HYDROGEN STORING METHOD AND UNIT

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ABSTRACT

The invention relates to a method for storing hydrogen and for producing hydrogen in which, for storing hydrogen, a unit (2) having: a cation donor, particularly of H⁺ ions, an anode (20), a cathode capable of storing atomic and/or molecular hydrogen, a wall (21) permeable to ions, having an electrical non-conducting but ionic conducting material, between the cathode and the cation donor, is subjected to an electric field allowing the formation, at least at the cathode and electrical non conducting material interface, of atomic and/or molecular hydrogen and storing said hydrogen at least in the cathode, and in which, to restitute hydrogen gas, the cathode is heated and/or depressed.

Diagram of the method and unit described in the patent.
HYDROGEN STORING METHOD AND UNIT

[0001] The present invention relates to the storage of hydrogen and more particularly the storage of hydrogen produced via electrochemical means, and the restitution of the stored hydrogen.


[0003] There is a need to have a storage unit that makes it possible to store a relatively large amount of hydrogen and that is capable of restoring it to the outside of the unit in the form of molecular hydrogen.

[0004] According to one of its aspects, the subject of the invention is thus a method for producing and storing hydrogen, in which, in order to store hydrogen, a unit comprising:

[0005] a cation donor, in particular a donor of H⁺ ions;

[0006] an anode;

[0007] a cathode capable of storing atomic and/or molecular hydrogen; and

[0008] a wall that is permeable to ions, comprising an electrically non-conducting but ion-conducting material, between the cathode and the anode donor, subjected to an electric field that enables the formation, at least at the interface of the cathode and of the electrically non-conducting material, of atomic and/or molecular hydrogen and the storage thereof within the cathode at least, and in which, in order to restore gaseous hydrogen, the cathode is heated and/or put under vacuum.

[0009] The term "storing" should be understood to mean a chemical or physical absorption or adsorption on an atomic level and/or in the porosities of the material.

[0010] The cathode may comprise a hydridable material.

[0011] The term "interface" between the cathode and the electrically non-conducting material should be understood to mean that there is a molecular contact phenomenon between the cathode and the electrically non-conducting material. Between the electrically non-conducting material and the cathode, the interface is produced so as to ensure the conversion of a hydrogen ion to a hydrogen atom on the surface of the cathode, the cathode being configured in order to absorb it straight away. The expression "electrically non-conducting material" should be understood to mean a material whose electrical conductivity is low enough not to take place to the detriment of the cation conduction.

[0012] The method according to the invention makes it possible to store hydrogen during its production and to restore it at will, depending on the requirements.

[0013] The storage may be carried out without causing the degradation of the cathode.

[0014] The present invention can find an application in numerous fields where gaseous hydrogen is necessary for producing energy, for example vehicles, electronic appliances or electricity generators. The invention also applies to the intermittent storage of any form of renewable energy, for example of wind turbine, tidal power or solar origin.

[0015] The wall that is permeable to ions may have a water permeability of less than 5% of the mass of hydrogen produced.

[0016] The cathode may contain less than 5 wt % of water.

[0017] The wall that is permeable to ions may have zero water permeability, measured under normal temperature and pressure conditions, with liquid water, or even water in vapor form, at a temperature of less than 900° C. and a pressure difference on both sides of the membrane that does not exceed 4 bar.

[0018] The total impermeability of the wall during the production and storage may make it possible to provide the storage of the atomic and/or molecular hydrogen formed within the cathode. The adsorption of hydrogen necessary for this purpose may depend on the nature of the cathode. Specifically, the presence of water in the cathode may risk preventing the establishment of molecular contact within the cathode, thus preventing the establishment of a satisfactory electrical conduction, and then preventing the formation of hydrogen in the cathode or at the interface. On the other hand, the presence of water at the interface of the cathode and of the proton exchange membrane may be of no consequence to the system. Specifically, the water behaves as the continuation of the ion-permeable wall due to its ion conductivity. Furthermore, insofar as, near the cathode, the medium is reducing due to the presence of the hydrogen, the presence of water is not troublesome for the storage.

[0019] The anode may be produced with any electrically conducting material compatible with the H⁺ ion donor, for example platinum, graphite, a thin film of a mixture of RuO₂, IrO₂ or of Ru₃O₇, IrO₂ and TiO₂ or of RuO₂, IrO₂ and SnO₂ lined with a sheet of porous from 30 to 50% for example) titanium or a conducting polymer, inter alia. The thin film may have a thickness between 5 μm and 20 μm, for example of around 10 μm.

[0020] The anode may be in contact with the electrically non-conducting material.

[0021] The cathode may have a solid, liquid or pulvulent form; a pulvulent form may facilitate the manufacture of the unit with very diverse shapes.

[0022] The cathode may comprise an intermetallic compound, in particular chosen from complex interstitial or metallic hydrides, for example chosen from the following list: of Al₂ type (A and B being metals), for example LaNi₅, phases of vanadium-based centered cubic solid solutions, BaReHₓ (the formula corresponding to the hydrided state), Mg₂FeH₄ (the formula corresponding to the hydrided state), NaAlH₄ (the formula corresponding to the hydrided state), LiBH₄ (the formula corresponding to the hydrided state), and all the compounds and derivatives thereof or alloys thereof.

[0023] The cathode may be embedded in a mass of boron nitride, the periphery of this mass of boron nitride forming the electrically non-conducting material. The electrode may comprise, for example, a metal foam or a foam of any conducting and hydridable material, embedded in a mass of boron nitride.

[0024] The electrically non-conducting material may comprise a ceramic, for example that comprises hexagonal boron nitride, preferably activated by an acid solution under an electric field, lithium nitride, boric acid, an ion-conducting polymer, and more generally any ion exchange material. The electrically non-conducting material may be chosen from ion exchange materials developed for PEMFC or PCFC cells.

[0025] The electrically non-conducting material may, for example, comprise turbostratic boron nitride, that is to say for which the crystallization planes may be slightly offset relative to the theoretical crystallization position, for example the
hexagonal crystallization position of boron nitride, with leads to the planes being held together less well, since the latter are further apart.

[0026] The electrically non-conducting material may comprise hexagonal boron nitride grains placed next to each other, for example grains having a size of around 100 µm, or else having a nanoscale size.

[0027] The boron nitride gains may be oriented, preferably, not all parallel to the wall, but for example perpendicularly, so as to ensure a better mechanical strength, or else heterogeneously, in order to ensure a better proton conduction.

[0028] The boron nitride may be in the form of grains, for example having an average size of around 7 to 11 µm. The weight proportion of boron nitride in the material may be between 5% and 100%, for example up to 70%. The wall may be entirely made of high-pressure sintered boron nitride powder. As a variant, it may comprise boron nitride and a binder, being manufactured by a HIP (hot isostatic pressure) process.

[0029] The electrically non-conducting material may comprise percolated boron nitride grains, for example that are held together by one another by a compound, for example a compound from the following list: nickel, boron oxide, calcium borate, ethyl cellulose, boracic acid, polyvinyl alcohol, vinylcaprolactam, PTFE (Teflon®), sulfonated polyethylic sulfone.

[0030] The electrically non-conducting material may be formed by boron nitride inserted in a binder, for example boracic acid or a polymer membrane, which may provide a very good proton conductivity to the electrically non-conducting material.

[0031] The polymer may be, for example, PVA (polyvinyl alcohol), vinylcaprolactam, PTFE (Teflon®), sulfonated polyethylic sulfone.

[0032] The polymer, for example PVA, may be used to plug the porosities present in the boron nitride. The addition of polymer may, for example, be carried out under vacuum, so that the latter is sucked into the porosities of the boron nitride.

[0033] The electrically non-conducting material may be obtained by the following process.

[0034] Boron nitride grains are mixed with a polymer binder in liquid form, this mixture being poured over a substrate, then heated at a sufficient temperature to cause the calcination of the binder, for example at a temperature of around 600 or 700°C, so that the boron nitride grains are percolated with one another on the substrate.

[0035] In a supplementary step, the result obtained is heated at a temperature between 800 and 1700°C, or even between 1000 and 1500°C, under an inert atmosphere, for example nitrogen or argon, giving rise to the sintering of the grains to one another.

[0036] Finally, in a supplementary step, the substrate is removed and a rigid boron nitride membrane composed of sintered grains is obtained.

[0037] The substrate may, for example, comprise a fine fabric, produced for example from nylon®, polyethylene-terephthalate, ethylene tetrafluoroethylene, polyethylene terephthalate or polyester.

[0038] In the foregoing, the boron nitride may have been activated beforehand or may be activated during or at the end of the process for manufacturing the electrically non-conducting material.

[0039] The term “activation” of the boron nitride is understood to mean a process that makes it possible to promote proton conduction in the boron nitride.

[0040] The boron nitride may, for example, be activated in an acid solution by being subjected to an electric field.

[0041] The boron nitride may also be activated in a solution of sodium hydroxide, with or without application of an electric field.

[0042] In yet another process, the boron nitride may be activated by being dipped in a solution, for example of water, in the presence of iron, for example an iron grid, and under application of an electric field.

[0043] The use of boron nitride in pulverulent form may facilitate the activation of the latter.

[0044] The boron nitride may be activated in its pulverulent form before insertion into a binder, for example into a polymer, or else after insertion into this binder, for example as a function of the binder used.

[0045] In the process described above, the boron nitride grains may be activated before their insertion into the polymer binder or after the sintering of the grains.

[0046] In the case of sintering, the activation may be carried out at the end of the process, in order to avoid the risk of it being destroyed by the sintering.

[0047] The wall that is permeable to ions may comprise one or more layers of different materials, at least one of these layers possibly exercising a cation-conducting function. Between the layer having this function and the electrolyte, the wall may comprise, for example, a porous layer having a support role.

[0048] The wall that is permeable to ions may cover, at least partially, better still entirely, the cathode, especially at least on its face pointing toward the anode.

[0049] The electrically non-conducting material of the ion-permeable wall may make it possible to prevent, in one exemplary embodiment, any contact between the cathode and the cation donor.

[0050] Furthermore, the electrically non-conducting material is preferably impervious to gaseous hydrogen, so as to more easily allow, during the restititution of the gaseous hydrogen, the evacuation of the latter to a gaseous hydrogen outlet and not toward the cation donor.

[0051] The cation donor may be an electrolyte, for example an acidic aqueous solution comprising, for example, at least one of the compounds from the following list: sulfuric acid, hydrochloric acid, weak acid, or else salts of a weak acid.

[0052] The cation donor may be liquid, as mentioned above, or as a variant may be solid, gaseous or in the form of plasma.

[0053] It is possible to circulate the cation donor in the unit, for example using a pump or a moving spindle. This circulation may remain inside the unit or take place partially outside of the unit, for example in a device for recharging the unit. Such a circulation may make it possible, for example, to avoid the formation of a gradient of H⁺ ions in the unit, considering the fact that the unit may consume water in order to ensure the formation of hydrogen. Furthermore, circulating the cation donor may make it possible to keep the characteristics of the exchange surface around the anode and the cathode substantially constant.

[0054] The voltage applied between the anode and the cathode during the production of hydrogen may be for example between 1 and 3000 V, better still between 1.24 and 200 V, preferably between 1.24 and 4 V.

[0055] The cathode may be heated in order to restore the gaseous hydrogen, for example at a temperature above 30°C,
better still 50°C, for example between 70 and 350°C, the temperature possibly being chosen as a function of the materials.

[0056] The heating may take place after draining the electrolyte, this draining possibly being carried out to the recharging device. As a variant, the cation donor is not drained for the heating that aims to release hydrogen.

[0057] The unit may also be heated at a temperature below that which yields the discharging, during the phase of hydrogen production and storage, in order to improve the latter.

[0058] The heating of the cathode may advantageously take place in a controlled manner, in order for example to act precisely on the amount of gaseous hydrogen released. As a variant or in addition, the unit, and especially the cathode, may be put under vacuum in order to facilitate the extraction of gaseous hydrogen.

[0059] The heating may be caused by the Joule effect during the circulation of an electric current, for example in a conductor integrated into the unit, for example that extends within the cathode. The heating may also be carried out by circulation of a hot fluid.

[0060] The atomic and/or molecular hydrogen may also be stored, if necessary, in the electrically non-conducting material of the ion-permeable wall.

[0061] The atomic or molecular hydrogen produced within the unit may be stored in the cathode only or, as a variant, both in the cathode and in the electrically non-conducting material.

[0062] Furthermore, the hydrogen may be stored in the cathode in atomic and/or molecular form, depending on the choice, in particular, of the material that forms the cathode.

[0063] The gaseous hydrogen leaving the cathode may be collected in order to be used in a fuel cell and/or as a fuel or reactant.

[0064] Another subject of the invention, independently of or in combination with the foregoing, is a unit for the storage and restitution of hydrogen comprising:

[0065] an anode;
[0066] a cathode capable of storing atomic and/or molecular hydrogen;
[0067] a cation donor, especially a donor of H⁺ ions;
[0068] a wall that is permeable to ions, comprising an electrically non-conducting but ion-conducting material between the cathode and the cation donor;
[0069] optionally a member for heating the cathode; and
[0070] an electrical connector that makes it possible to electrically power the anode and the cathode in order to create an electric field between them that enables the formation of atomic and/or molecular hydrogen at least within the cathode and the storage thereof at least in the cathode,

the unit being arranged in order to collect the gaseous hydrogen released by the cathode at least during the heating of the latter,

the unit comprising, in addition:

[0071] a fluid connector that makes it possible to channel the gaseous hydrogen thus released to the outside of the unit.

[0072] The unit for the storage and restitution of hydrogen may comprise an outer envelope for housing at least the anode, the cathode, the cation donor, the electrically non-conducting but ion-conducting material, the optional heating member, and optionally also the electrical connector. This outer envelope may be produced, at least partially in a synthetic or metallic material.

[0073] The anode of the unit for the storage and restitution of hydrogen may be porous and/or pierced with orifices, for example being produced in mesh form or in the form of metal or metallized foam.

[0074] The heating member may comprise an electrical resistance element, and be inside or outside of the outer envelope.

[0075] The heating member may, for example, make it possible to heat the unit to a temperature greater than or equal to 30°C, better still 50°C, for example between 70 and 350°C.

[0076] The heating member may comprise an electrical resistance element that is at least partially positioned in the cathode or in an element in contact with it, for example in an elastically deformable member that makes it possible to apply the cathode against the electrically non-conducting but ion-conducting material and to compensate for the variations in volume of the cathode.

[0077] When the heating member is positioned at least partially in the cathode, it may for example comprise a resistive wire running through the cathode and electrically insulated from the latter.

[0078] The unit may also comprise a temperature sensor, better still a device for regulating the temperature of the cathode, in order for example to control the heating of the cathode in order to adapt the temperature to the desired flow rate of hydrogen.

[0079] The unit may be configured in order to allow an expansion of the cathode during its operation, and especially to provide a permanent contact between the cathode and the electrically non-conducting but ion-conducting material.

[0080] The unit may comprise an elastically deformable member on the side of the cathode opposite the electrically non-conducting material of the ion-permeable wall, arranged in order to make the cathode bear against this electrically non-conducting material. Such an elastically deformable member may be elastically deformed in order to compensate for a variation in the volume of the cathode, for example, when the cathode swells due to the hydrogen accumulated.

[0081] The elastically deformable member is, for example, made at least partially with an elastically deformable metallic material, for example spring steel, or with an elastomer having sufficient thermal resistance, for example based on silicone which can withstand a temperature of at least 250°C.

[0082] In one exemplary embodiment, the cathode is tubular, for example surrounding an interior space that allows its expansion. Such a configuration is desirable when the cathode comprises one or more intermetallic compounds capable of expanding during the accumulation of hydrogen, for example by around 25% to 30% by volume.

[0083] The interior space may house the elastically deformable member, which is present, for example, in the form of an elastomeric sleeve.

[0084] The interior space may also house, for example, the heating member and/or the temperature sensor.

[0085] The unit may comprise a connector for filling and/or purging of the cation donor, optionally equipped with a valve that opens during the connection with a filling or purging system outside of the unit.

[0086] The unit may comprise a hydrogen outlet coupling that makes it possible to convey the gaseous hydrogen released to the outside of the unit.

[0087] These filling and/or purging and hydrogen outlet connectors may be equipped with appropriate sealing systems, such as O-rings, for example.
Another subject of the invention is a device for recharging a unit as defined above, comprising at least one housing for receiving the storage unit and at least one electrical connector to be connected to the electrical connector of the unit in order to generate an electric field between the cathode and the anode and, where appropriate, heating the cathode.

The recharging device may comprise several housings that make it possible to recharge several units simultaneously or successively.

On the other hand, the recharging device may comprise one housing that makes it possible to receive a reserve of water or of electrolyte that makes it possible to supply the unit or units via an internal circuit and optionally to recover the electrolyte during the emptying of these units.

The recharging device may be arranged in order to monitor the charge and interrupt it when certain conditions are achieved.

The recharging device may comprise one or more end of recharging indicators, for example, one or more light-emitting diodes and/or a pressure-detecting device. Detection of the increase in the pressure may convey a saturation of the cathode with hydrogen and the end of the storage capacity.

The recharging device may be arranged in order to cut the power supply starting from a certain value of the pressure.

The recharging device may comprise, for example, at the bottom of each of the housings intended for receiving a unit, at least one connector to be coupled to the hydrogen outlet and/or with the filling and/or purging connector or connectors mentioned above. One or more valves may be activated during the installation of a recharge into the recharging device.

Another subject of the invention is a method comprising a step that consists in supplying a fuel cell with hydrogen extracted from a storage unit as defined above.

In the case where the unit is intended to be introduced into an electrical appliance, the storage unit may, before its introduction, be emptied of the cation donor, especially in the case where the latter is a liquid. This emptying may take place into the aforementioned recharging device for example.

Another subject of the invention is an electrical appliance, in particular a cell phone or a laptop computer, comprising at least one housing that makes it possible to receive at least one storage unit as defined above.

The unit may be configured in order to operate at ambient temperature, or even at a temperature greater than 60°C, for example above 100°C, and for example at an internal pressure between 0.1 bar and 100 bar. The storage in the cathode may be improved under pressure.

The unit may, where appropriate, be coupled to a fuel cell, for example within a one-piece assembly.

The fuel cell may share an envelope with the unit for producing and storing hydrogen, where appropriate.

In such a case, the discharging of hydrogen is carried out toward the fuel cell without exiting the envelope that contains the storage unit and the fuel cell.

The invention will be better understood on reading the detailed description that follows, the non-limiting exemplary embodiments of the latter, and on examining the appended drawing, in which:

FIG. 1 represents, in a schematic and simplified manner, units for storing and producing hydrogen, and also the associated recharging device;

FIG. 2 is a view similar to FIG. 1, the units for producing and storing hydrogen being withdrawn from the recharging device;

FIG. 3 is an exploded view representing an assembly, comprising a storage and production unit and a fuel cell;

FIG. 4 represents the assembly from FIG. 3, in the assembled state;

FIG. 5 represents an embodiment variant of the unit;

FIG. 6 is a schematic and partial longitudinal cross section of the unit from FIG. 5;

FIG. 7 is a schematic and partial cross section of an embodiment variant of the unit; and

FIG. 8 represents examples of hydrogen charging rates as a function of time, according to several voltages applied between the anode and the cathode.

Represented in FIG. 1 is a system comprising two removable units for producing and storing hydrogen and a recharging device that makes it possible to recharge these units with hydrogen between two successive uses.

The recharging device may comprise, as can be seen in FIG. 2 in particular, housings for each receiving a unit and it may comprise a reservoir which may be filled with a liquid intended for the units, for example the electrolyte.

In one variant, the recharging device comprises a single housing.

Each unit may, as illustrated in FIGS. 3 and 4, be arranged in order to be coupled, during use, to a fuel cell, for example within an assembly comprising at least one fluid connector that makes it possible to recover the hydrogen produced by the unit in order to inject it into the fuel cell and an electrical connector that makes it possible to electrically power the unit, in order for example to give rise to, via heating, the release of the stored hydrogen.

The assembly may comprise, as illustrated in FIG. 4, an electrical connector that enables the fuel cell to electrically power the electrical appliance into which the assembly is introduced.

Represented in FIG. 3 is another example of a unit that has a generally cylindrical shape.

This unit comprises an outer envelope which has a cover at one end. Of course, the invention is not limited to the particular form of envelope, and the latter may be in one-piece form, where appropriate.

The envelope houses, in the example in question, an anode which is advantageously perforated in order to increase the exchange surface area, a wall that is permeable to ions, comprising an electrically non-conducting but ion-conducting material, a cathode made from a material that allows the storage of hydrogen and an elastic return member.

The material of the wall that is permeable to ions, which is placed in contact with the cathode, is electrically non-conducting but ion-conducting, in order to be able to be passed through by H⁺ ions. The storage of hydrogen is favored when the contact surface area between the cathode and this electrically non-conducting material is large.

The wall has, for example, a tubular shape sealed by a base, on the side opposite the cover.

The non-conducting material of the wall may comprise hexagonal boron nitride, activated by the electrolyte by being left for several hours in contact with it, under an electric field.
The return member 24 is, for example, a sleeve made from an elastomeric material such as silicone, capable of withstanding the temperature at which the cathode 22 is heated in order to release hydrogen.

The wall 21 and the return member 24 may trap between them the cathode 22 when this is liquid or pulvulrent.

The return member 24 makes it possible to press the cathode 22 against the wall 21, in order to ensure a contact between the two despite the expansions of the cathode 22.

The unit 2 may house a heating member 25 that makes it possible to heat the cathode 22 in order to give rise to the release of the accumulated hydrogen.

The unit 2 may also be equipped with a temperature sensor 26, represented very schematically in FIG. 6, in order to avoid any overheating and/or to control the flow rate of hydrogen released owing to a regulation of the heating of the cathode 22.

The hydrogen may exit the unit via an orifice 27 which forms or is equipped with a male or female connector, optionally provided with a valve.

The circulation of electrolyte may take place through the unit, by means of orifices 14. The circulating electrolyte comes into contact with the anode 20 and the wall 21.

In accordance with one aspect of the invention, the cathode 22 is made from a material capable of storing hydrogen, for example a hydridable material. Under the effect of an electric field created between the anode 20 and the cathode 22, the anode being connected to the positive terminal of an electric generator which is, for example, integrated into the recharging device 3, and the cathode being connected to the negative terminal of this electric generator, the H⁺ cations contained in the electrolyte migrate through the wall 21 toward the cathode 22 and are reduced to atomic hydrogen at the interface of the cathode 22 and the wall 21.

The atomic and/or molecular hydrogen thus generated is directly stored in the cathode 22, and optionally in the wall 21 if this is produced in accordance with Application WO 2006/003328.

The hydrogen is preferably stored in the cathode in the form of atomic hydrogen, being fixed directly, via adsorption, in the cathode. In the case where the cathode comprises an intermetallic compound, the hydridation of the cathode may take place via a chemisorption reaction, the molecular hydrogen splitting into atomic hydrogen on contact with the intermetallic compound. In order to favor this chemisorption reaction, the hydridable cathode may optionally be heated and/or put under pressure.

When the diameter of the pores of the wall 21 is less than the dimensions of the H₂O⁺ ions contained in the H⁺ ion donor, the intensity of the electric field applied between the anode and the cathode must be sufficient to give rise to the rupture of the H₂O⁺ ions according to the reaction:

\[
\text{H}_2\text{O}^+ \rightarrow \text{H}_2\text{O} + \text{H}^+
\]

The reaction consumes water, which is preferably present in the electrolyte.

The reaction for producing hydrogen also gives rise to a gaseous emission of oxygen. This gaseous emission may result in the formation of bubbles at the anode 20, in the electrolyte.

The gaseous oxygen formed during the production of hydrogen may be recovered at a corresponding outlet arranged in the unit, and stored or used directly, or else released into the atmosphere.

It is possible to extract the hydrogen thus stored by heating the cathode and/or by putting the latter under vacuum, in order to supply, for example, a fuel cell and/or to use the hydrogen as a fuel or reactant.

Preferably, the unit is emptied of electrolyte before the cathode is heated. This emptying may be made into the recharging device for example.

The flow rate of extracted hydrogen may be controlled by actuating, for example, on the heating temperature of the cathode.

In one variant that is not illustrated, the heating member is outside the envelope 15.

In the variant illustrated in FIG. 7, the heating member 25 is positioned within the cathode 22.

Also illustrated in this figure is the option for the anode 20 to be supported by the wall 21 that is permeable to ions.

The anode 20 is passed through by the electrolyte 40, which may communicate, where appropriate, with a reserve located on the side of the anode 20 which is opposite the cathode 22.

The wall 21 that is permeable to ions may have a multilayer structure, with for example, as illustrated in FIG. 7, a support layer 21a and a layer 21b made of an electrically non-conducting but ion-conducting material.

The support layer 21a may be composed of a porous ceramic, for example.

The presence of the support layer 21a may make it possible to reduce the thickness of the layer 21b providing the support function of this layer 21b.

The layer 21a may also make it possible to use an anode 20 that has a lower mechanical strength, by supporting the latter.

FIG. 8 represents an example of results obtained with a unit similar to that of the example from FIG. 6, with the exception of the heating member, placed outside of the envelope.

The anode used is made of graphite. The wall 21 is made of hexagonal boron nitride activated by being left for three hours in contact with the electrolyte under a voltage of 50 V. The wall 21 is, for example, produced by machining a bar, with a thickness of 1 mm. The electrolyte is 5 N sulfuric acid. The cathode 22 is based on pulverulent LaNi₅ used in NiMH batteries.

Of course, the invention is not limited to the examples which have just been described.

The unit may be produced with different shapes and sizes and with other materials. Where appropriate, the anode and the cathode may be interdigitated. The unit may comprise several production and storage cells that each comprise a cathode and an anode. The electrolyte may be located internally, being surrounded by the anode, the ion-permeable wall and the cathode, which is thus external relative to the anode and may itself be surrounded by an elastically deformable member.

The expression “comprising” should be understood as being synonymous with “comprising at least one”, unless otherwise specified.
1.-29. (canceled)

30. A method for storing and producing hydrogen comprising:

- subjecting to an electric field a unit comprising:
  - a cation donor;
  - an anode;
  - a cathode configured for storing atomic and/or molecular hydrogen; and
  - a wall that is permeable to ions, comprising an electrically non-conducting but ion-conducting material, between the cathode and the cation donor, wherein the electric field causes the formation, at least at the interface of the cathode and of the electrically non-conducting material, of atomic and/or molecular hydrogen;
- storing the hydrogen at least within the cathode; and
- restoring gaseous hydrogen by heating the cathode and/or putting the cathode under vacuum.

31. The method of claim 30, wherein the cation donor is a donor of H⁺ ions.

32. The method as claimed in claim 30, wherein the wall that is permeable to ions has a water permeability of less than 5% of the mass of hydrogen produced.

33. The method as claimed in claim 32, wherein the cathode contains less than 5 wt % of water.

34. The method as claimed in claim 30, wherein the wall that is permeable to ions has zero water permeability.

35. The method as claimed in claim 30, wherein the cathode comprises an intermetallic compound chosen from the following list: of AB₅ type (A and B being metals), LaNi₅, phases of laves (Zr, Ti), (Mn, V, Cr, Ni), ZrMn₅, or TiMn₅, Mg, TiFe, MgNi, the vanadium-based centered cubic solid solutions, BaRhH₄ (the formula corresponding to the hydrided state), Mg₂FeH₄ (the formula corresponding to the hydrided state), NaAlH₄ (the formula corresponding to the hydrided state), LiBH₄ (the formula corresponding to the hydrided state), and all the compounds and derivatives thereof or alloys thereof.

36. The method as claimed in claim 30, wherein the electrically non-conducting material comprises a ceramic.

37. The method of claim 36, wherein the ceramic comprises hexagonal boron nitride.

38. The method of claim 37, wherein the boron nitride is activated boron nitride, the activated boron nitride being activated by an acid solution under an electric field.

39. The method as claimed in claim 30, wherein the wall that is permeable to ions comprises one or more layers of different materials, at least one of these layers exercising a cation-conducting function.

40. The method as claimed in claim 30, wherein the wall comprises a porous layer having a support role between the layer that has the cation-conducting function and the electrolyte.

41. The method as claimed in claim 30, wherein the cation donor is an acidic aqueous solution.

42. The method as claimed in claim 30, wherein the cation donor is circulated in the unit.

43. The method as claimed in claim 30, wherein the voltage applied between the anode and the cathode during the production of hydrogen is between 1 and 300 V.

44. The method as claimed in claim 30, wherein the cathode is heated at a temperature greater than 30° C. in order to produce gaseous hydrogen.

45. The method as claimed in claim 44, wherein the cathode is heated by a Joule effect during the circulation of an electric current.

46. The method as claimed in claim 44, wherein the cathode is heated after draining the electrolyte.

47. The method as claimed in claim 44, wherein the unit is heated at a temperature below that which yields the discharging of hydrogen, during a phase of hydrogen production and storage.

48. The method as claimed in claim 30, wherein the atomic and/or molecular hydrogen is also stored in the electrically non-conducting but ion-conducting material.

49. A unit for the storage and restitution of hydrogen comprising:

- an anode;
- a cathode capable of storing atomic and/or molecular hydrogen;
- a cation donor;
- a wall that is permeable to ions, comprising an electrically non-conducting but ion-conducting material between the cathode and the cation donor;
- an electrical connector to electrically power the anode and the cathode in order to create an electric field between them that enables the formation of atomic and/or molecular hydrogen at least within the cathode and the storage thereof at least in the cathode, the unit being configured to collect the gaseous hydrogen released by the cathode at least during the heating of the latter; and
- a fluid connector to channel the gaseous hydrogen thus released to the outside of the unit.

50. The unit as claimed in claim 49, further comprising an electrical resistance element for heating the cathode.

51. The unit as claimed in claim 50, further comprising a device for regulating the temperature of the cathode.

52. The unit as claimed in claim 49, wherein the cathode comprises an intermetallic compound.

53. The unit as claimed in claim 49, wherein the electrically non-conducting material comprises a ceramic.

54. The unit as claimed in claim 49, wherein the cation donor is an aqueous acid solution.

55. The unit as claimed in claim 49, further comprising an elastic return member configured to make the cathode bear against the electrically non-conducting but ion-conducting material.

56. The unit as claimed in claim 49, further comprising a connector for filling and/or purging of the cation donor.

57. The unit as claimed in claim 49, further comprising a coupling that enables the extraction of the gaseous hydrogen stored.

58. The unit as claimed in claim 49, wherein the anode is supported by the wall that is permeable to ions.

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