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(71) Applicant: **THE ROYAL INSTITUTION FOR THE ADVANCEMENT OF LEARNING / MCGILL UNIVERSITY** [CA/CA]; 845 Sherbrooke Street West, James Administration Building, Room 429, Montreal, Québec H3A 0G4 (CA).

(72) Inventors: **TROWELL, Keena**; 7957 Rue St-Denis, Montreal, Québec H2R 2G2 (CA). **BERGTHORSON, Jeffrey Myles**; 115 Strathearn Ave North, Montreal-West, Québec H4X 1X8 (CA). **FROST, David**; 7276 Champlain Blvd., Verdun, Québec H4H 1B2 (CA). **GOROSHIN, Sam**; 3055 Ernest-Hemingway, Apt 101, St-Laurent, Québec H4R 0A8 (CA).

(74) Agent: **NORTON ROSE FULBRIGHT CANADA LLP S.E.N.C.R.L., S.R.L.**; Suite 2500, 1 Place Ville-Marie, Montréal, Québec H3B 1R1 (CA).

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Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
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(54) **Title:** METHOD FOR HYDROGEN PRODUCTION VIA METAL-WATER REACTION

(57) **Abstract:** Hydrogen gas is produced by exposing a metal to an aqueous solution, wherein the aqueous solution is under supercritical conditions or is at a temperature of at least 200°C and at a pressure of at least the saturated vapor pressure of water at said temperature. Metals include A1, B, Mg, Si, Ti, Mn, and Zn. Metal oxides and/or metal hydroxides may also be recovered. The process may potentially be used to produce hydrogen on demand with applications in producing clean energy.

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METHOD FOR HYDROGEN PRODUCTION VIA METAL-WATER REACTION

[0001] The present application claims priority from US provisional patent application serial no. 62/826,173, filed March 29, 2019 and entitled "METHOD FOR HYDROGEN PRODUCTION VIA METAL-WATER REACTION", the disclosure of which is hereby incorporated by reference in its entirety.

FIELD OF THE DISCLOSURE

[0002] The disclosure relates to a method designed to oxidize metals to produce heat, hydrogen and metal oxides/hydroxides.

BACKGROUND OF THE DISCLOSURE

[0003] The shift away from fossil fuels to more sustainable energy sources is inevitable. Hydrogen has the potential to replace fossil fuels in many applications requiring high power owing to its high specific energy density. Currently, over 85% of the hydrogen produced today is produced via the reformation of methane (CH_4), a process which releases greenhouse gasses (GHGs) and is still reliant on fossil fuels. As the price of renewables comes down, the economic argument for using electricity to make fuels (rather than fossil fuels to make electricity as is currently the case with coal- and gas-fired plants) strengthens.

[0004] Hydrogen can also be produced via hydrolysis, a technique which uses an electric current to split a water molecule into its constituent hydrogen and oxygen. Hydrolysis releases no process GHG emissions but, like methane reformation, requires the hydrogen to be stored and transported which introduces a host of safety concerns.

[0005] There remains a need to produce hydrogen on-demand, *in-situ*, therefore preventing the need to store or transport hydrogen, while generating no GHGs.

SUMMARY OF THE DISCLOSURE

[0006] An aspect of the disclosure relates to a process for producing hydrogen gas, comprising exposing a metal capable of generating hydrogen to an aqueous solution under supercritical conditions or to an aqueous solution at a temperature of at least 200°C and a pressure of at least the saturated vapour pressure of the water at said temperature.

BRIEF DESCRIPTION OF FIGURES

[0007] FIGS 1A, 1B and 1C present the normalized hydrogen yield, as a percentage of full yield, for various aluminum morphologies.

[0008] FIGS 2A and 2B present the normalized hydrogen yield for various common aluminum alloys

[0009] FIGS 3A and 3B present the normalized hydrogen yield for zinc and magnesium respectively

[0010] FIG 4 shows the SEM image of the reaction products from aluminum in accordance with one embodiment of this disclosure.

DETAILED DISCLOSURE

[0011] "Metals" may be effective and clean energy carriers because metals are energy dense, have high specific energy densities, and they provide a convenient package with which to store and transport energy. These metals can be produced from clean electricity without GHG emissions, storing the energy for later use. By casting metal fuels as the energy carrier, rather than hydrogen, the major obstacles surrounding a sustainable hydrogen economy are addressed; that is the need to store and transport hydrogen is negated. Rather, the metal is oxidized in water to produce hydrogen on demand.

[0012] The present disclosure provides a process by which hydrogen can be produced with high efficiency from metals capable of generating hydrogen through the reaction of the metals with supercritical water and/or high-temperature, high-pressure water.

[0013] In one embodiment, there is provided a process for producing hydrogen from a metal, such as Al, B, Mg, Si, Ti, Mn, Zn, or a combination thereof or their alloys thereof. It is contemplated that the metal is preferably in solid state at the process temperature and may have a coating of the oxide of the selected metal/alloy. In this method, there is no requirement to embed, dissolve, or incorporate the metal with/in another material inert to water under the process conditions herein described.

[0014] Other optionally recoverable products of the process include heat, and metal oxides/hydroxides. The process is conducted in water at elevated temperatures and pressures.

[0015] In one embodiment, the reaction is carried out under supercritical water conditions; that is, at temperatures above the critical temperature of about 373°C, and pressures adequate to keep the water near to or above the critical specific density of 0.003106 m^3/kg, for example pressures of at least 100 atm.

[0016] In another embodiment, the temperatures will be of at least about 200°C, or ranging from 200°C to 400°C, and the pressure is at minimum the saturated vapour pressure of the water at the corresponding temperature, or adequately high to ensure the presence of liquid water or saturated liquid-vapour mixture.

[0017] The process described herein is a catalyst-free, and additive-free process. In particular, the process is conducted without requiring the addition of externally supplied non-metal (ceramic) such as, aluminum hydroxide(s) and/or aluminum oxide(s). In addition, the process is conducted without requiring the addition of an inorganic base, such as caustic base (NaOH or KOH). The process is also conducted without the mechanical manipulation of the metal prior to reaction, manipulation(s) intended to disrupt the passivating oxide layer. The process does not require alloying of the fuel metal with highly reactive metals such as Li or Na .

[0018] The process as provided herein further does not require the “metal capable of generating hydrogen” to be used with a passivating-oxide preventing agent such as gallium, gallium-indium,

gallium-indium-tin and other suitable alloys that are liquid at low temperatures (e.g. below 373K) and that are substantially inert to water from a standpoint of splitting water into hydrogen.

[0019] The process even allows for the use of coarsely produced metal powders, chips, or scrap fragments. It is believed that this is possible under supercritical conditions because the hydroxides formed in the reaction dissolve in the fluid rather than protecting the metal from further oxidation.

[0020] The aqueous solution for use in this disclosure is not especially limited and may be tap water, and even sea water. The water may also be purified to some extent e.g. by reverse osmosis water (i.e. deionized (demineralized) water) if desired.

[0021] The metal-water reaction process herein may chemically be depicted by the general equation:

$$xM + yH_2O \rightarrow yH_2 + M_xO_y + \text{heat}$$

[0022] Metals such as Al, B, Mg, Si, Ti, Mn, Zn are thermodynamically predicted to react with water in temperatures above 200°C. In the following examples, the process has been experimentally demonstrated for Al, Mg and Zn. B, Si, Ti, Mn, or any combination of those or together with a combination Al, Mg and Zn are embodiments of this disclosure. Under the process conditions, the metals listed are predicted to occupy a higher energy state when exposed to an aqueous solution, than their oxides and hydrogen gas, therefore the oxidation reaction is thermodynamically predicted to proceed under the process conditions. For example, at 300°C, manganese and water are at a higher energy state than manganese oxide and hydrogen therefore the reaction to split the water molecule and oxidize the metal will occur.

[0023] As an exemplary metal, in accordance with this disclosure, hydrogen can be produced with high efficiency from coarse aluminum powders, and even aluminum scrap, through the reaction of the metals with high-temperature/high-pressure water and supercritical water. In particular, the use of supercritical water may provide a full hydrogen yield for a range of

aluminum powders, for aluminum slugs of several millimeters or larger, and scrap aluminum cans.

[0024] The reactions follow one of two pathways depending on the temperature and pressure of the reaction:

$$2Al + 6H_2O \rightarrow 3H_2 + 2Al(OH)_3 + 871kJ \quad \text{Eq. 1}$$

$$2Al + 4H_2O \rightarrow 3H_2 + 2AlOOH + 846kJ \quad \text{Eq. 2}$$

[0025] As can be seen from Eq.1 and Eq2, 1 mole of aluminum yields 1.5 moles of hydrogen. This means that 1 kg of aluminum yields 1.2 cubic metres of hydrogen (at standard conditions), regardless of pathway. Furthermore, there is no release of process CO_2 or other GHGs in the reaction. The hydroxides formed in the reaction are inert and readily recyclable, because there is no addition of a catalyst,.

[0026] It was surprisingly found that an increase in reaction temperature has led to a significant increase in heat and hydrogen yield of the reaction. It is believed that once in the supercritical regime, water becomes a solvent for non-polar species such as the oxides and hydroxides that form as a result of the reaction. Because of this change in property, the products do not adhere to the surface of the unreacted metal, but rather dissolve into the water. This would explain that this continual exposure of reactive metal to the oxidizing fluid results in full yield, regardless of initial particle size. When the temperature is reduced to subcritical levels (for example from 373°C to 200°C), the solid reaction products precipitate out of the liquid. The following examples have shown that the reaction efficiency for coarse metal powders or even metal scrap is drastically improved as the reaction temperature increases. Metal scrap and macroscopic metal slugs are shown to be converted to hydrogen with 100% efficiency in supercritical water. For finer powders/materials, full yield can be obtained under subcritical water conditions (for example from 200°C to 373°C).

EXAMPLES

[0027] The experiments were carried out using a high-pressure confined gasket closure reactor (High Pressure Equipment Company GC-1 reactor). The reactor is housed in a heating mantle which is heated by a resistive heater. A dual element K-type thermocouple (Omega CAXL-116-U-12-DUAL) and a pressure transducer (WIKA A-10), both connected to a digital oscilloscope (Yokogawa DL750 ScopeCorder), are used to monitor the conditions inside the reactor during experiments and to record data. The oscilloscope was replaced with a Raspberry Pi microcomputer with an analogue to digital converter chip (MCP3008) to capture the signal from the pressure transducer and a chip to capture the temperature signal (MAX31855).

[0028] In each experiment, a measured amount of metal and deionized water was placed inside the reactor cell and the reactor was sealed. Each experiment used approximately 1 g of metal and 27 ml of deionized water. The amount of water was calibrated to ensure that liquid water was always present at temperatures below the critical temperature and that at the critical temperature the water density was equal to the critical density. To ensure that any hydrogen produced by the reaction was recorded by the instruments, the system was pressurized with an initial amount of hydrogen and this initial pressure, p1, was recorded. The reactor was then heated to the desired temperature and held at that temperature until the pressure reading becomes constant. The constant pressure at a constant temperature was an indication that the reaction had quenched. The apparatus was then cooled to the initial temperature and a second pressure reading, p2, recorded. Yield was determined using the ideal gas law to calculate hydrogen evolution based on the difference between p1 and p2.

[0029] Three micron-scale aluminum powders shown in FIG 1A produced by Valimet (Stockton, CA) and are referred to as H10, H50 and H95 with nominal diameters of 12, 55 and 120 micron respectively. According to Valimet's literature, these powders are 99.7% pure aluminum and have no coating other than the naturally occurring passivation layer of aluminum oxide on the surface of the powder.

[0030] The above experimental conditions was repeated using different types and shapes of aluminum as well as other metals and water source as reagent. The same protocol as described above was used for all shapes and metals The results are described below.

[0031] The aluminum plate and slugs (i.e. of generally cylindrical shape) used in FIG 1B and FIG 1C, respectively, were procured from Alfa Aesar and have a 99.99% metals basis purity.

[0032] The alloy used to obtain the results shown in FIG 2A was procured from a common aluminum beverage can (LaCroix brand).

[0033] The aluminum alloys 5052 and 6061, the zinc and magnesium slugs used herein (results shown in FIG 2B, 3A and 3B) were procured from Alfa Aesar

[0034] FIGS. 1A-1C present the normalized hydrogen yield, as a percentage of full yield, for various aluminum morphologies.

[0035] FIG. 1A are the yields for three aluminum powders ranging in nominal size from 12 micron to 120 micron. As can be seen in the figure, the smallest particle reacted fully at temperatures of about 275°C, while the largest particle only begins reacting at that temperature.

[0036] FIG 1B shows the yield for an aluminum plate with a thickness of 2mm, width of approximately 10mm and length of approximately 100mm. At 200°C there is no reaction with the water and as temperature increases so does the yield. Complete reaction is achieved at temperatures above 350°C.

[0037] FIG. 1C shows the yield for aluminum slugs measuring approximately 3mm in diameter and 4 mm in length. Again, as temperature increased, so did the yield. Full yield was even achieved at supercritical temperatures. Experiments were also conducted following the same methodology but replacing the reverse osmosis water with salt water. The salt water has the same salinity as sea water (35 parts per thousand). The results showed a similar trend with yield occurring in supercritical fluid.

[0038] FIGS. 2A-2B present the normalized hydrogen yield for aluminum obtained from a commercial can and two further aluminum alloys.

[0039] FIG. 2A shows the yield for a common aluminum beverage can. The walls of the can were cut into strips measuring approximately 3mm in width and 30mm in length. As can be seen in FIG. 2A, there was no reaction in the water until the supercritical regime is reached, after which was observed 100% yield of hydrogen.

[0040] The reaction products of the 380°C experiment, as shown by the SEM image in FIG 4, were a very fine powder with particles as small as 1 micron. This confirms that the aluminum oxides and hydroxides that form during the aluminum-water reaction dissolve in the supercritical water. This enables highly efficient hydrogen production from coarse aluminum powders and waste aluminum under supercritical water conditions.

[0041] FIG 2B shows the yields for two common aluminum alloys, Alloy 5052 and Alloy 6061. The plates used in these experiments were approximately 1–2 mm thick, approximately 10mm wide and approximately 100mm long. Alloy 5052 is more reactive than Alloy 6061, they both show an increase in hydrogen yield as temperature increases.

[0042] FIGS. 3A-3B present the normalized hydrogen yield for two other metals, zinc and magnesium.

[0043] FIG 3A shows the yield for zinc slugs, approximately 3mm in diameter and 4mm in length. Yield increases with temperature and full yield is achieved in the supercritical regime.

[0044] FIG 3B shows the yield for magnesium slugs, approximately 3mm in diameter and 4 mm in length. While yield increases with temperature, magnesium is shown to be more reactive than the other metals tested. Full yield is reached at 200°C.

CLAIMS

1. A process for producing hydrogen gas, comprising exposing a metal capable of generating hydrogen to an aqueous solution under supercritical conditions or to an aqueous solution at a temperature of at least 200°C and a pressure of at least the saturated vapour pressure of the water at said temperature.

2. The process of claim 1. comprising exposing a metal capable of generating hydrogen to an aqueous solution under supercritical conditions.

3. The process of claim 2, wherein the supercritical conditions is comprising a temperatures above about 373°C.

4. The process of claim 2 or 3, wherein the supercritical conditions is comprising a pressure adequate to keep the water near to or above the critical specific density of 0.003106 m3/kg.

5. The process of claim 4, wherein the pressure is at least 100 atm.

6. The process of claim 1 comprising exposing a metal capable of generating hydrogen to an aqueous solution under a temperature of at least 200°C and a pressure of at least the saturated vapour pressure of the water at said temperature.

7. The process of claim 6, wherein the temperature is ranging from 200°C to 400°C.

8. The process of claim 7, wherein the pressure is a pressure is at least the saturated vapour pressure of the water at said temperature.

9. The process of claim 7, wherein the pressure sufficient to have liquid water or saturated liquid-vapour mixture.

10. The process of any one of claims 1 to 9, wherein said metal capable of generating hydrogen is Al, B, Mg, Si, Ti, Mn, Zn, or a combination thereof or their alloys thereof.

11. The process of any one of claims 1 to 9, further comprising recovering at least heat and metal oxides and/or hydroxides resulting from the process.

12. The process of any one of claims 1 to 11, wherein the aqueous solution is comprising salt water.

13. The process of any one of claims 1 to 11, wherein the aqueous solution is comprising deionized water.

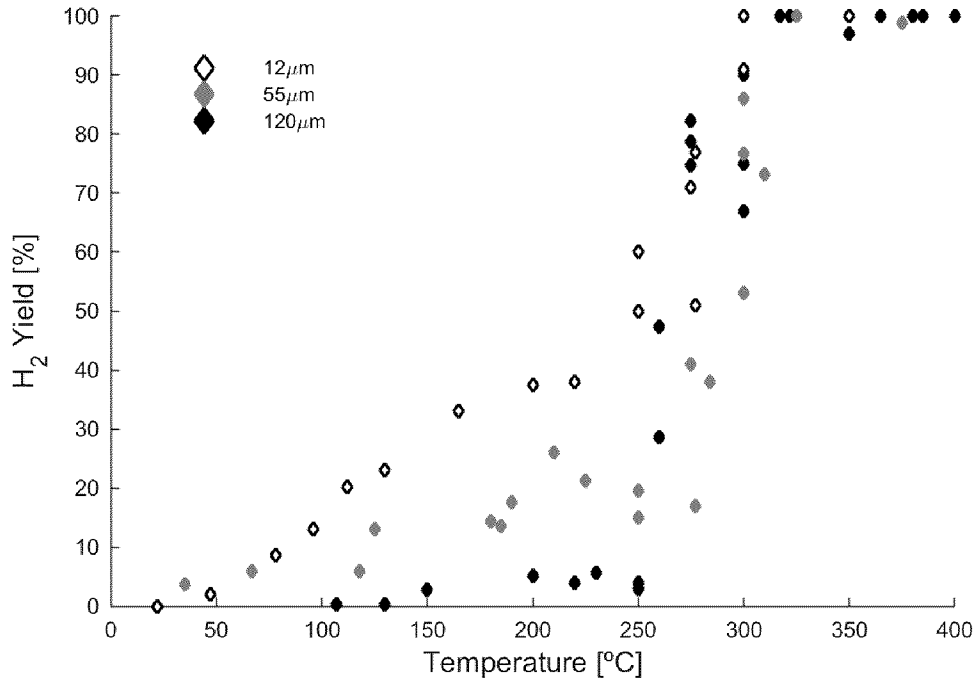
12μm
55μm
120μm
H2 Yield [%]
Temperature [°C]
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

FIG. 1A

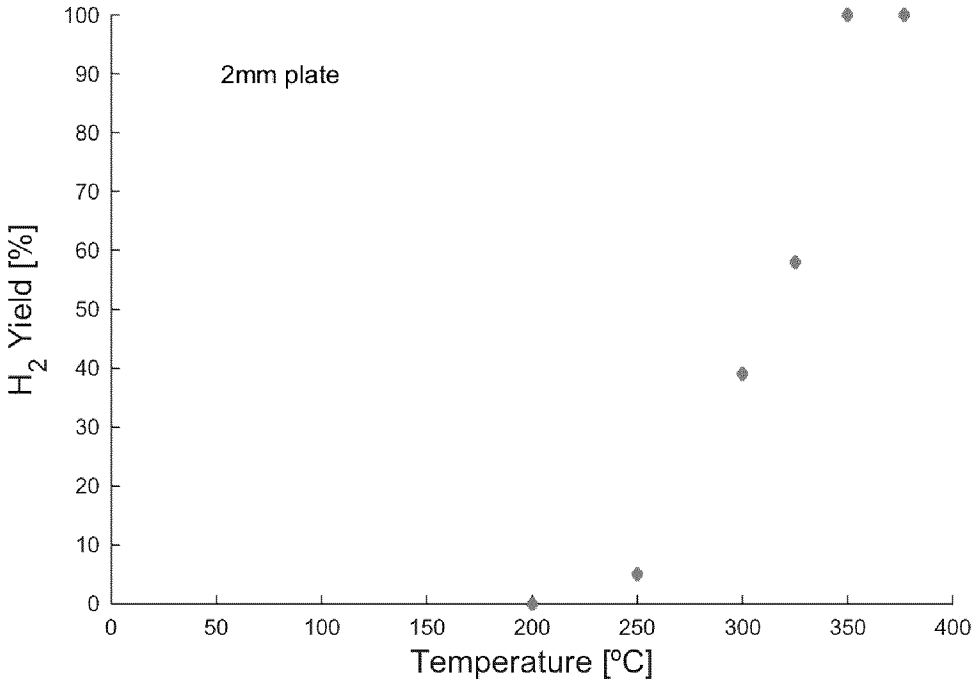
2mm plate
H2 Yield [%]
Temperature [°C]
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

FIG. 1B

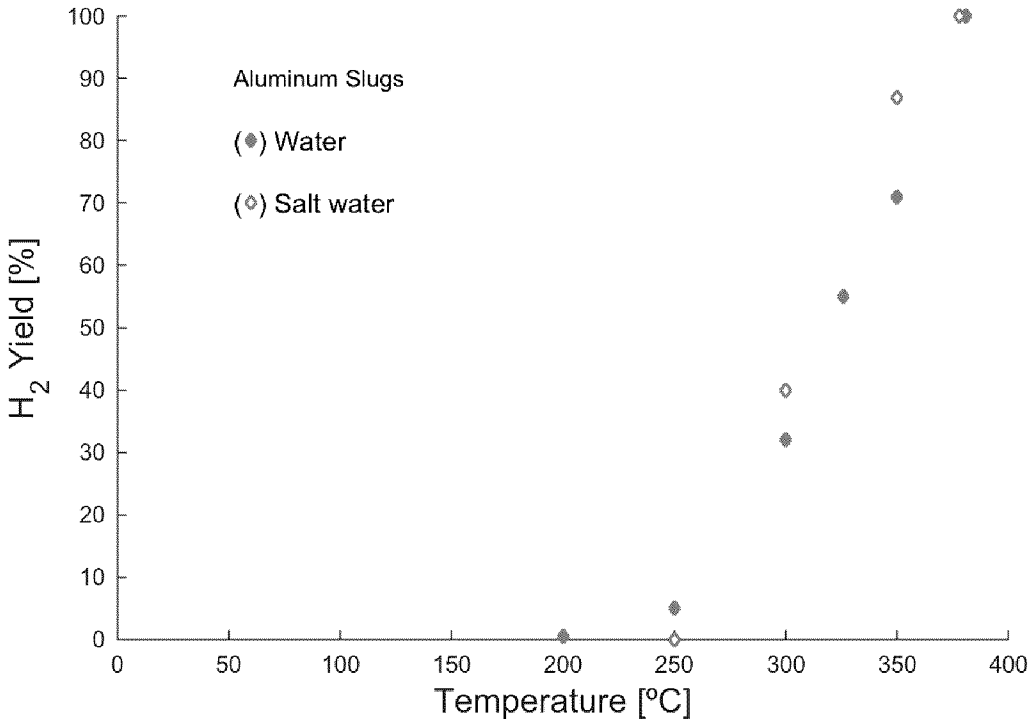
Aluminum Slugs
(♦) Water
(◇) Salt water
H_2 Yield [%]
Temperature [°C]
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

FIG. 1C

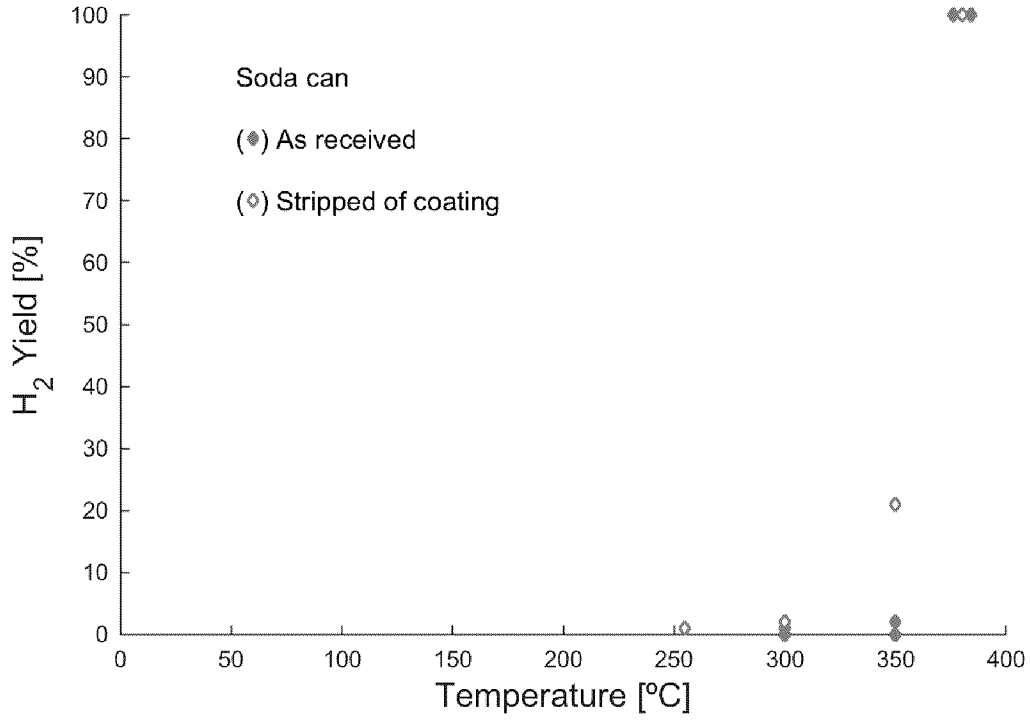
Soda can
(♦) As received
(◇) Stripped of coating
H_2 Yield [%]
Temperature [°C]
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

FIG. 2A

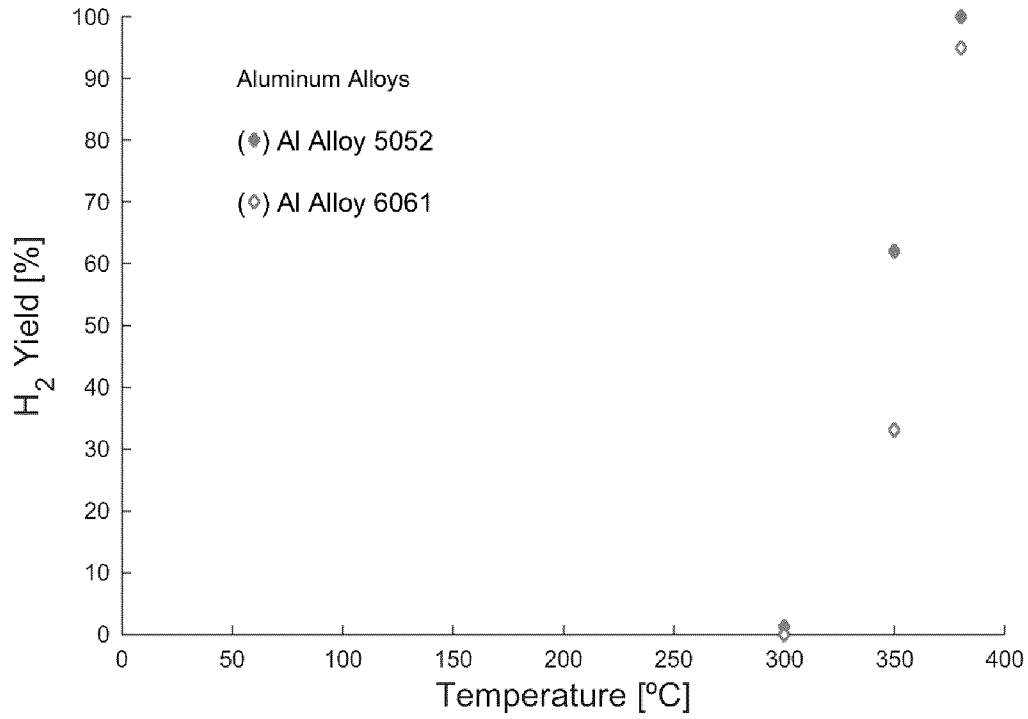
Aluminum Alloys
(♦) Al Alloy 5052
(◇) Al Alloy 6061
H_2 Yield [%]
Temperature [°C]
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

FIG. 2B

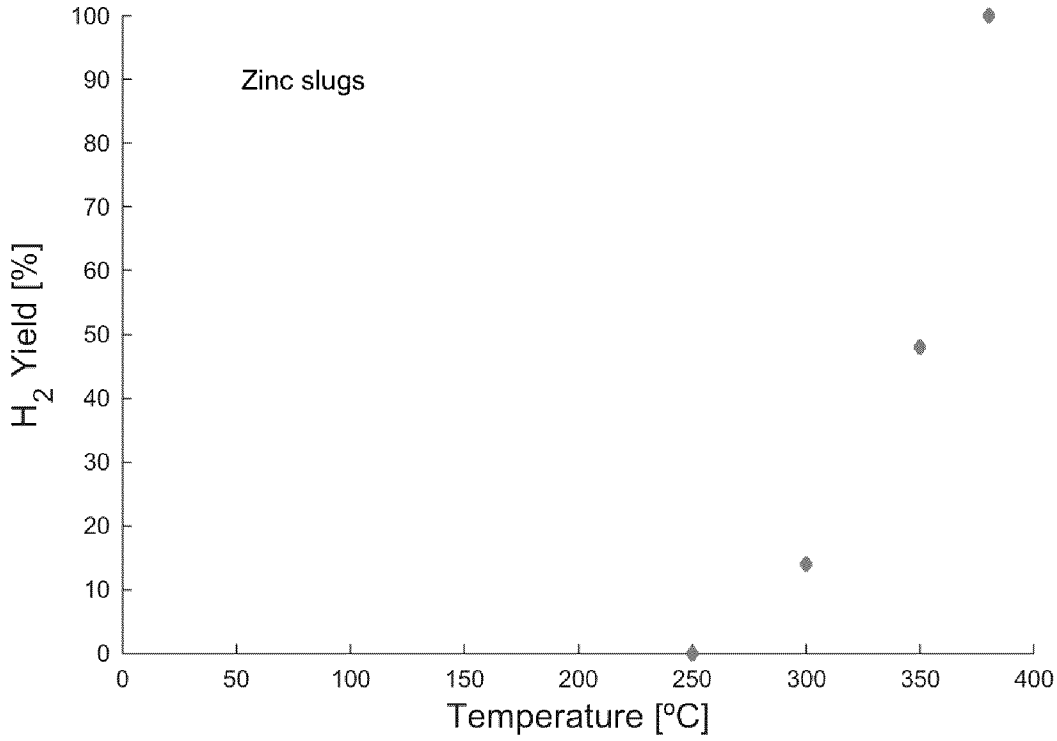
Zinc slugs
H_2 Yield [%]
Temperature [°C]
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

FIG. 3A

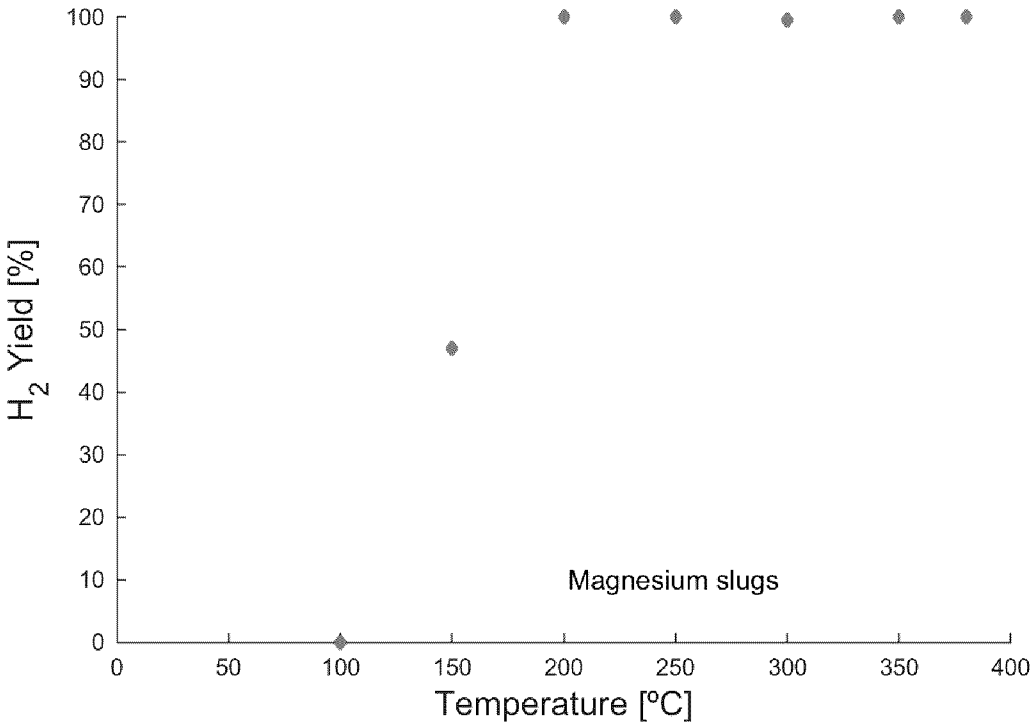
100
90
80
70
60
50
40
30
20
10
0
H_2 Yield [%]
Magnesium slugs
0
50
100
150
200
250
300
350
400
Temperature [°C]

FIG. 3B

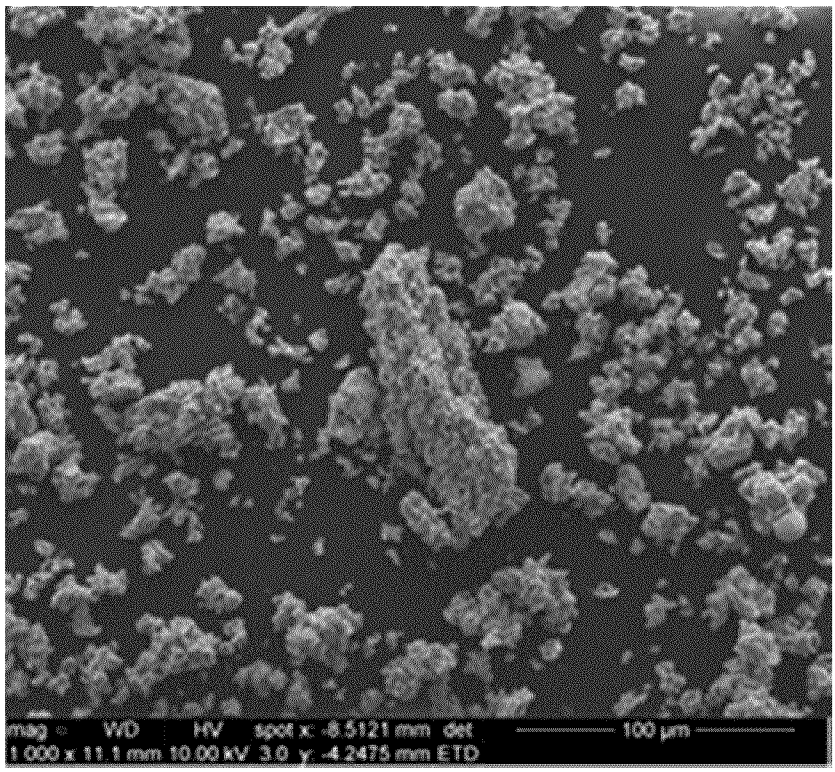
100 µm

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2020/050392

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C01B 3/08*** (2006.01) , ***C01B 3/02*** (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2006.01): C01B 3/08, C01B 3/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Keywords used across the whole IPC.

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Databases: Canadian Patents Database, Questel Orbit, Google Scholar
Keywords: "hydrogen production", "hydrogen gas production", "metal-water reaction", supercritical, water, "aqueous solution", hydrogen, metal, reaction

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VOSTRIKOV, A.A. et al., "The Formation of Al2O3 Nanoparticles in the Oxidation of Aluminum by Water Under Sub- and Supercritical Conditions", *Russian Journal of Physical Chemistry B*, 19 January 2011 (19-01-2011), Vol. 4, pp. 1051-1060. * Page 1051, column 2, paragraph 2; page 1052, column 2, paragraph 4.	1-13
A	BERGTHORSON, J.M. et al. "Metal-Water Combustion for Clean Propulsion and Power Generation", *Applied Energy*, 4 November 2016 (04-11-2016), Vol. 186, pp. 13-27. * The same applicant * * The whole document *	1-13
A	ALINEJAD, B. et al. "A Novel Method for Generating Hydrogen by Hydrolysis of Highly Activated Aluminum Nanoparticles in Pure Water", *International Journal of Hydrogen Energy*, 14 August 2009 (14-08-2009), Vol 34, pp. 7934-7938. * The whole document *	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"D"	document cited by the applicant in the international application	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"E"	earlier application or patent but published on or after the international filing date	"&"	document member of the same patent family
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 04 May 2020 (04-05-2020)	Date of mailing of the international search report 04 June 2020 (04-06-2020)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 819-953-2476	Authorized officer Kevin Anderson (819) 639-8409