



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

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<p><b>(21) International Application Number:</b> PCT/EP92/01302 <b>(22) International Filing Date:</b> 11 June 1992 (11.06.92)</p> <p><b>(71) Applicant (for all designated States except US):</b> PEGOL BJHQ COMPANY LIMITED [LI/LI]; Residence Trust Aktiengesellschaft, Austrasse 52, FL-9490 Vaduz (LI).</p> <p><b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> NAIDENOV, Stefan, Nikolov [BG/BG]; Zona B-5 Block 23, Sofia 1303 (BG).</p> <p><b>(74) Agents:</b> RAMBELLI, Paolo et al.; Jacobacci-Casetta &amp; Perani S.p.A., Via Alfieri, 17, I-10121 Torino (IT).</p> <p><b>(81) Designated States:</b> AU, BG, BR, CA, CS, FI, HU, JP, KP, KR, MN, NO, PL, RO, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).</p>		<p><b>Published</b> <i>With international search report.</i></p>
<p><b>(54) Title:</b> A METHOD FOR THE PRODUCTION OF HYDROGEN FROM A WATER MEDIUM</p> <p><b>(57) Abstract</b></p> <p>A method for the production of hydrogen from a water medium comprising introducing a palladium sponge in a water medium comprising heavy water thereby to cause hydrogen evolution. The palladium sponge is preferably obtained by subjecting a palladium powder to implantation of palladium ions.</p>		

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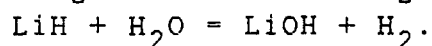
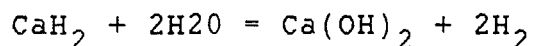
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A method for the production of hydrogen from a water  
medium

The present invention relates to a method for the production of hydrogen from a water medium.

Many methods are known for obtaining hydrogen from water:

1. interaction between water and hydrides; most often calcium hydride ( $\text{CaH}_2$ ) is used and lithium hydride ( $\text{LiH}$ ) is particularly valuable. Hydrogen production takes place according to the following reactions:

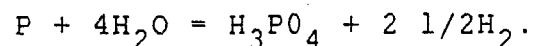


These methods are not very productive and also are very expensive since the hydrides are expensive substances.

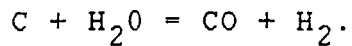
2. Interaction between water and metals. Some of the metals decompose water at ordinary temperature, e.g. sodium ( $\text{Na}$ ), potassium ( $\text{K}$ ) or lithium ( $\text{Li}$ ), according to the reaction:  $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$ .

Other metals decompose water at high temperature, e.g. iron ( $\text{Fe}$ ) according to the reaction  $3\text{Fe} + 4\text{H}_2\text{O} = 4\text{H}_2$  at about  $500^\circ\text{C}$ .

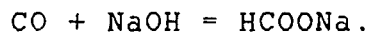
3. Interaction between water and metalloids. This method has been developed particularly on the basis of the interaction between water and phosphorus ( $\text{P}$ ) vapours at about  $400$ - $600^\circ\text{C}$  according to the reaction:



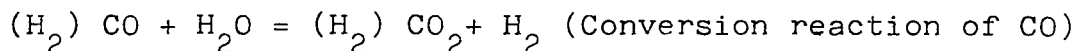
A more important method is the interaction between carbon (C)-coke, anthracite and water vapours at the temperature of about 1100°C according to the reaction:



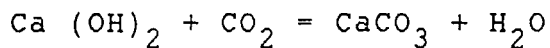
The obtained gas mixture is known under the name of water gas. The removal of CO, e.g. by means of its liquefaction is not of practical importance. It is carried out by cooling the gas to about -200°C (Frank-Karo - Linde's method). Carbon monoxide trails are removed by passing the gas through appropriate sodium hydroxide heated up to 80° - 85° C according to the reaction:



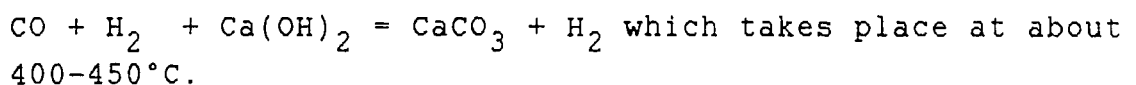
Most often carbon monoxide is removed according to the following method: the water gas is mixed with a given amount of water vapour and this mixture is passed over a catalyst heated up to 450-500°C, (usually  $\text{Fe}_2\text{O}_3$  activated with  $\text{Cr}_2\text{O}_3$  or  $\text{NiO}$ ) and the following reaction takes place:



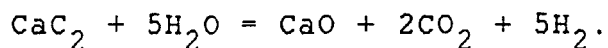
$\text{CO}_2$  from the mixture  $\text{CO}_2 + \text{H}_2$  is removed by its dissolution under pressure (about 2.5 MPa) in cold water and its trails are removed by gas scrubbing with  $\text{Ca}(\text{OH})_2$ :



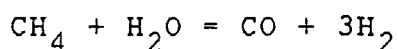
Small quantities of carbon monoxide are removed by passing the gas through an ammonia solution of copper chloride ( $\text{CuCl}$ ). The following reaction may also be used for CO removal from water gas:



4. Interaction between water and carbides. Most often calcium carbide is used ( $\text{CaC}_2$ ), according to the reaction:



5. Interaction between water and methane. The mixture of water vapours and methane is passed over a suitable catalyst, such as platinum or iron, heated up to  $1000^\circ\text{C}$  according to the reaction:



The carbon monoxide is removed in the same manner as described above.

6. Water electrolysis.

Water including an alkali base, such as potassium hydroxide (KOH) or sodium hydroxide (NaOH), is subjected to electrolysis with production of hydrogen at the cathode. The hydrogen obtained in this manner is rather pure in comparison with that obtained by other methods; however, the method is expensive and energy consuming.

7. Water electrolysis (or overheated vapour heated at  $700-1000^\circ\text{C}$ ) by creation of a high frequency ionising field, as well as magnetic pulsating field. Apparatuses to carry out such method are available, for instance filter-press type EP-24/12-12 having a capacity of  $24 \text{ m}^3$  hydrogen/hour and  $12 \text{ m}^3$  oxygen/hour with an energy consumption of 2390 A/hour. Cell tension 1.18V or 2,9 Kw/hour per  $\text{m}^3$  of hydrogen.

8. The cold nuclear synthesis of Pons and Fleishmann wherein hydrogen from heavy water and heavy water electrolysis is obtained with two different electrodes

made of platinum and palladium respectively. This method, even if already proved, has no practical significance since only heavy water ( $D_2O$ ) must be used.

The object of the present invention is to provide a very simple method for obtaining hydrogen from water, which is cheaper in comparison with all other up to date methods.

It has been surprisingly discovered that when a palladium sponge is introduced into a water medium including a volume of heavy water, hydrogen and oxygen evolution takes place from the water medium.

Accordingly the invention provides a method for the production of hydrogen from a water medium, which method comprises introducing a palladium sponge in a water medium comprising heavy water, thereby to cause hydrogen evolution.

The initial concentration by volume of heavy water in the ordinary water medium is not particularly critical; however it is preferred that such volume concentration be in the range from 2 to 2.2 % by volume; particularly preferred is a volume ratio between ordinary and heavy water of 50:1.

The process takes place at room temperature and atmospheric pressure, by simply introducing the palladium sponge within the heavy water containing water medium. It has been observed that evolution of hydrogen, oxygen and helium as well as gamma radiation start within 3-4 minutes from the introduction in the water medium of the palladium sponge. On a background of 3-4 impulses in an hour, the gamma radiation reaches 1800-2300 impulses.

A further subject of the invention is a palladium sponge which is particularly adapted to carry out the method of the invention. Such palladium sponge is preferably obtainable by subjecting a palladium body, preferably powdered palladium, to an accelerated ion beam. Methods for subjecting a body to an accelerated ion beam of different chemical elements are known in the art and microelectronic devices are made available to carry out such methods. Such methods provide for a modification of the target substance by relying on phenomena which take place in a vacuum medium as the result of the interaction between accelerated ions and a hard body. Available methods, which are adapted for obtaining the palladium sponge to be used in the method of the invention, include ion implantation, ion lithography, molecular-radiant epitaxy, ion-radiant mixing, as well as methods for pickling (etching) and direct doping (alloying) with a fine focused and computer controlled ray. The ion-radiant synthesis of compounds and especially of dielectric layers from  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  by reagent ion implantation e.g. by introducing accelerated chemical active ions of carbon, nitrogen and oxygen in a monocrystal silicon, has been the subject of a particular scientific and practical interest during the last years. Practically significant is the fact that the above-mentioned compounds may be synthesised on the silicon surface as well as at a certain depth under the surface, so that the above mentioned methods provide the possibility to form surface or hidden layers. Ion implantation, which is described in the Kirk-Othmer Encyclopaedia of Chemical Technology, third edition, volume 13, page 706-719 (incorporated hearing by reference) is the preferred method to obtain the palladium sponge to be used in the method of the invention. Ion implantation has recognised advantages such as that of being a pure vacuum process, of allowing a precise control

of the parameters and high degree of reproducibility of the results. Such a technique allows to introduce ions through thin passivating surface layers of the target body and allows to handle the distribution profile at depth by changing the accelerating tension, thus allowing to achieve high concentrations in spite of the limits provided by the chemical solubility.

Preferably the palladium sponge is obtained by implantation of palladium ions into a palladium powder without using Argon.

The method of the invention will be thoroughly described by means of the following examples.

Example 1: procedure for obtaining a palladium sponge.

A conventional twin-beamed ion implanter is used with the following raw materials:

Pd: purity 99.95%

PdO: palladium-oxide-salt

Argon: argon gas, purity 99.99%

Pd: powder with grain size of from about 1 to about 1.05 micron.

An amount of 0.4 up to 0.6 e.g. of palladium powder is introduced in the target chamber of the ion implanter. 4g PdO and 4 cm<sup>3</sup> argon gas are introduced in the sputter ion source of the ion implanter; the Ar gas is not an obstruction on the Pd<sup>+</sup> way.

Implantation is carried out consequently with Pd<sup>+</sup> (palladium cation) and argon gas. The energy accompanying the implantation is 150-200 KeV; dose 5.10<sup>17</sup>-2.5.10<sup>18</sup>



cm<sup>-2</sup>.

Implantation temperature: 500-600°C.

Annealing: 1150-1410°C.

Annealing duration: 0.5 up to 6 hours.

Elaboration of the computer program to manage the implantation algorithm: building of small channels with length of 1005.4A (Angstrom) under an angle of 105.4°; channel width: 105.4A.

The implantation of palladium cations, in the presence of Ar (molecular argon) aims at forming a sponge under the influence of the inert gas argon. The thus obtained palladium sponge was used in the process of the invention for the production of hydrogen and oxygen at mild conditions with the use of ordinary water and heavy water at room temperature.

#### Example 2

##### Production of hydrogen

One litre of ordinary water and 20 ml of heavy water (D<sub>2</sub>O) are introduced into a lead glass container with thickness of the lead glass of about 3-4 mm.

1.8-2.3 g. of palladium sponge as obtained by the above described ion implantation technique are introduced into the water medium.

Within 3-4 minutes hydrogen and oxygen in a volume ratio of 2:1 and a small quantity of helium are formed and emission of gamma radiation takes place. As the times goes on, in about 1 hour, the heating of the water medium takes place and the temperature reaches 62-67°C. It has been

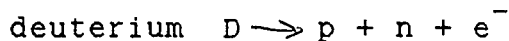
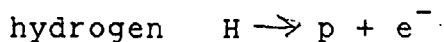
noticed that with an increased initial amount of the palladium sponge a higher exothermic effect is obtained; for instance with 3.6-4.6 g of palladium sponge the temperature of the water medium reaches 92-93°C and water evaporation starts. Evaporation of water is however not desirable since the main purpose is to produce hydrogen and oxygen.

After the start of the reaction the pouring of additional quantities of water and the changing of the ordinary water/heavy water ratio do not play any significant role and are not susceptible to cause a reduction or interruption of the reaction rate. Such a reaction may work for a long time and experiments up to one year and 4 months of continuous running have been carried out.

If the palladium sponge is removed from the water medium the reaction stops and the gamma radiation disappears. The palladium sponge as well as the water medium are not radioactive. When the palladium sponge is introduced again into the water medium, the reaction starts and addition of heavy water ( $D_2O$ ) is not necessary. We have not noticed any significant loss of weight of the palladium sponge after its continuous use, and theoretically it may be presumed that the palladium sponge does not substantially wear out. Palladium has the natural property of strong affinity to hydrogen and deuterium and is able to absorb a volume of hydrogen or deuterium equal to about 3000 times its own volume.

Although the applicant does not wish to be bound to any specific explanation of the reaction mechanism, it is believed that a chemical catalytic and naturally handled nuclear reaction takes place.

The involved species are:



wherein

p stands for proton

n stands for neutron

and  $e^{-}$  stands for electron.

More specifically it is believed that the two cycles are involved, namely:

- 1) p-p from  $H_2O + H_2O$
- 2) p-p-n from  $H_2O + D_2O$

Initially, the first cycle p-p takes place, with heavy water consumption in the amount of about 81-85% for a period of about 96 hours, (as determined on samples periodically taken from the  $H_2O$  and  $D_2O$  solution) after which the second cycle p-p-n takes place where new  $D_2O$  starts forming.  $D_2O$  recovery takes place in the amount of 24-32% and in this way the reaction is looking for resonance regime of work with a maximum formation of hydrogen and oxygen. The starting of the reaction and its duration is due to the natural properties of palladium and of the specially prepared lattice of palladium sponge which creates gravitational collapse (shrinkage) of  $H_2$  and D; the great pressure between the ions leads to the release of energy in the amount of 26.7 MeV (mega electron volts) and this energy is susceptible to cause the joining of two or more protons. Helium is formed together with gamma radiation, which however occurs at a very low level which cannot be compared with that of an uncontrollable nuclear reaction.

As it is known in nuclear physics, the binding energies

have an order of magnitude of million electron volts (MeV). The kinetic energy of the electron is 1 MeV. The binding energy (E) of  $e^-$ , that is, connected with the mass is 0.51 MeV.

The binding energy of helium is 27 MeV.

It is known that light hydrogen  $H_2$  at electrolysis is formed at the cathode with a rate which is 5-6 times higher than that of heavy hydrogen ( $D_2$ ). If the atomic ratio of  $H_2$  to  $D_2$  is 5000:1, the electrolysis of 6 litres of ordinary water results in  $1 \text{ cm}^3$  of pure heavy water  $D_2O$ .

The new isotopes of hydrogen and helium are: tritium  $1H^3$  and  $2He^3$  however such isotopes are present in only trace amount and do not play any role in the present case.

The helium may be detected by gas-mass spectrometry and is the results of the joining of two protons. The absorbed radiation of 26.7 MeV destroys new water molecules and creates free radicals, thus making possible the joining of new protons. In this way conditions are available for the beginning of the second cycle p-p-n and  $D_2O + H_2O$  are obtained.

The increase of the concentration of  $D_2O$  is a confirmation that the second cycle takes place. The  $D_2$  nucleus has  $D = p + n$  and the binding energy is 22.24 MeV. The He nucleus has  $He = 2p + 2n$  and the binding energy is 28.30 MeV. These reactions take place on a micro-molecular level in the crystal lattice of the palladium sponge.

Evidence that the above mentioned reactions take place

under the described conditions, with the use of a palladium sponge and a water medium comprising ordinary water and a limited amount of heavy water is provided by the evolution of hydrogen, oxygen and helium, as determined by gas-mass spectrometry and by the emission of gamma-radiation.

Thus, the invention provides a method for the production of hydrogen which is adapted to be industrially exploited.

The formed gases are not radioactive and the palladium sponge, when taken out from the water medium is not radioactive. Also the water medium is not radioactive.

The gamma-radiation emission takes place at a micro molecular level in the crystal lattice of the palladium sponge when immersed into the water solution.

CLAIMS

1. A method for the production of hydrogen from a water medium comprising introducing a palladium sponge in a water medium comprising heavy water thereby to cause hydrogen evolution.

2. A method according to claim 1, wherein said water medium comprises of from 2 to 2.2 % by volume of heavy water.

3. A method according to claims 1 or 2, wherein said palladium sponge is obtained by subjecting a palladium body to an accelerated twin beamed ion beam.

4. A method according to claim 3, wherein said palladium sponge comprises implanted palladium ions.

5. A method according to any of claims 1 to 4, wherein said palladium sponge is obtained by subjecting a palladium powder to implantation of palladium ions.

6. A method according to claim 5, wherein implantation is carried out in the presence of inert gas argon.

7. A palladium sponge as obtainable by ion implantation of palladium ions into a palladium powder.

8. A palladium sponge according to claim 7, wherein the palladium sponge after having been subjected to ion implantation is subjected to annealing at a temperature of from 1150 to 1410°C for a time of from 0.5 to 6 hours.

9. The use of a palladium sponge according to claims 7 or 8 for the production of hydrogen in a water medium comprising heavy water.

## INTERNATIONAL SEARCH REPORT

PCT/EP 92/01302

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C01B3/04; C23C14/48		
II. FIELDS SEARCHED		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C01B ; G21B ; C23C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	GB,A,2 223 422 (DORYOKURO KAKUNENRYO KAIHATSU JIGYODAN) 11 April 1990 see page 2, paragraph 4 - page 4, paragraph 1 see page 6, paragraph 1 - page 7, paragraph 1 see claims 1,4 ---	1,9
A	US,A,4 121 984 (H.J.GOMBERG ET AL.) 24 October 1978 see claims 1-6 ---	1
A	DATABASE WPIL Week 9050, Derwent Publications Ltd., London, GB; AN 90-370753/50 & JP,A,2 266 291 (SUMIMOTO ELEC IND KK) see abstract ---	1,7,9
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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A	MACHINE DESIGN vol. 58, no. 6, 20 March 1986, CLEVELAND US pages 61 - 65 P.SIOSHANSI 'Surface Modification by Ion Implantation' see the whole document ---	3,6,8
A	WO,A,9 101 037 (G.E.SHAFER) 24 January 1991 see page 3, paragraph 3 see claims 1-3,14,15 ---	1,3,9
A	JOURNAL OF ELECTROANALYTICAL CHEMISTRY vol. 261, 1989, LAUSANNE pages 301 - 308 M.FLEISCHMANN, S.PONS 'Electrochemically induced nuclear fusion of deuterium' see the whole document -----	1



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9201302  
SA 61118

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE-A- 3932670	05-04-90
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		US-A- 5093302	03-03-92
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