(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 October 2009 (22.10.2009)

PCT

(10) International Publication Number
WO 2009/127828 A2

(51) International Patent Classification:
C01B 3/08 (2006.01)

(21) International Application Number:
PCT/GB2009/000980

(22) International Filing Date:
15 April 2009 (15.04.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0806810.8 15 April 2008 (15.04.2008) GB

(71) Applicant *(for all designated States except US)*: **H2RENEW, LTD** [GB/GB]; 72 Main Street, Solihull, West Midlands B90 1UA (GB).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **WOODWARD, Jonathan** [GB/GB]; H2Renew, Ltd, 72 Main Street, Solihull, West Midlands B90 1UA (GB).

(74) Agent: **FORRESTER KETLEY & CO**; Chamberlain House, Paradise Place, Birmingham B3 3HP (GB).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: HYDROGEN PRODUCTION

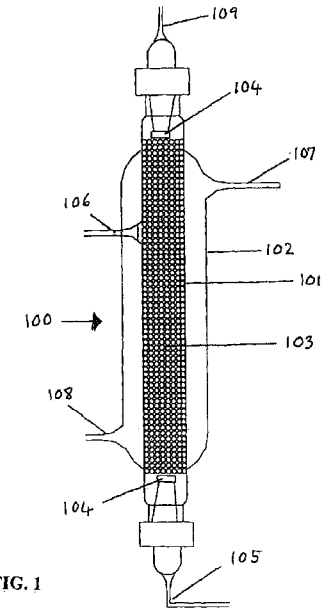

FIG. 1

(57) Abstract: A method for production of hydrogen comprising: i) providing one or more permeable vessel, the permeable vessel containing a plurality of entrapped metal particles; ii) causing an acid to permeate the permeable vessel, wherein the entrapped metal particles react with the acid to generate hydrogen, and wherein the metal particles are exposed to a reducing atmosphere.

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HYDROGEN PRODUCTION

Hydrogen use as a renewable fuel for transportation and fuel cells has the potential to solve several major challenges facing the world today: dependence on fossil fuels, poor air quality resulting from their burning, and greenhouse gas emissions. To realize the full benefits of a hydrogen economy, hydrogen must be produced cleanly, efficiently and affordably from regionally available, renewable resources. Currently, the dominant hydrogen production technology is reforming of natural gas due to cost advantages over electrolysis and other renewable technologies. However, renewable technologies attract tremendous interest with companies that use readily available and renewable sources of energy such as solar, biogas and biomass to produce hydrogen in large quantities. Using hydrogen for energy applications requires a more efficient, lower cost production process, with low or no CO_2 emissions.

It is known that some metals can displace hydrogen from water or acid solutions. In water or acid the metal will lose electrons to become a positively charged metal ion. The electrons will reduce protons formed by the dissociation of the acid and molecular hydrogen will be generated.

Getty et al. (U.S. Patent 6,395,252) discloses hydrogen production by reaction of metallic iron with an organic acid to generate a metal oxide and hydrogen, in which the organic acid is consumed in regenerating the metal.

Hopkins et al. (WO 2006/127775 A3) also discloses hydrogen production by reaction of a metal with an organic acid, resulting in the precipitation of the metal oxide.

Because metals are expensive, their consumption in hydrogen production makes such known processes expensive.

There is therefore a need for an approach in which the metal is inexpensively regenerated.

In a first aspect, therefore, a method is provided for production of hydrogen comprising: providing one or more permeable vessel, the permeable vessel containing a plurality of entrapped metal particles; causing an acid to permeate the permeable vessel, wherein the entrapped metal particles react with the acid to generate hydrogen, and wherein the metal particles are exposed to a reducing atmosphere.

The method may also include collecting the hydrogen.

In the inventive approach, hydrogen gas is generated by reaction between an acid and the metal entrapped in the permeable vessel, in which the resulting metal oxide is constantly exposed to a reducing atmosphere provided by the hydrogen generated inside the permeable vessel, and is thereby reduced back to the metal. Hydrogen diffuses out of the permeable vessel and can be collected, and the metal is regenerated and is reusable.

The present invention thus provides a method for the sustainable production of hydrogen by the reaction of acid with metal particles entrapped inside a permeable vessel.

The approach exploits the fact that hydrogen is produced within the permeable vessel, and the entrapped metal oxides will be under a reducing atmosphere, causing the oxidised metal product inside the permeable vessel to be reduced back to the metallic state.

Thus, the present approach provides a method whereby hydrogen is generated without significant consumption of metal.

Without being bound to any particular theory, in the reducing conditions of the present inventive approach, it is believed that electrons become reattached to the metal ion to regenerate the metal and a dynamic equilibrium is established where the rate at which the metal ions are formed approximately equals the rate at which they are reduced back to the metallic state.

For example, metallic iron in water or acid will lose electrons and go into solution as Fe^{2+} ions, and the electrons will reduce protons formed by the dissociation of the acid to generate molecular hydrogen. Under reducing conditions however, some electrons are transferred back to the metal ion to regenerate metallic iron.

In alternative embodiments of the present invention, the steps of providing one or more permeable vessel containing a plurality of entrapped metal particles, and causing an acid to permeate the permeable vessel, are either performed continuously or performed as a batch process.

It will be evident to those skilled in the art that the inventive approach is amenable to a continuous process, permitting the continuous permeating of the permeable vessel with an acid, such as by flowing the acid over the permeable vessel, and collecting (or using) the hydrogen continuously from the vessel.

Equally, the method may comprise a batch process in which an acid is made to contact the permeable vessel containing the entrapped metal particles and the required quantity of hydrogen generated therefrom.

In another embodiment, the steps of providing one or more permeable vessels containing a plurality of entrapped metal particles, and causing an acid to permeate the permeable vessel, are carried out in anaerobic conditions.

For example, using acid that has first been deaerated, using a vacuum to remove dissolved gas in the liquid, helps ensure that little or no oxygen comes into contact with the surface of the metal within the permeable vessel.

In a further embodiment, the steps of providing one or more permeable vessel containing a plurality of entrapped metal particles, and causing an acid to permeate the permeable vessel, are carried out in a temperature-controlled environment.

The temperature may be controlled by a means for maintaining a fixed temperature such as a jacket surrounding the permeable vessel through which water is circulated at a given temperature.

In one embodiment, the temperature is about 80°C.

For example, the permeating of the permeable vessel with acid may be carried out at in a temperature-controlled environment, wherein the temperature is 40, 50, 60, 70 or 80°C.

In another embodiment, the steps of providing one or more permeable vessel containing a plurality of entrapped metal particles, and causing an acid to permeate the permeable vessel, are carried out in an environment of approximately neutral pH.

In a further embodiment, the permeable vessel is a gel bead or a slab.

In a further embodiment, the permeable vessel is made of one or more of: an alginate, a gelatin, a gum, a polysaccharide, a heteropolysaccharide and a resin.

For example, the permeable vessel may be made of sodium alginate, guar gum, gum arabic, carrageehan, pectin, tragacanth gum, xanthan gum, or deacylated chitin (chitosan).

In one embodiment, the entrapped metal particles are one or more of: silver, palladium, platinum, copper, nickel, lead, antimony, iron, zinc, aluminium, magnesium, gallium, calcium and sodium silver, palladium, platinum, copper, nickel, lead, antimony, iron, zinc, aluminium, magnesium, gallium, calcium, sodium, mixtures thereof and metal alloys.

It will be evident to those skilled in the art that alloys of metal may be suitable for the present inventive approach wherein at least one metal in the alloy is capable of acting as described above.

In a further embodiment, the entrapped metal particles are iron.

In yet another embodiment, the entrapped metal particles are of a mesh size of between 2500 and 4.

In a further embodiment, the entrapped metal particles are of a mesh size of between 2500 and 100.

The entrapped metal particles may be, for example, microparticles or nanoparticles.

In one embodiment, the acid is one of or a mixture of: gluconic acid, ascorbic acid, oxalic acid, citric acid, succinic acid, acetic acid, formic acid, a carboxylic acid and a precursor thereof.

In a further embodiment, the acid is gluconic acid.

In yet another embodiment, the acid is degassed to permeating the permeable vessel.

For example, before contacting the entrapped metal particles, the acid may be deaerated using a vacuum that removes the dissolved gas in the liquid by decompression, to help ensure that little or no oxygen comes into contact with the surface of the metal within the permeable vessel.

However, it should also be noted that hydrogen diffuses at a faster rate than any other gas, ensuring anaerobic conditions surrounding the metal component, so that during the metal acid reaction any metallic ion is reduced in situ in the reducing atmosphere.

The permeable vessel is, for example, a gel bead, and the metal is, for example, iron, and the acid, is for example, a weak organic acid, such as gluconic acid.

Alternatively, aluminium powder may be entrapped within the permeable vessel, either alone or in combination with iron particles or another appropriate metal such as gallium.

Alternatively, the entrapped metal particle is an alloy or a mixture of suitable metals.

For example, when a solution of gluconic acid is flowed over gel beads, made from propylene glycol alginate and bone gelatine, containing iron particles, hydrogen production from within the beads make the microenvironment within the beads anaerobic and reducing. Gluconic acid is a renewable organic acid formed by fermentation of sugar (glucose) and is oxidised in the process forming 2-keto-D-gluconic acid.

In one embodiment, a plurality of the permeable vessels containing entrapped metal particles is provided.

In a further embodiment, the method further comprises the step of separating the metal particles from the permeable vessel for subsequent reuse for hydrogen production.

In a second aspect of the invention is provided a permeable vessel containing entrapped metal particles for hydrogen gas production, the vessel comprising one or more of: propylene glycol alginate, sodium alginate, bone gelatin, guar gum, gum arabic, carrageehan, pectin, tragacanth gum, xanthan gum, deacylated chitin (chitosan), cellulose and combinations thereof; and a plurality of entrapped metal particles contained in the permeable vessel.

It will be evident to those skilled in the art that the permeable vessel may contain more than a single number of entrapped metal particles, as befitting the use thereof.

Such a permeable vessel may be made inexpensively, used, recovered easily and reused, or dried for ease of transportation to the site of hydrogen gas production.

For example, the permeable vessel may comprise gel beads that can be dehydrated and rehydrated for their transportation and storage.

It is also envisaged that the gel beads could be used to store hydrogen, which has been generated by the reaction of an organic acid with metal (e.g. iron) micro/nanoparticles entrapped within them, perhaps following a dehydration step.

In one embodiment, the permeable vessel is a gel bead having a diameter of between 0.2 mm and 5.0 mm.

The gel bead may be made of a gel forming polymer which forms a gel upon contact with a gelling inducer and is compatible with the metal particle to be encapsulated. For example, the gel forming polymer can be an ionotropic gel forming polymer such as a polysaccharide.

Suitable polysaccharides include those typically extracted from vegetable matter and include sodium alginate, guar gum, gum arabic, carrageehan, pectin, tragacanth gum, xanthan gum, and deacylated chitin (chitosan).

Exemplary gel beads may be manufactured out of propylene glycol alginate and bone gelatine and may have a diameter ranging from 200 microns to 5 mm.

Exemplary gel beads may contain iron powder particles (10-40 microns) or nanoparticles of iron (20-40 nm).

The gel beads may be manufactured by forcing a stream of gel through a nozzle which can be vibrated at a given frequency by ultrasound to control the dimensions of the gel beads, or for example, as described in the examples below.

It will be evident to those skilled in the art that the inventive approach contemplates providing a plurality of the permeable vessels containing a plurality of entrapped metal particles inside a reactor.

Thus, in a third aspect of the invention is provided system for production of hydrogen gas comprising: at least one reactor containing one or more of a permeable vessel containing a plurality of entrapped metal particles; the reactor having at least a first outlet for discharging generated hydrogen.

In one embodiment, the reactor is configured for a continuous process, and further comprises a first inlet for flowing an acid into the reactor and a second outlet for egress of the acid.

In another embodiment, the system further comprises a pump in connection with the first inlet for pumping the acid into the reactor.

In yet another embodiment, the reactor is a batch process reactor and is configured for an acid to be added to the reactor to cause hydrogen production.

In yet a further embodiment, the reactor further comprises an outer container in connection with the reactor, the outer container being enabled to flow a liquid (e.g. water) around the reactor for temperature control.

It will be evident to those skilled in the art that the inventive system may amount to the one or more permeable vessels containing the entrapped metal particles being housed in a reactor, and the reactor being housed in an outer container, the outer container being configured to permit the flow of water through it to provide temperature control of the reaction, and the reactor being, for example, a columnar container, such as a glass column, containing a plurality of the permeable vessel containing the entrapped metal particles. The glass column may be thermo-jacketed for temperature control. The reactor may be enabled for an acid to be flowed through it.

During hydrogen production, the entrapped metal particles will be under a hydrogen atmosphere since hydrogen is produced within the permeable vessels, ensuring reducing conditions around the metal particles. Hydrogen diffuses rapidly into the fluid phase of the reactor (the fluid phase being the acid surrounding the permeable vessels), bubbles out of the reactor and is collected or used.

The acid, for example, may be a dilute solution of a weak organic acid such as gluconic acid, and may be continuously passed through the reactor, while the hydrogen generated is collected from some point of egress out of the reactor, or used.

The buoyancy of hydrogen means it can pass out of the reactor quickly, such as by a point of egress at the top of the reactor, and be easily separated from the solution for subsequent storage, if desired.

Thus the inventive approach provides for the continuous production of hydrogen gas in which the metal components are not consumed, because some of the hydrogen generated within the reducing environment of the entrapped metal particles results in the electrochemical reduction of the ionic metal products. Thus, in such a system the metal is regenerated to be reusable or renewable.

It is known that some metals reactive with acids form an oxide layer (e.g. magnetite, in the case of iron) upon oxidation in weak acids such as water and organic acids. During hydrogen production within the permeable vessel (e.g. gel beads) of the present invention, a reducing environment produced by (for example) gluconic acid and the evolved hydrogen, slows down this oxidation process and results in yields of hydrogen from the metal and the acid. Stoichiometric (or even greater than stoichiometric) yields are possible. The permeable vessel provides a form of enclosed environment which facilitates the reduction of the metal oxide.

The metal particles may be iron powder, for example, and upon passage through the reactor of an acid, such as for example a dilute solution of weak acids, such as gluconic and ethanoic acids, hydrogen is generated.

The (preferential) gel beads also offer a means of entrapping the metal particles, which can easily be recovered (after their use for extracting hydrogen from organic acids) by simple techniques such as sieving/filtration. At that stage, any oxidised metal particles not reduced during the regenerative process can be reduced back to their metal state, for re-use. As nanoparticles of metal (e.g. iron) can be used, their entrapment within the permeable vessel (e.g. gel bead) also offers a significant safety and handling advantage. Metal nanoparticles, by virtue of their extreme small size (hence large reactive surface area) and nature show an extreme susceptibility to oxidation and it is known that exposure to atmospheric air/oxygen can cause spontaneous combustion. Containing the metal particles within the permeable vessel (e.g. gel bead) prevents or greatly reduces the risk of this occurring.

By continuous passage of the acid through the reactor, such as by flowing the acid through the reactor at specific flow rates, continuous production of hydrogen gas is enabled.

The reactor may be made of any dimensions to suit, and may be made of glass or any appropriate material that does not react with an organic acid.

The pH in the reactor may be neutral.

The temperature of the acid may be between 20 °C and 80 °C.

The acid may first be deaerated prior to being introduced into the reactor.

The hydrogen that evolves from the reactor may then either be stored or used immediately in a fuel cell application.

The amount of hydrogen generated may be made to depend upon the dimensions of the reactor, such as the dimensions of the cylindrical column.

In a fourth aspect of the invention, a kit is provided comprising a plurality of the permeable vessel described above, packaged.

For example, the kit may a plurality of gel beads as described herein. After preparation, beads may be packaged in plastics (polythene) bags in air, in nitrogen or in carbon dioxide or under vacuum, at a minimum humidity. Such packaging prevents deterioration during storage.

Specific and non-limiting embodiments of the invention are illustrated by way of example only with reference to the following figures.

Figure 1 – shows a diagram of a reactor system of the present invention.

Figure 2 - shows an exemplary gel bead producing apparatus in accordance with present invention.

Figure 3 - shows a photograph of exemplary 2 mm diameter gel beads containing iron particles.

Figure 4 - shows a photograph depicting the appearance of exemplary hydrated and dehydrated gel beads of the present invention.

Figure 5 - shows a graph of an exemplary hydrogen production in accordance with the present invention.

When metals react with for example, acid they donate electrons to form positive ions. The electrochemical series for various metals, shown in Table 1 below, shows the ability of certain metals to displace hydrogen

from acid solutions. The standard electrode potential (E°) of a metal/metal ion combination is the emf measured when the metal/metal ion electrode is coupled to a hydrogen electrode under standard conditions. Metals towards the top of the series are good reducing agents, donating electrons more easily to become positively charged metal ions, in which state they may for example form an oxide. The reducing ability of a metal increases the higher up the series it is. Metal ions at the bottom of the series are good electron acceptors, and are thus, good oxidising agents. The oxidising ability of the metal ions increases the lower down the series they are. The more negative the E° value, the more the position of equilibrium lies to the left, or the more readily the metal loses electrons. The more negative the value, the stronger the reducing capability. The more positive the E° value, the more the position of equilibrium lies to the right, or, the less readily the metal loses electrons, and the more readily its ions accept electrons.

The metal iron (Fe) in water or a weak acid solution iron will lose electrons and go into solution as Fe^{2+} ions. The electrons will reduce protons formed by the dissociation of the acid, generating molecular hydrogen. However, under reducing conditions, some electrons can remain attached to the metal, the metal is regenerated. A dynamic equilibrium is established where the rate at which ions are formed is equal to the rate at which they are removed by reduction to the metallic state.

Table 1-The electrochemical series

equilibrium	E° (volts)
$Li^{+}_{(aq)} + e^{-} \rightleftharpoons Li_{(s)}$	-3.03
$K^{+}_{(aq)} + e^{-} \rightleftharpoons K_{(s)}$	-2.92
$Ca^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Ca_{(s)}$	-2.87
$Na^{+}_{(aq)} + e^{-} \rightleftharpoons Na_{(s)}$	-2.71
$Mg^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Mg_{(s)}$	-2.37

$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	-1.66
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	-0.76
$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}$	-0.44
$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)}$	-0.13
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$	0
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77
$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$	+1.36
$Au^{3+}_{(aq)} + 3e^- \rightleftharpoons Au_{(s)}$	+1.50

A less reactive metal will dissociate into its ionic state less readily and it follows therefore that any ions formed are more likely to reclaim their electrons and regenerate the metal. The position of the iron equilibrium:

$Fe^{2+} + 2e^- \leftrightarrow Fe$

will be to the left and the free electrons will reduce protons to produce hydrogen:

$2H^+ + 2e^- \leftrightarrow H_2$

The position of any equilibrium can be changed by changing its conditions. Changing the concentration of the protons in solution is one of the ways of changing the position of equilibrium. Iron (II) ions are easily oxidised to iron (III) ions, and iron (III) ions are fairly easily reduced to iron (II) ions. The equilibrium is:

$2Fe^{3+} + 2e^- \leftrightarrow 2Fe^{2+}$

The redox potential (E) (in volts) measures the tendency of a substance to donate or accept electrons. The standard redox potential Eo′ refers to standard conditions (all reactants at 1.0 Molar; 1 atm pressure; pH 7.0;

25°C or 298°K). Values in Table 1 are given relative to the standard electrode which is 1.0 molar H^+ ions in equilibrium with H_2 gas at 1 atm pressure and by definition has $E^o = 0$. It should be noted that the pH is not 7 but pH 0, due to the 1.0 molar acid. At pH 7, E^o becomes $E^{o'}$ and for $H_2/H+$ this is -420mV, no longer zero. Under the latter conditions, therefore, the reduction of Fe^{2+} to Fe (especially in the presence of a high hydrogen gas concentration) becomes possible. This, together with a reducing potential of gluconic acid of approximately -4.5mV, forms the basis of the herein described invention.

Specific and non-limiting embodiments of the present invention are now exemplified by means of the following examples.

Example 1. Hydrogen production system

Figure 1 shows an exemplary system (100) comprising reactor (101), suitable for hydrogen gas generation, surrounded by water jacket (102). Reactor (101) contains propylene glycol bone gelatine gel beads (103) which enclose entrapped iron particles manufactured, as described below. The volume of beads in the reactor will depend on the working volume of the reactor as will be understood by those skilled in the art. The beads are held in place by two sintered discs (104) positioned at either end of reactor (101) providing a barrier plug for keeping the beads (103) in place in the reactor, but also optionally providing temperature insulation, and filtration of liquids. At one end of reactor (101) is fluid inlet means (105) for the introduction of acid and fluid outlet means (106) for egress of acid. Water is circulated at a given temperature through jacket (102) surrounding reactor (101) via water inlet means (107) and water outlet means (108). Gluconic acid is pumped into one end of the reactor (105) at a flow rate of 0.5 cm^3 min^{-1} and out of distal end of the reactor (106) using a peristaltic pump. This flow rate can be varied to provide optimal hydrogen production. The concentration of gluconic acid can also be determined enzymatically.

Hydrogen gas exits the reactor from gas outlet (109) and is collected in a measuring vessel (by water displacement) from which the rate and amount of hydrogen gas production can be measured. The purity of the hydrogen is checked by GC/MS. Reactor (101) can be built to any specifications depending on the hydrogen production requirement.

Example 2. Manufacture of propylene glycol alginate bone gelatine beads containing iron particles

Figure 2 shows an exemplary bead producing apparatus (200) of the present invention. Propylene glycol alginate, de-ionised bone gelatine, iron particles, glutaraldehyde, and mineral oil are all obtained commercially. A suspension containing propylene glycol alginate (2%) bone gelatine (14.5%), and iron particles (10 microns or less) in water at 40 °C is stirred in magnetic stirrer receptacle (201) until everything except the iron particles dissolves. The viscous suspension is transferred to feed reservoir (202) and kept at 40 °C, having air or nitrogen circulated via inlet (203). Beads are formed by using 20 lb/in^2 of gas pressure (nitrogen) via pressure gauge (204) to force the viscous suspension along flexible tubing (205) and through a nozzle (206) (0.25-0.78 mm diameter) as discrete droplets which fall into magnetic stirrer bath (207) containing 500 cm^3 of mineral oil on the surface of 200 cm^3 of cold water, stirred by magnetic stirrer (208). Temperature control is via circulating fluids means (209). Flow of the viscous suspension via flexible tubing (205) is also controlled by sonic vibration transducer (210) and vibration frequency control (211). The volume of gel beads produced is dependent on the volume of the suspension. The diameter of the beads ranges between 0.5 to 3.0 mm depending on the frequency at which the nozzle is vibrated which must also be tuned the velocity and fluid properties of the gel suspension. The beads are removed from the oil/water interface and stored for 20 h at 23 °C in 0.5% (w/v) solution of glutaraldehyde at pH 7.0. The beads are then

washed four times with 0.5 L of water and stored in water or dried in air.

Alternatively, high intensity ultrasonic liquid processors may be used that atomize the liquid into micro-droplets whose median drop size can be 100 microns. The latter would be suitable for entrapment of nanoparticles of iron (20-40 nm).

Exemplary gel beads are shown in Figure 3. Figure 4 shows an example of hydrated (Fig. 4a) and dehydrated gel beads (Fig. 4b). The beads are made from materials such as carrageenan, alginates and gelatines which can be dehydrated for storage and transportation with subsequent rehydration. They may be packed into a tubular column made out of glass, although other corrosion resistant materials such as nickel alloys can be substituted for glass. Specific numbers of the beads can be made for the production of specific amounts of hydrogen for specific applications.

A working reactor may contain gel beads the diameter of which could range from 100 microns to 1 mm formed by high intensity ultrasonic liquid processors. Exemplary gel beads with entrapped iron powder may have a particle size of 20 nm, 40 nm or 10-40 microns. Alternatively, the gel beads contain aluminium powder.

Example 3. Hydrogen production

The gel beads are placed into the reactor shown in Figure 1 until full and then the reactor is closed by means of the sintered discs. Water is then circulated around the reactor at a temperature of between 20 and 80°C, and a 0.5M solution of gluconic acid solution is pumped into the reactor using a peristaltic pump at a flow rate of 0.5 $cm^3 min^{-1}$.

The gluconic acid solution may optionally be degassed. Prior to flowing the gluconic acid through the reactor, it may be deaerated using a vacuum that removes the dissolved gas in the liquid by decompression. This also helps to ensure that little or no oxygen comes into contact with the surface of the iron within the bead. However, because hydrogen diffuses at a faster rate than any other gas which helps to ensure the anaerobic conditions within the reactor. During the reaction oxidised iron is reduced in situ by the reducing atmosphere and the reducing potential of gluconic acid.

The gluconic acid solution permeates the gel beads and contacts the iron particles. Hydrogen gas is generated within the beads and diffuses out into the solution. The hydrogen gas exits the top of the reactor because of its buoyancy and is collected and stored or even used immediately in a fuel cell application. The solution leaving the bottom of the reactor may be stored for further processing or even returned to the reactor continuously until all the gluconic acid has been oxidised by the process.

The graph shown in Figure 5 illustrates a hydrogen production with respect to time, in which 3.5 g of entrapped iron inside the beads of the present invention are contacted with acid using a reactor configuration as exemplified in Figure 1, by flowing 0.5 M gluconic acid at a pH of 1.86 and at a working temperature of 75°C over gel beads containing the entrapped iron. From the graph it can be seen that hydrogen production increases with time for a constant quantity of iron, without consumption of the iron metal.

Other organic acids such as ascorbic, oxalic, citric, succinic, and ethanoic acids may also be used as alternatives.

The reaction may, for example, take place in a warmed environment of temperature of up to 80 °C, at ambient pressure, and at neutral pH. For example, a solution of 1 M gluconic acid solution at pH 7.0 is pumped through the reactor at a flow rate of 1.0 cm^3min^{-1}, where the temperature of the water jacket is 40°C.

Example 4. Optimisation of hydrogen production

Different mesh sizes of iron particles (see Table 2 below) which represent different surface area to volume (mass) ratios are commercially available. A higher mesh size corresponds to a higher surface area to volume ratio. Although the smallest size of particle shown in the table is 5 microns, nanoparticles of iron are also available in the range of 20-40 nm with a surface area of 30-50 m^2g^{-1}. Higher surface area to volume ratios for the iron particles will result in a greater yield of hydrogen per g of iron and a higher surface area in contact with hydrogen and gluconic acid for the regeneration of iron in situ.

Table 2 – Correlation between mesh and particle size

Mesh	Micron	Inches
4	4760	0.185
6	3360	0.131
8	2380	0.093
12	1680	0.065
16	1190	0.046
20	840	0.0328
30	590	0.0232
40	420	0.0164
50	297	0.0116
60	250	0.0097
70	210	0.0082
80	177	0.0069
100	149	0.0058
140	105	0.0041
200	74	0.0029
230	62	0.0023
270	53	0.0021
325	44	0.0017
400	37	0.0015
625	20	0.0008
1250	10	0.0004
2500	5	0.0002

The optimum rate of hydrogen production and the amount of hydrogen produced can be determined by water displacement and may be measured as a function of one or more of the following: 1. bead diameter; 2. size of iron particles; 3. temperature; 4. acid concentration; 5. pH; and 6. flow rate.

An exemplary pH is that of the gluconic acid diluted with fresh water supplied to the laboratory, giving a pH of approximately 7.0.

Example 5. Working reactor

A working reactor volume of a 2 cm diameter and 20 cm length glass cylinder (similar to that exemplified in Fig. 1) is 62.84 cm^3. Gel beads of diameter 2 mm (0.2 cm) with a volume of 0.0042 cm^3 per bead can fill 53% of the cylinder volume - the number of beads in the reactor will be approximately 7,930. These beads will contain 2.51 g of iron powder particles, or 316.5 μg per bead. A deaerated gluconic acid solution in water at a concentration of 0.5M and pH 7.0 is pumped through the reactor containing the beads at a flow rate of 0.5 cm^3min^{-1}. The thermojacket maintains the reactor and its contents at a constant temperature of 50 °C. Hydrogen is produced and collected in a measuring cylinder by water displacement. This allows the rate and amount of hydrogen production to be calculated, as follows: one mole of iron will generate 1 mol of hydrogen gas or 22.4 litres. Since the 0.5 M gluconic acid solution is the source of protons for the reduction by iron, approximately 0.13 litres of hydrogen (approximately 4 standard cubic feet (scf)) is generated by this reactor used in batch mode. 1kW h is provided by 25-27 scf hydrogen.

Example 6. Working reactor

A working reactor volume of 100 cm diameter and 1000 cm length cylinder is 7.855 x 10^6 cm^3. The number of beads filling this volume is

991 x 10^6, containing 105 kg iron (1873.4 moles). Approximately 1.9 x 10^3 moles of hydrogen gas is produced (in batch mode), or 42.6 x 10^3 litres of gas, or 1.28 x 10^6 scf of hydrogen (equivalent to 51,200 kW h)

The working reactor may be designed in order to produce a given volume of hydrogen gas for a given application and power requirement.

Optionally, other liquid media may be also introduced into the reactor, including, but not restricted to water, and sea water.

The produced hydrogen may for example, be stored for later use in cylinders under pressure or as a hydride, or for example, may be immediately used to provide electricity by a fuel cell, where the size of the reactor used will depend on the power output of the fuel cell. Exemplary uses of the produced hydrogen include but are not limited to fuel cell applications for electricity (power) generation in transport, domestic and industrial heating systems. A further exemplary use of the produced hydrogen is for combustion engines where hydrogen is burnt to provide engine power in lieu of gas or petrol, in automobiles and planes and trains and boats, space crafts, as public transport systems worldwide move toward hydrogen-powered engines as an alternative to petrol engines.

CLAIMS

1. A method for production of hydrogen comprising:
   i) providing one or more permeable vessel, the permeable vessel containing a plurality of entrapped metal particles;
   ii) causing an acid to permeate the permeable vessel, wherein the entrapped metal particles react with the acid to generate hydrogen, and wherein the metal particles are exposed to a reducing atmosphere.

2. The method of claim 1 further comprising:
   iii) collecting the hydrogen.

3. The method of claim 2, wherein steps ii) and iii) are performed continuously.

4. The method of claim 2, wherein steps ii) and iii) are performed as a batch process.

5. The method of any preceding claim, wherein the acid is flowed over the permeable vessel.

6. The method of any of claims 2 to 5, wherein steps ii) and iii) are carried out in anaerobic conditions.

7. The method of any of claims 2 to 6, wherein steps ii) and iii) are carried out in a temperature-controlled environment.

8. The method of claim 7, wherein the temperature is about 80°C.

9. The method of any of claims 2 to 8, wherein steps ii) and iii) are carried out in an environment of approximately neutral pH.

10. The method of any preceding claim, wherein the permeable vessel is a gel bead or a gel slab.

11. The method of any preceding claim, wherein step i) further comprises providing the plurality of the permeable vessel containing the entrapped metal particles, in a reactor.

12. The method of any preceding claim, further comprising the step of separating the metal particles from the permeable vessel for subsequent reuse for hydrogen production.

13. The method of any preceding claim, wherein the entrapped metal particles are one or more of: silver, palladium, platinum, copper, nickel, lead, antimony, iron, zinc, aluminium, magnesium, gallium, calcium, sodium, mixtures thereof and metal alloys.

14. The method of any preceding claim, wherein the entrapped metal particles are iron.

15. The method of any preceding claim, wherein the entrapped metal particles are of a mesh size of between 2500 and 4.

16. The method of any preceding claim, wherein the entrapped metal particles are of a mesh size of between 2500 and 100.

17. The method of any preceding claim, wherein the acid is one of or a mixture of: gluconic acid, ascorbic acid, oxalic acid, citric acid, succinic acid, acetic acid, formic acid, a carboxylic acid and a precursor thereof.

18. The method of any preceding claim, wherein the acid is gluconic acid.

19. The method of any preceding claim, wherein the acid is degassed prior to permeating the one or more permeable vessel.

20. The method of any preceding claim, wherein the permeable vessel is made of one or more of: an alginate, a gelatin, a gum, a polysaccharide, a heteropolysaccharide and a resin.

21. A permeable vessel containing entrapped metal particles for hydrogen gas production, the vessel comprising one or more of: propylene glycol alginate, sodium alginate, bone gelatin, guar gum, gum arabic, carrageehan, pectin, tragacanth gum, xanthan gum, deacylated chitin (chitosan), cellulose and combinations thereof; and a plurality of entrapped metal particles contained in the permeable vessel.

22. The permeable vessel of claim 21, wherein the metal particles are one of or a mixture of: silver, palladium, platinum, copper, nickel, lead, antimony, iron, zinc, aluminium, magnesium, calcium and sodium.

23. The permeable vessel of either of claims 21 and 22, wherein the metal particles are microparticles or nanoparticles.

24. The permeable vessel of any one of claims 21-23, wherein the permeable vessel is a gel bead or gel slab.

25. The gel bead of claim 24, having a diameter of between 0.2 mm and 5.0 mm.

26. A hydrogen gas production system for providing hydrogen gas comprising: at least one reactor containing one or more of a permeable vessel containing a plurality of entrapped metal particles; the reactor having at least a first outlet for discharging generated hydrogen.

27. The system of claim 26, wherein the reactor is configured for a continuous process, and further comprises a first inlet for flowing an acid into the reactor and a second outlet for egress of the acid.

28. The system of claim 27, further comprising a pump in connection with the first inlet for pumping the acid into the reactor.

29. The system of claim 28, wherein the reactor is a batch process reactor, and is configured for an acid to be added to the reactor to cause hydrogen production.

30. The system of any one of claims 26-29, the reactor further comprising an outer container in connection with the reactor, the outer container being enabled to flow water around the reactor for temperature control.

31. A permeable gel bead or slab containing entrapped metal particles for use in hydrogen gas production by reaction of the metal with an acid.

32. A kit comprising a plurality of the permeable vessel of any one of claims 21-25, packaged.

33. A method, a permeable vessel, a system, a gel bead or slab, or a kit, substantially as described herein and with reference to the drawings.

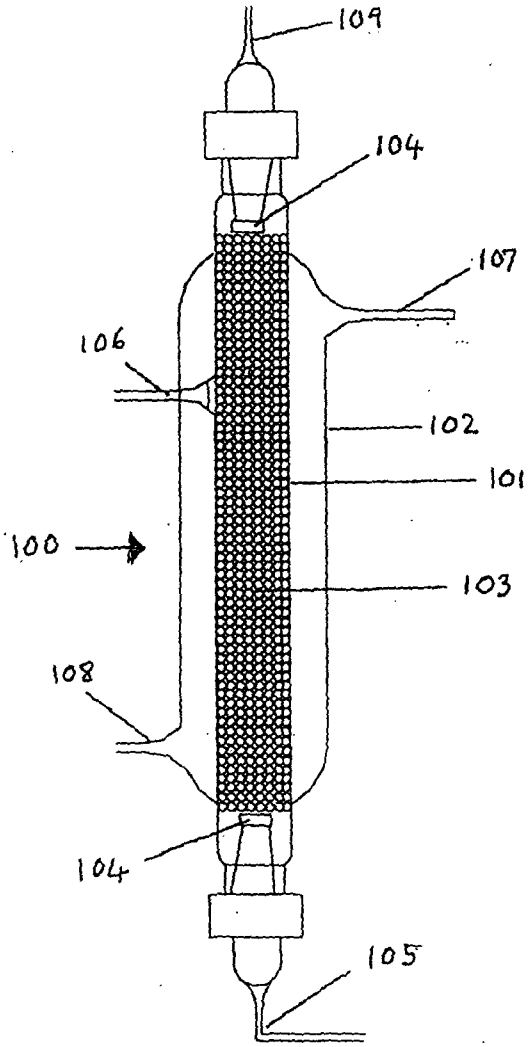

FIG. 1

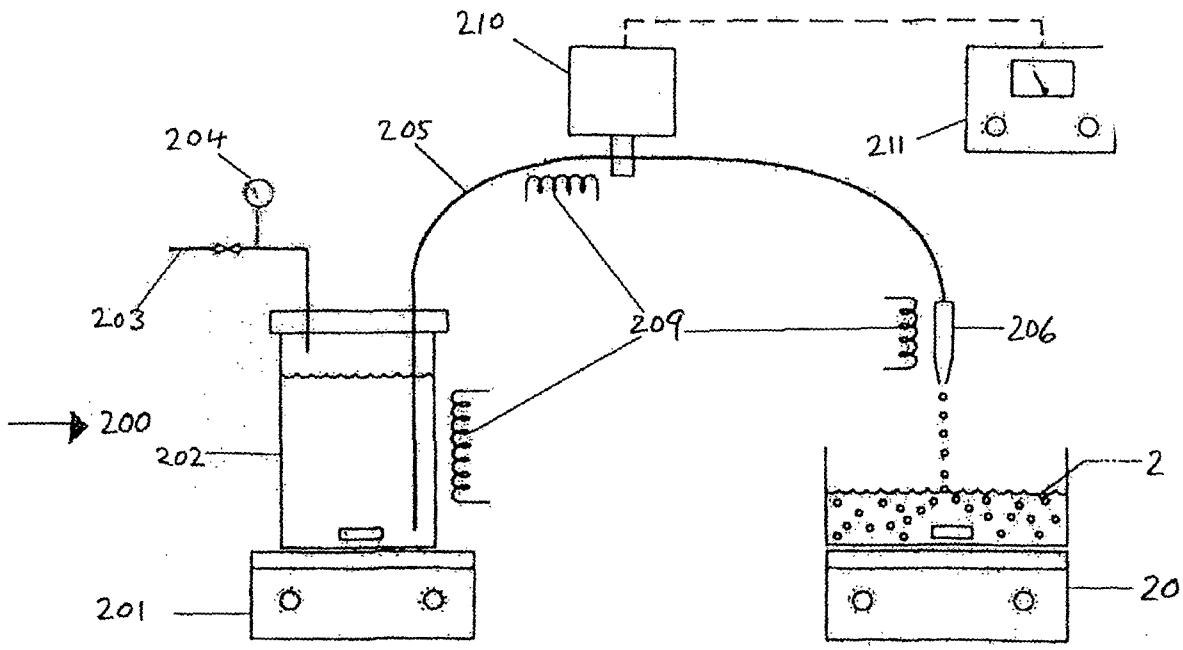

FIG. 2

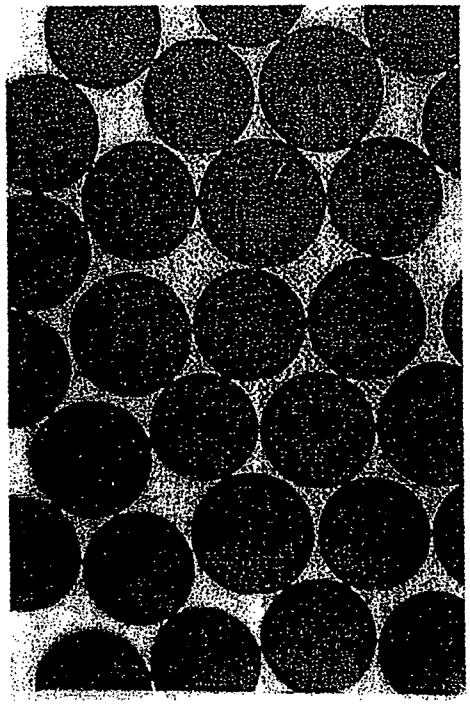

FIG. 3

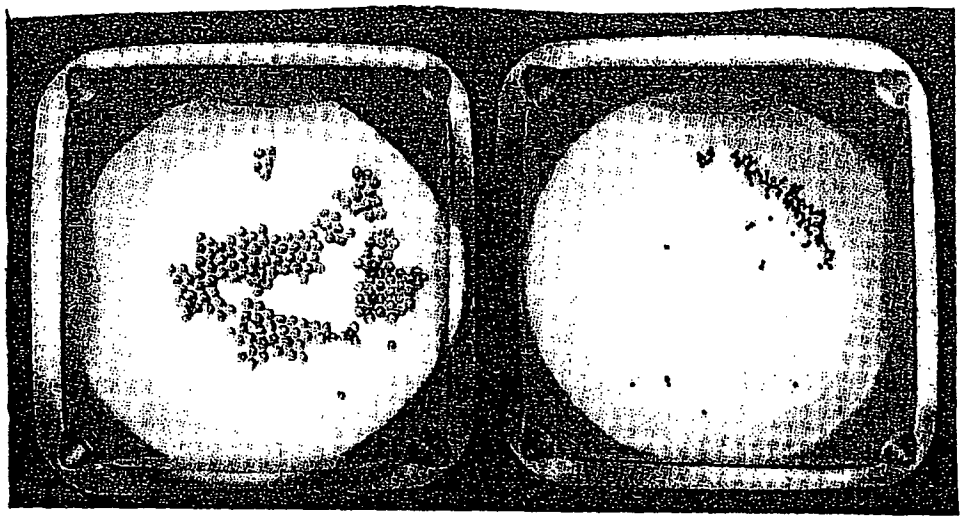

FIG 4(a) FIG 4(b)

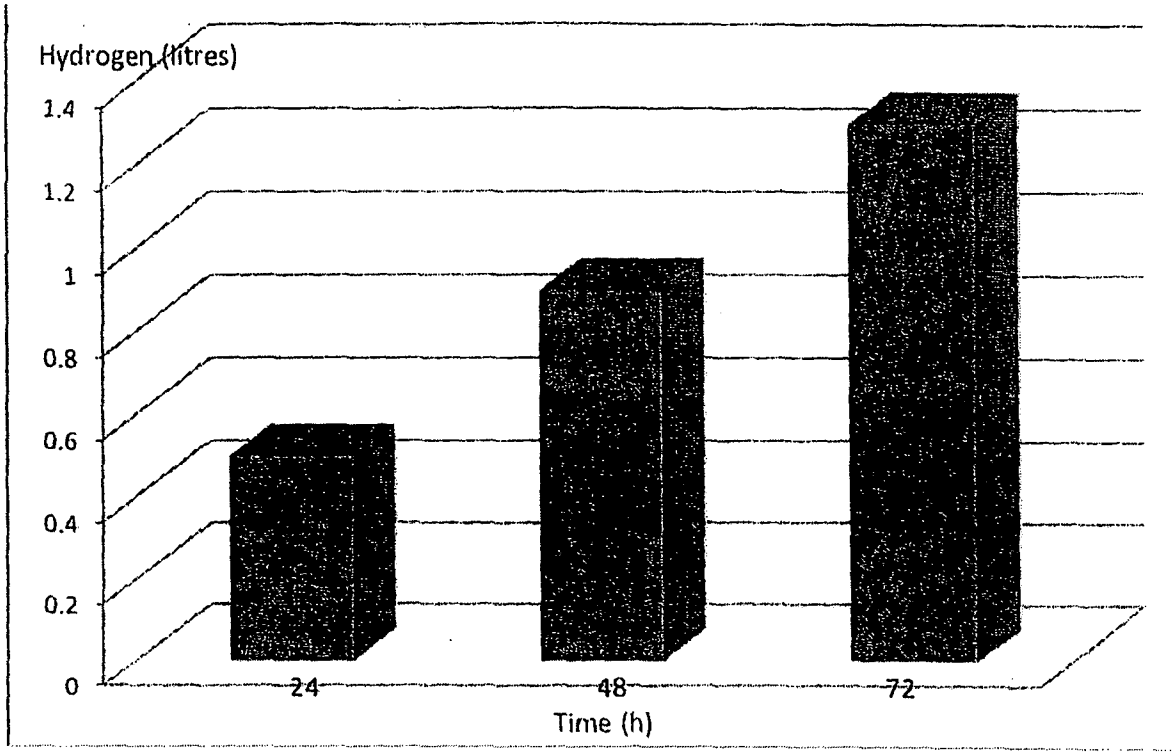

FIG. 5