making a hydride having a low enough decomposition temperature (i.e. 60 to 120 °C) by traditional routes would be prohibitively expensive.

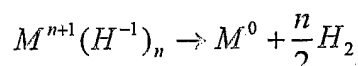
The present invention also resides in a vehicle which is at least partially powered by a system according to the second aspect of the invention. The vehicle may be entirely powered by a system according to this aspect of the invention.

The temperature, T_{dec} , at which binary chemical hydrides decompose to their constituent elements and molecular hydrogen, represents one key parameter for their ultimate potential use as hydrogen-storage materials for mobile and stationary applications. Ideally, T_{dec} should be within the range 60–100 °C for the use of a hydride material with polymer electrolyte (proton exchange) membrane fuel cells.

It can be demonstrated from thermodynamic considerations that in order to reach an equilibrium pressure of 1 bar at 27 °C, the standard enthalpy of hydride formation should be close to 4.7 kcal molH⁻¹. Yet, the precise guidance as to how to control T_{dec} chemically (i.e. by judicious choice and combination of chemical elements) has not yet been forthcoming.

The inventors have made the surprising discovery that T_{dec} correlates closely with the electronic properties of the metal or non-metal centre bound to the hydride ion in binary (MH_n) species, more specifically with the value of the standard redox potential (E^0) for the M^{n+}/M^0 redox pair in acidic aqueous solutions.

T_{dec} decreases monotonically with an increasing value of E^0 . The thermal decomposition of a hydride, described by the general equation:



is facile for chemical hydrides containing cations such as, for example, Hg^{2+} or Sb^{3+} which facilitate the oxidation of hydride anions, but inhibited for hydrides containing cations which are difficult to reduce, for example Li^+ or Ba^{2+} .

The Figure shows the relationship between T_{dec} and E^0 for various binary metal hydrides. In addition, the graph indicates the operating temperatures of various types of hydrogen fuel cells (A-alkaline; B-polymeric electrolyte membrane; C-phosphoric acid; D-solid oxide (low temperature variants; E-molten carbonate).

It will be seen from the graph that the relationship between T_{dec} and E^0 holds over a range from approximately 700K to -100K in T_{dec} and from -3.5 to 1.5V for E^0 .

Several binary and ternary hydrides which have T_{dec} values suitable for incorporation into low-temperature fuel cells are known. Such hydrides include ZnH_2 [$T_{\text{dec}} = 90\text{ }^{\circ}\text{C}$], $Zn(BH_4)_2$ [$T_{\text{dec}} = 85\text{ }^{\circ}\text{C}$], $KSiH_3$ [$T_{\text{dec}} = 70\text{ }^{\circ}\text{C}$], CuH [$T_{\text{dec}} = 60\text{ }^{\circ}\text{C}$], and $LiGaH_4$ [$T_{\text{dec}} = 50\text{ }^{\circ}\text{C}$]. Unfortunately, with the exception of $Zn(BH_4)_2$ (8.4 wt % hydrogen), these compounds do not store a sufficiently high wt % of hydrogen to reach the US Department of the Environment target of 6.5 wt % for use in hydrogen fuel cells. Also, their decomposition is irreversible and they are expensive to produce by traditional methods.

However, the correlation between T_{dec} and E^0 suggests that the use of compounds of Ga^{3+} , V^{3+} , Yb^{3+} and particularly those of the cheap and readily available metals Zn^{2+} , Cd^{2+} , Ti^{3+} , Ti^{4+} , Fe^{2+} and Fe^{3+} may be useful in the production of hydrogen fuel cells. For example, the metal hydrides may be produced according to the method of the first aspect.

In addition, such metal hydrides (whether or not produced by the method of the first aspect) may be useful as catalysts to facilitate hydrogen evolution (at a usefully low

temperature) from readily available and relatively low cost metal hydride hydrogen stores such as, for example, NaBH_4 , NaH , LiAlH_4 , and MgH_2 which have a T_{dec} normally considered outside the desirable range for use in low temperature hydrogen fuel cells. It will be apparent that such an approach will allow relatively cheap, high storage (but high T_{dec}) hydrides (such as NaBH_4 , MgH_2 , and AlH_3) to be combined with hydrides of more electronegative elements which have a lower T_{dec} but lower hydrogen storage capacity to provide a source of hydrogen in the electrical energy generating system according to the second aspect of the present invention.

Furthermore, a hydrogen store can be envisaged in which compounds such as NaH and LiH (high T_{dec}) whose decomposition is theoretically reversible can be combined with the electronegative element hydrides (low T_{dec}) to produce a hydrogen store which can be regenerated.

Embodiments of the invention will now be described by way of example only.

Example 1:

Production of $\text{Zn}(\text{BH}_4)_2$:

ZnO (81.4 g) and NaBH_4 (75.6 g) is high-energy ball-milled at room temperature in a laboratory planetary miller (Pulverisette, Fritsch) for from about 1 hr to about 20 hrs at a rotation speed of from 100 to 300 rpm to yield predominantly $\text{Zn}(\text{BH}_4)_2$, and Na_2O with a small proportion of unreacted starting materials remaining.

Alternatively, the ZnO can be replaced by 136.3 g of ZnCl_2 to yield predominantly $\text{Zn}(\text{BH}_4)_2$, and NaCl .

Example 2:

Production and testing of $\text{Zn}(\text{BH}_4)_2$:

Loading of the planetary ball mill reactor was carried out under an inert atmosphere of dry argon. In a typical procedure, 3.907 g of zinc chloride (Alfa Aesar) was dried in a vacuum oven to remove traces of water. This freshly dried ZnCl_2 was placed in either a stainless steel agate-lined (99.9% SiO_2) or sintered corundum (99.7% Al_2O_3) grinding jar.

Commercial sodium tetrahydroborate (Aldrich Chemicals) was recrystallized from diglyme. 2.111 g of this NaBH_4 was then added to the 250 ml grinding jar and the lid sealed (with an atmosphere of argon inside) with a positive O-ring seal.

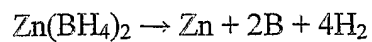
Mechanical treatment of a ZnCl_2 - NaBH_4 mixture was then performed in a Retsch Planetary Ball Mill (PM400; Retsch, Haan-Germany). Both stainless steel, chrome steel tungsten carbide and zirconia grinding balls with diameters of 4, 9 and 12 mm were used. The grinding balls describe a semi-circular movement, separate from the inside wall and collide with the opposite surface at high impact energy. The mechanical treatment was effected between 30 to 300 rpm, but a typical speed was 175 rpm, this speed kept constant via an electronic controller. The duration of the mechanical treatment varied from 0.5 minutes to 4 hrs, with a typical time being between 0.5 min to 2 hours. The ZnCl_2 : NaBH_4 molar ratio was 1:2 and the total weight of the net load was 6.018 g.

After this mechanical treatment, the reaction mixtures (generally colourless powders) were carefully separated from the packing container and balls and subjected to physicochemical analysis. X-ray powder diffraction analysis was carried out on a Bruker-Siemens D-5005 diffractometer (CuK_α radiation). IR spectra were recorded on a Pye-Unicam spectrophotometer in the range $400\text{--}4000\text{ cm}^{-1}$; the samples are suspensions in mineral oil dried with finely-dispersed metallic sodium.

A range of experiments was carried out in which the parameters of mechanical treatment (e.g. duration of ball milling, diameter of grinding balls, various grinding balls etc.) of the 1:2 mixture of ZnCl_2 - NaBH_4 mixtures were varied. Attempts were made to ascertain the completeness of the reaction, as monitored by the characteristic IR spectra of the BH_4^- anion. The BH_4^- ion in NaBH_4 has a characteristic band at 2290 cm^{-1} , and in $\text{Zn}(\text{BH}_4)_2$ the anion exhibits characteristic vibrations at approximately 2100 cm^{-1} (bridging B-H bonds) and approximately 2450 cm^{-1} (terminal B-H bonds).

Analysis revealed that the synthesis reaction for $\text{Zn}(\text{BH}_4)_2$ goes to completion within 1 hour of milling, but a significant proportion of the product can appear before that time. Control experiments were also carried out using different-sized grinding balls (as so-called "activating packing volumes"), and the duration of the mechanical milling was varied between 0.5 min to 2 hours. Increasing the reaction time (for a given grinding ball size) gives rise to a noticeable change in the colour of the reaction mixture, for example, from white

(5-10 min), through grey (30-60 min), to finally black, probably due to the partial/complete thermochemical decomposition, probably via the following reaction



X-ray diffraction analysis of one milled batch (conditions as above) revealed the presence of zinc borate and sodium chloride, as well as unreacted sodium borohydride.

CLAIMS

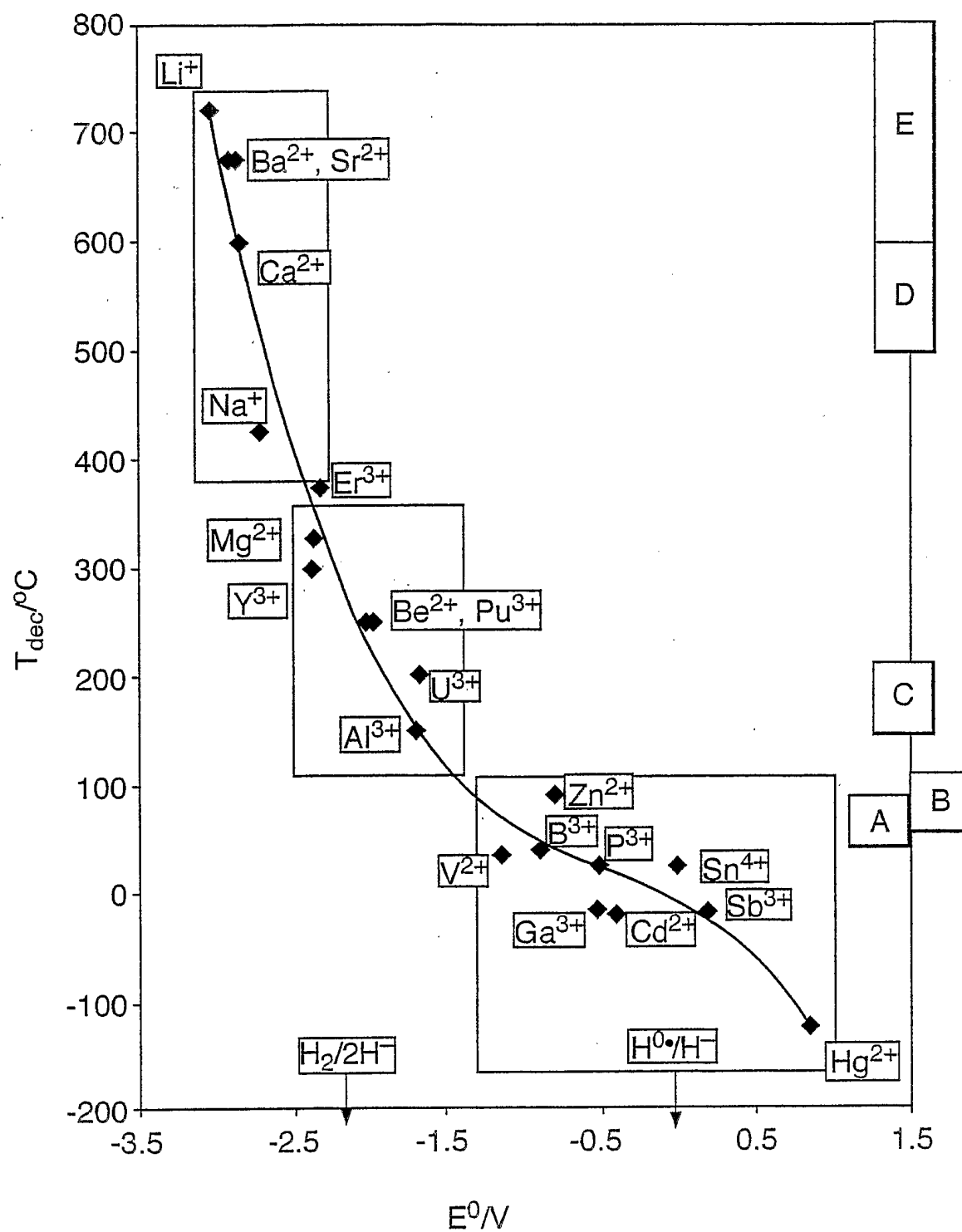
1. A process for producing a metal hydride, which process comprises mechanically grinding or milling a compound of a first metal with a hydride of a second metal to produce an intimate mixture of said first metal compound and said second metal hydride, such that *in situ* generation of the hydride of the first metal occurs.
2. A process according to claim 1 wherein the compound of the first metal is an oxide or a halide of the first metal.
3. A process according to claim 2 wherein the compound of the first metal is an oxide.
4. A process according to any one of the preceding claims wherein the second metal hydride is selected from NaH, NaBH₄ and LiAlH₄.
5. A process according to any one of the preceding claims wherein the mechanical grinding or milling is conducted such that substantially all reacting particles have a particle size of up to 50 µm.
6. A process according to claim 5 wherein substantially all the reacting particles have a particle size of from 5 to 40 µm.
7. A process according to claim 5 or claim 6 wherein the reacting particles comprise smaller grains or domains having a size of from 1 to 65 nm.
8. A process according to any one of the preceding claims wherein the step of mechanically grinding or milling comprises a ball-milling process.
9. A process according to any one of the preceding claims which proceeds without the addition of energy.

10. An electrical energy generating system comprising:
- (i) a hydrogen fuel cell having an inlet for hydrogen gas; and
 - (ii) a storage vessel containing a solid metal hydride material, said solid metal hydride material being substantially free from solvent, said storage vessel being connected to the inlet of the hydrogen fuel cell;
- wherein the solid metal hydride material thermally decomposes to release hydrogen gas at a temperature within the operating range of the hydrogen fuel cell.
11. A system according to claim 10 wherein the active hydrogen content of the at least one solid metal hydride is at least 6.5 wt%.
12. A system according to claim 10 or claim 11 wherein the hydrogen fuel cell is a polymeric-electrolyte-membrane cell or an alkaline fuel cell.
13. A system according to any one of claims 10 to 12 wherein the operating range of the hydrogen fuel cell is from 60 to 120 °C.
14. A system according to any one of claims 10 to 13 wherein the solid metal hydride material comprises at least two solid metal hydrides, and wherein at least one of the solid metal hydrides is selected from hydrides of Ga^{3+} , V^{3+} , Yb^{3+} , Zn^{2+} , Cd^{2+} , Ti^{3+} , Ti^{4+} , Fe^{2+} and Fe^{3+} .
15. A system according to claim 14 wherein at least one of the solid metal hydrides is $\text{Zn}(\text{BH}_4)_2$.
16. A system according to claim 14 or claim 15 wherein at least one of the solid metal hydrides is selected from NaBH_4 , MgH_2 and AlH_3 .
17. A system according to claim 14 or claim 15 wherein at least one of the solid metal hydrides undergoes reversible decomposition.

18. A system according to claim 17 wherein the at least one solid metal hydride which undergoes reversible decomposition is selected from NaH and LiH.
19. A vehicle powered at least in part by an electrical energy generating system according to any one of claims 9 to 18.

1/1

Fig. 1.



INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/GB2004/001579

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B6/00 C01B6/21 H01M8/06 B60L11/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B H01M B60L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MAL'TSEVA, N. N. ET AL: "Syntheses of Zn(BH ₄) ₂ and RbBH ₄ .18C6 using mechanochemical activation" RUSSIAN JOURNAL OF COORDINATION CHEMISTRY (TRANSLATION OF KOORDINATSIONNAYA KHIMIYA), 25(4), 246-248 CODEN: RJCCEY; ISSN: 1070-3284, 1999, XP009033242	1,2,4,8,9
A	the whole document	3,5-7
X	US 3 812 244 A (DANIELS A ET AL) 21 May 1974 (1974-05-21)	1,2,4,8,9
A	column 1, line 60 - column 2, line 21; examples 1,8	3,5-7
X	US 3 423 192 A (SNOVER JOHN A) 21 January 1969 (1969-01-21)	1,2,4,8,9
A	example 1	3,5-7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

7 July 2004

Date of mailing of the international search report

12.9.04

Name and mailing address of the ISA

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Authorized officer

Werner, H

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2004/001579

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-9

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-9

A process for producing a metal hydride by milling or grinding a metal compound with a different metal hydride.

2. claims: 10-19

An electrical energy generating system using a hydrogen fuel cell. The hydrogen is released from a solid metal hydride material.

A vehicle powered by an electrical energy generating system using a hydrogen fuel cell where the hydrogen is released from a solid metal hydride material.

INTERNATIONAL SEARCH REPORT

International Application No
PC 1 / GB2004/001579

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 565 183 A (KNOTT WILFRIED) 15 October 1996 (1996-10-15) example 1	1,2,8
A	----- WO 99/19250 A (UNIV MCGILL ; ZALUSKA ALICJA (CA); ZALUSKI LESZEK (CA); STROEM OLSEN J) 22 April 1999 (1999-04-22) page 5, lines 3-16; example 1 -----	1-9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2004/001579

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3812244	A	21-05-1974	NONE	
US 3423192	A	21-01-1969	NONE	
US 5565183	A	15-10-1996	DE 4336602 A1 CA 2131870 A1 DE 59401155 D1 EP 0650924 A1 JP 7149502 A	04-05-1995 28-04-1995 09-01-1997 03-05-1995 13-06-1995
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