



HYDROGEN GENERATOR AND METHOD OF OPERATING IT

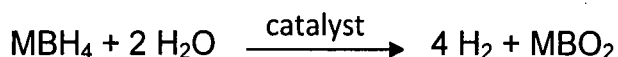
FIELD OF THE INVENTION

5 The invention relates to a hydrogen generator which can be a hydrogen generator comprising a container for containing an aqueous solution of at least one metal hydride, a reactor chamber containing a catalyst, a pump for pumping the aqueous solution from the container to the reactor chamber, a first liquid collecting area communicating with the reactor chamber for
10 collecting the reaction exhaust products, an exhaust products outlet exiting from the collecting area and a gas outlet for extracting the gaseous products, or a hydrogen generator comprising a container for containing a liquid reaction agent, a reactor chamber containing at least one metal hydride in solid form, a pump for pumping the liquid reaction agent from the container to the reactor
15 chamber, a first liquid collecting area communicating with the reactor chamber for collecting the reaction exhaust products, an exhaust products outlet exiting from the collecting area and a gas outlet for extracting the gaseous products, and to a method of operating it.

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BACKGROUND OF THE INVENTION

Hydrogen generators of the kind mentioned above usually serve to supply fuel cells with gaseous hydrogen, e.g. for vehicles such as small aircrafts. Particularly for this purpose low volume and light weight are essential.
25 Hydrogen is chemically generated by a following reaction



where MBH_4 and MBO_2 respectively represent a metal borohydride and a
30 metal metaborate. While H_2 is the useful product, MBO_2 and residual water, partly in the form of steam, are exhaust products. These exhaust products, dissolved in aqueous solution, have a high tendency to crystallize.



According to US 2004/0009379 A1 the exhaust product is separated into dry residuals which are collected in a special vessel, and steam which can be vented to the atmosphere. The drying equipment and the mentioned vessel lead to a bulky and heavy construction.

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According to US 2006/0225350 A1, the exhaust is processed in a gas / liquid separator and the exhaust is drained to a collecting tank. Again, the construction is unfavourable with respect to size and weight. This prior art, further, uses a closed loop control of the pressure and the temperature in the reaction chamber, mentioned pressures are from 0 to 41 kPa and mentioned temperatures are 20 to 50°C.

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Due to US 7,083,657 B2, the exhaust product is separated into its gaseous and liquid components, the liquid component being fed back to the reaction chamber. In this prior art, the problem is further discussed that in the reaction exhaust products the salt product tends to crystallize, thereby clogging the reaction chamber or the downstream conduits and apparatus.

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20 SUMMARY OF THE INVENTION

It is an object of the invention to provide for a compact, lightweight hydrogen generator. For such compact generators with small sized element, it is particularly necessary to avoid crystallization of the reaction exhaust products which, in this case hypercritically congests the conduits. For preventing the crystallization, the conduit extending from the exhaust products outlet via the controllable valve to a conduit end carries heating devices at least along part of its length, an elevated temperature counteracts the crystallization.

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To obtain such compact and lightweight generator, according to the invention, in the generator the exhaust products outlet opens to the environment via a controllable valve. By such disposals, the components for separating or drying the exhaust products are no longer necessary.

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A further aspect with reference to the compactness is the fact that the saturation water vapour partial pressure depends on the temperature but keeps materially constant if the gas pressure of the mixture containing the water vapour in the reaction chamber is increased. Upon hydrolyses, it is possible to generate the hydrogen under a high pressure in the reaction chamber by controlling the flow rate of the pump and the power of heating devices of the reaction chamber, where a preferred temperature is at least 70°C. For this reason, the reactor chamber preferably contains temperature and pressure sensors, it is coupled to temperature adjusting devices, and the sensors are connected to a control unit controlling the pump and the temperature adjusting devices.

For maintaining the desired pressure in the reaction chamber the first liquid collecting area contains first liquid level sensors coupled to a control unit controlling the controllable valve which opens and closes in intervals.

In the generator the gas outlet is coupled via a cooling device to a gas / liquid separator containing a second liquid collecting area including second liquid level sensors, as is known in the prior art; To said area a discharging conduit is connected which leads via a controllable valve, which opens and closes in intervals, alternatively to the environment or to a point upstream of the pump. The liquid is almost pure water which, if conducted to the environment, is discharged similarly as the reaction exhaust products, and if conducted to a point upstream of the pump, can be used for diluting the fuel, similarly to the prior art US 7,083,657 B2, or for a cleaning cycle

For avoiding crystallization of the reaction exhaust products in the reaction chamber and its downstream elements, high pressure and high temperature according to mutual relations are preferably used, as characterized in claims 9 to 11.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and further objects, features and advantages of the present invention will become apparent from the following description of preferred
5 embodiments with reference to the accompanying drawings.

Fig. 1 shows an embodiment of the hydrogen generator of the invention

Fig. 2 shows a section view of an alternative embodiment of the invention

Fig. 3 shows a section view of another alternative embodiment of the invention

10 Fig. 4 shows a graph of the correlation between pressure and temperature

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

15 A hydrogen generator 1 according to fig. 1 comprises a bag shaped fuel container 2 that contains an aqueous solution of a metal hydride, in the present example sodium borohydride, which via a conduit 3 and a check valve 4 is conducted to a pump 5, here a peristaltic pump, which pumps the solution under pressure via a conduit 6 to a reaction chamber 7. Contained in the
20 reaction chamber is a fixed bed catalyst device 10, e.g. consisting of porous ceramic substrates with a supported catalyst of known kind. An alternative catalyst device, not shown, consists of movable catalyst supports to be immersed into the solution in the reaction chamber. The reaction chamber can be heated by a heater 11 and can be cooled by fans 12. According to
25 alternatives not shown, the heater 11 and the cooling fans 12 can be replaced by heat pipes. In the reaction chamber, the reaction mentioned above takes place, releasing hydrogen and reaction exhaust products.

The hydrogen escapes the reaction chamber through a gas outlet 13, flows
30 through a cooling coil 14 and is fed into a gas / liquid separator 19. In this separator, the hydrogen is withdrawn through filter units 20 and a pressure regulator 21 and fed via a conduit 22 to a fuel cell system 23.

The reaction chamber 7 contains a pressure sensor 27 and temperature sensors 28. A control unit 29 in the hydrogen generator 1 picks up the values of the pressure sensor 27 and the temperature sensors 28 and regulates the flow rate of the pump 5 as well as the power of the heater 11 and of the fans 12 according to a given program.

In the lower part of the reaction chamber 7 there is a first liquid collecting area 30 wherein the slurry like exhaust products 31 accumulate. An exhaust products outlet 32 at the bottom of area 30 extends to a conduit 36 and further via a controllable valve 37 to a conduit end 38 that is located outside the casing of the hydrogen generator 1. In area 30 two liquid level sensors 39, 40 are arranged at slightly different level heights and are connected to the control unit 29, which controls the valve 37. When the higher liquid level sensor 40 gives a signal, the control unit 29 opens the valve 37 between conduit 36 and conduit end 38, discharging the exhaust products 31 through end 38 into the surrounding environment. As surrounding environment the atmosphere is usually defined; also the surrounding environment can be a collection container open to atmosphere, that is no part of the hydrogen generator and not shown in the figures, wherein the exhaust products are accumulated. When the lower liquid level sensor 39 gives a signal, the control unit 29 closes the valve 37. To maintain the predefined pressure in the reaction chamber 7 the level difference between the sensors 39,40 is small as well as the discharged amount, keeping the gas volume in chamber 7 almost constant. The frequency of opening the valve 37 is rather high and the duty rate can be in the order of 1:10. The path from the outlet 32 to the conduit end 38 is short and does not contain complex elements, thereby almost preventing the danger of crystallization. As a further measure the conduit 36 and the valve 37 are at least partially heated.

In the lower part of gas / liquid separator 19, the water condensed from the mixture of hydrogen and steam and cooled in the cooling coil 14 accumulates in a second liquid collecting area 45. In the bottom of area 45, a discharging conduit 46 is connected that leads to the valve 37. Two level sensors 47, 48 are placed in the area 45 and connected to the control unit 29, working similar

to level sensors 39, 40. The valve 37, controlled by control unit 29, can block the exit of the liquid through the discharging conduit 46, can connect the discharging conduit 46 to the conduit end 38 so as to discharge the condensed water or can connect the discharging conduit 46 to a conduit 49, located to a point upstream of the pump 5 either into the fuel container 2 or directly into pump 5. The latter can be suitable for a cleaning cycle for restarting the generator after an interruption, thus preventing clogging of the system by crystallization; or for diluting the solution of the metal hydride.

According to different embodiment shown in fig. 2, located directly in the reaction chamber 7 and fixed by fixing devices 51 there is a solid block 52 of a chemical hydride. A reaction agent in the fuel container 2 that is an aqueous acidic solution such as phosphoric acid to which possibly a catalyst is added, is transported via the conduit 3 to the check valve 4 and pump 5 and further to a distributor 53, that is located at the top of reacting chamber 7 and arranged to spray the reaction agent to the solid block 52 thereby originating the reaction. The gas outlet 13 in this embodiment is situated near the bottom of the chamber 7, but above the liquid collecting area 30 as in the embodiment of fig. 1.

Fig. 3 shows a still different constellation of the reaction chamber 7, which is supplied by the fuel solution of fig. 1 and is equipped with the fixed bed catalyst device 10 and comprises cooling ribs 54, and the liquid collecting area 30 is constructed as a separate container 55 connected to the catalyst device 10 by a tube 56. The gas outlet 13 is arranged in the top part of the container 55, and the exhaust products outlet at the lower part of the container 55 at a level lower than the lower level sensor 39.

In the graph of fig. 4, the pressure in kPa at the ordinate is plotted against the temperature in °C at the abscissa. Three curves 60, 61, 62 show limits of the correlation between pressure and temperature. Curve 60 shows generally the

temperature limit dependent on the pressure, in the area left of curve 60 (lower temperatures) the danger of crystallization is too high. Curve 61 and 62, referring to the embodiment of fig. 1, show limits of the correlation of pressure and temperature for different concentrations of sodium borohydride in water, i.e. curve 61 for a 25% and curve 62 for a 20% solution, wherein for both cases the operating points should be selected between curve 60 and curve 61 or respectively 62 for obtaining optimal conditions to avoid crystallization of the exhaust products. These curves appear in the tables of claims 10 to 12.

REFERENCE LIST

	1	hydrogen generator
	2	fuel canister
5	3	conduit
	4	check valve
	5	pump
	6	conduit
	7	reaction chamber
10	10	fixed bed catalyst device
	11	heater
	12	fans
	13	gas outlet
	14	cooling coil
15	19	gas / liquid separator
	20	filter units
	21	pressure regulator
	22	conduit
	23	fuel cell system
20	27	pressure sensor
	28	temperature sensors
	29	control unit
	30	first liquid collecting area
	31	exhaust products
25	32	exhaust products outlet
	36	conduit
	37	controllable valve
	38	conduit end
	39	lower liquid level sensor
30	40	higher liquid level sensor
	45	second liquid area
	46	conduit
	47	level sensor
	48	level sensor

	49	conduit
	51	fixing devices
	52	solid block
	53	distributer
5	54	cooling ribs
	55	container
	56	tube
	60	curve
	61	curve
10	62	curve

CLAIMS

1. Hydrogen generator (1) comprising a container (2) for containing an aqueous solution of at least one metal hydride, a reaction chamber (7) containing a catalyst (10), a pump (5) for pumping the aqueous solution from the container to the reactor chamber, a first liquid collecting area (30) communicating with the reactor chamber for collecting the reaction exhaust products (31), an exhaust products outlet (32) exiting from the collecting area and a gas outlet (13) for extracting the gaseous products, characterized in that the exhaust products outlet opens to the environment via a controllable valve (37).
2. Hydrogen generator (1) comprising a container (2) for containing a liquid reaction agent, a reaction chamber (7) containing at least one metal hydride in solid form (52), a pump (5) for pumping the liquid reaction agent from the container to the reaction chamber, a first liquid collecting area (30) communicating with the reactor chamber for collecting the reaction exhaust products (31), an exhaust products outlet (32) exiting from the collecting area and a gas outlet (13) for extracting the gaseous products, characterized in that the exhaust products outlet opens to the environment via a controllable valve (37).
3. The generator according to claim 1 or 2, characterized in that the reaction chamber (7) contains temperature (28) and pressure sensors (27).
4. The generator according to claim 3, characterized in that the reaction chamber (7) is coupled to temperature adjusting devices (11, 12).
5. The generator according to claim 4, characterized in that the sensors (27, 28) are connected to a control unit (29) controlling the pump (5) and the temperature adjusting devices (11, 12).

6. The generator according to any of claims 1 to 5, characterized in that the first liquid collecting area (30) contains first liquid level sensors (39, 40) coupled to a control unit (29) controlling the controllable valve (37).

5 7. The generator according to any of claims 1 to 6, characterized in that a conduit (36) extending from the exhaust products outlet (32) via the controllable valve (37) to a conduit end (38) carries heating devices at least along part of its length.

10 8. The generator according to any of claims 1 to 7, characterized in that the gas outlet (13) is coupled via a cooling device (14) to a gas/ liquid separator (19) containing a second liquid collecting area (45) including second liquid level sensors (47, 48), to said area a discharging conduit (46) is connected which leads via a controllable valve (37) alternatively
15 to the environment or to a point upstream of the pump (5).

9. The generator according to any of claims 1 to 8, characterized in that the exhaust products outlet (32) opens via a controllable valve (37) to a container open to atmosphere that accumulates the reaction exhaust
20 products (31).

10. A method of operating the hydrogen generator according to claim 5 or any of claims 6 to 9 if referred to claim 5, characterized in that the reaction in the reaction chamber (7) is carried out at a temperature, the
25 minimum temperature being defined by a curve (60) connecting the points of the following table:

Temperature (°C)	70	85	100	115
Pressure (kPa)	100	300	800	1200

11. The method of claim 10 if referred to claim 1, characterized in that when using a 25% sodium borohydride (NaBH₄) solution in water
30 (H₂O) the pressure in the reaction chamber (7) is controlled by the

pump (5) dependent on the maximum temperature according to a curve (61) connecting the points of the following table:

Temperature (°C)	85	100	115	130
Pressure (kPa)	300	550	800	1050

12. The method of claim 10 if referred to claim 1, characterized in that when using a 20% sodium borohydride (NaBH_4) solution in water (H_2O) the pressure in the reaction chamber (7) is controlled by the pump (5) dependent on the maximum temperature according to a curve (62) connecting the points of the following table:

Temperature (°C)	70	85	100	115	130
Pressure (kPa)	100	150	230	350	500

13. A method of operating the hydrogen generator according to claim 6 or according to any of claims 7 to 12 if referred to claim 6, characterized in that the controllable valve (37) connected to the exhaust products outlet (32) of the first liquid collecting area (30) opens and closes in intervals controlled by the first liquid level sensors (39, 40).

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14. A method of operating the hydrogen generator according to claim 8 or according to any of claims 9 to 13 if referred to claim 8, characterized in that the controllable valve (37) connected to the discharging conduit (46) outlet of the second liquid collecting area (45) opens and closes in intervals controlled by the second liquid level sensors (47, 48).

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