

HYDROGEN GENERATOR AND METHOD OF OPERATING HYDROGEN GENERATORS



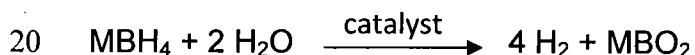
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5 FIELD OF THE INVENTION

The invention relates to a hydrogen generator comprising a container for containing an aqueous solution of at least one metal hydride, a reaction chamber containing a catalyst arrangement, an exhaust products outlet exiting from the reaction chamber and a gas outlet for extracting the gaseous products and a flow conduit connecting the container with the reaction chamber, and to a method for operating a hydrogen generator.

BACKGROUND OF THE INVENTION

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



where MBH_4 and MBO_2 respectively represent a metal borohydride and a metal metaborate. While H_2 is the useful product, MBO_2 and residual water, are exhaust products.

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According to US 6,534,033, B1, a supply of solution is used which communicates with the catalyst until the metal hydride is consumed to some degree. The solution contains a stabilizing agent providing a pH value of 7 or greater to avoid unintentional decomposition of the hydride. This generator is rather bulky and has a permanent high weight.

US patent 7,530,931 B2 teaches a hydrogen generator using a spent fuel container which is adapted to collect the exhaust products from the catalyst



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chamber. However, these exhaust products still contain residual feed material thereby reducing the overall yield.

Due to US 7,540,892 B2, a fuel storage chamber containing a membrane at the other side of which a hydrogen separation chamber is arranged wherein the exhaust products accumulate. Again, there is no optimal yield of the hydride.

All the above hydrogen generators are of low efficiency and have a not optimal weight and volume.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a compact, lightweight hydrogen generator and a method of use which allows such lightweight hydrogen generators. A compact, lightweight hydrogen generator is possible by providing for a faster reaction which can be obtained by using an aqueous solution of the at least one metal hydride having a pH value of between 5.5 and 7, preferably between 6.2 and 7. This is that the aqueous solution is not stabilized or even slightly de-stabilized. Thereby the catalyst and reaction chamber volume and weight can be reduced while having a reaction with the same degree of completeness, particularly if utilising the hydrogen already generated in the container. Such hydrogen generation already starts in non-operation mode and depends on the temperature. In many applications this consequence is of minor importance, e.g. in a cold environment or in cases where the starting materials, i.e. the metal hydride and the water, are mixed and filled into the container shortly before use.

If using such non-stabilized or de-stabilized solution, it is useful that the container for containing the aqueous solution, besides a first outlet communication with the flow conduit for liquid output to the reaction chamber, comprises a second outlet for gaseous output, the second outlet being connected to a valve. This valve allows the release of the hydrogen generated in the container into the surrounding or into the main hydrogen outlet. Further, it may be advantageous to feed this hydrogen to an additional small fuel cell,

which may be a passive fuel cell known in the art. The current generated thereby can be used to charge a battery.

5 A further aspect with reference to the compactness and high efficiency is the fact that the reaction chamber is divided into a first and second volume, the first volume containing a first, upstream catalyst and the second volume containing a second, downstream catalyst, the first volume being smaller than the second volume. The catalysts, known in the art, can be transition metal catalysts, i.e. ruthenium and nickel on a support substrate like carbon or silicon carbide. The first, upstream catalyst preferably presents 70 to 80% of the total catalyst of the reaction chamber. The two-catalyst reaction chamber provides for a more complete exploitation of the hydrogen stored in the metal hydride and is particularly of interest if using a non-stabilized metal hydride solution, which is led through the reaction chamber at a relatively high speed compared to conventional systems.

Preferably the second volume of the reaction chamber comprises a liquid collecting area for collecting an intermediate, partially reacted solution. Thereby, the drainage of the exhaust products can be easily controlled upon using an exhaust outlet valve located downstream of the exhaust products outlet and controlled by a control unit, and a liquid level sensor located in the liquid collecting area and coupled to the control unit. When the accumulated liquid reaches a predetermined level, the control unit opens the exhaust outlet valve. If the hydrogen generator has a determined orientation when in use, the accumulating liquid has a level rising up to the liquid level sensor, and the gas outlet is positioned above the liquid level sensor.

If the aqueous solution of the container is not transported by gravity to the reaction chamber, a pump, preferably a controllable pump is positioned between the container and the first volume of the reaction chamber.

For using such two-catalyst-reaction chamber, and a non-stabilized metal hydride solution, it is of advantage, that the ratio of the time of stay of the aqueous solution of the at least one metal hydride in the first volume

containing the first, upstream catalyst to the time of stay of the aqueous solution of the at least one metal hydride in the second volume containing the second, downstream catalyst is larger than 1 to 4, preferably larger than 1 to 10 and even more preferably larger than 1 to 30. In the upstream catalyst, the hydrogen generated therein is more than the hydrogen generated in the downstream catalyst for the reason that the solution if brought in contact with the upstream catalyst is immediately decomposed to a high degree.

10 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 embodiments with reference to the accompanying drawings.

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

Fig. 2 shows an alternative embodiment of the reaction chamber

20 DETAILED DESCRIPTION OF PREFERRED EMBOMENTS

A hydrogen generator according to fig. 1 comprises a fuel container 1 that contains an aqueous solution 2 of a metal hydride, in the present example sodium borohydride, which is contained in the solution at a concentration of 25%, which via a first outlet 3 and a check valve 4 is conducted to a pump 5, here a peristaltic pump, which pumps the solution via a flow conduit 6 to a reaction chamber 7. The fuel container 1 has a filler cap assembly 10, a dip tube 11, one end connected to the first outlet 3 for liquid output and the other end remaining at the bottom of the interior of the fuel container 1, and a second outlet 12 for gaseous output, connected to a relief valve 13.

In the prior art the solution 2, besides the metal hydride, contains a stabilizing agent, usually sodium hydroxide for avoiding unintended decomposition. The

solution used in the described example does not use any stabilizing agent or even a small amount of a de-stabilizing agent, which is an acid, so as to speed up and enhance the reaction and whereby a smaller and lighter weight reaction chamber suffices.

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Considering the unintended decomposition in the fuel container 1, the operator fills in the materials for the metal hydride solution, i.e. the sodium borohydride and the water, short time before demand of the hydrogen through the filler cap assembly 10. Depending on the temperature inside the container, the time of stay of the solution should be short, so as to avoid premature generation of hydrogen. Still, some hydrogen arises in the container 1 and is discharged via second outlet 12 and valve 13. This hydrogen, in the present embodiment, is conducted to a secondary, passive fuel cell 14 charging a battery. The main hydrogen mass flow produced in the reaction chamber 7 may serve as fuel for a primary, active fuel cell (not shown). Alternatively the second output 12 can release the hydrogen via valve 13 into the surrounding (not shown).

The reaction chamber 7 is contained in a housing 20 and is divided into a first volume 21, the first volume containing a first, upstream catalyst 22, and into a second volume 23 containing a second, downstream catalyst 24. The first catalyst 22 consists of a packed bed of catalyst elements, the packed bed almost completely filling the first volume 21 and being supported by a first mesh 25 fixed to the housing 20. And the second catalyst 24 also consisting of a packed bed of catalyst elements, in the described embodiment, fills the bottom part of the second volume 23 and is supported by a second mesh 26 also fixed to the housing 20. The housing 20 has an solution inlet 31 connected to the conduit 6, an exhaust product outlet 32 connected to the exhaust outlet valve 33 and a gas outlet 34 for extracting the useful product, i.e. the generated hydrogen possibly still containing some water vapour. If desired, dehumidifying devices are added (not shown). Further, if desired, the second output 12 of the container 1 is coupled with the gas outlet 34 of the reaction chamber 7

The second volume 23, partly already filled with the second catalyst 24, constitutes a liquid collecting area 35. A liquid level sensor 36 is placed at the top end of the liquid collecting area 35 and is connected to the control unit 37, controlling the valve 33. It also controls the pump 5 dependent on the demand of hydrogen.

The aqueous solution 2 that reaches the reaction chamber 7 via the inlet 31 meets the first catalyst 22 and immediately begins to react, releasing about 90% of the gaseous products. When the intermediate, partially reacted solution exits the first volume 21 through the first mesh 25, it still contains non-reacted starting material. It enters the second volume 23 and contacts the second catalyst 24 for almost completing the reaction and obtaining additional 9% of hydrogen. The second volume 23 having about the same size as the first volume 21, but contains only 20 to 30 % of the complete catalyst arrangement.

The time that the reacting solution needs to flow through the first catalyst 22 and then to remain in the second volume 34 depends on the amount of hydrogen that is produced and withdrawn from the hydrogen generator. At maximum hydrogen mass flow rate the reacting solution flows through the first catalyst 22 in 2 to 3 seconds, while remaining in the second volume 34 much longer, i.e. for about 45 seconds. If only partial hydrogen mass flow rate is desired the length of stay in the first 21 and second volume 23 elongates inversely proportional, i.e. half of the mass flow rate doubles the time of stay in both volumes 21 and 23. The times of stay in both volumes 21 and 23 are determined by controlling the pump 5 and the exhaust outlet valve 33, as well as by mutual sizes of the volumes 21 and 23.

As usual, the reaction chamber is operated under elevated temperature of e.g. 80°C and of elevated pressure of 450 kPa (4.5 bar). Devices for temperature and pressure regulation are associated to the reaction chamber in a usual manner (partially not shown).

Fig. 2 shows an alternative embodiment of the reaction chamber 7 wherein same reference numbers designate same components. According to fig. 2 the second, downstream catalyst 24 is not filling the bottom part of the second

volume 23 but constitutes aligning along the wall of the housing 20 resulting in the shape of a pan.

According to a further alternative embodiment (not shown) the second,
5 downstream catalyst can be a packed bed filling the complete second volume.
The catalyst arrangement, in this case, can provide a concentration gradient.

REFERENCE LIST

	1	fuel container
	2	aqueous solution
5	3	first outlet
	4	check valve
	5	pump
	6	flow conduit
	7	reaction chamber
10	10	filler cap assembly
	11	dip tube
	12	second outlet
	13	valve
	14	secondary fuel cell
15	20	housing
	21	first volume
	22	first upstream catalyst
	23	second volume
	24	second downstream catalyst
20	25	first mesh
	26	second mesh
	31	solution inlet
	32	exhaust products outlet
	33	exhaust outlet valve
25	34	gas outlet
	35	liquid collecting area
	36	liquid level sensor
	37	control unit

CLAIMS

1. Hydrogen generator comprising a container (1) for containing an aqueous solution (2) of at least one metal hydride, a reaction chamber (7) containing a catalyst arrangement (22, 24), an exhaust products outlet (32) exiting from the reaction chamber and a gas outlet (34) for extracting the gaseous products and a flow conduit (6) connecting the container with the reaction chamber, characterized in that the reaction chamber (7) is divided into a first (21) and second volume (23), the first volume containing a first, upstream catalyst (22) and the second volume containing a second, downstream catalyst (24), the first volume being smaller than the second volume.
2. The hydrogen generator according to claim 1, characterized in that the second volume (23) comprises a liquid collecting area (35) for collecting an intermediate, partially reacted solution.
3. The hydrogen generator according to claim 2, characterized in that the exhaust product outlet (32) downstream of the second volume (23) of the reaction chamber (7) is connected to an exhaust outlet valve (33) controlled by a control unit (37).
4. The hydrogen generator according to claim 3, characterized in that the liquid collecting area (35) contains a liquid level sensor (36) coupled to the control unit (37) for controlling the exhaust outlet valve (33).
5. The hydrogen generator according to claim 4, characterized in that in an orientation determined reaction chamber (7), the gas outlet (34) is positioned above the liquid level sensor (36).
6. The hydrogen generator according to any of claims 1 to 5, characterized by a pump (5) for pumping the aqueous solution (2) from the container (1) to the first volume (21) of the reaction chamber (7).

7. Hydrogen generator, if desired according to any of claims 1 to 6, comprising a container (1) for containing an aqueous solution (2) of at least one metal hydride, a reaction chamber (7) containing a catalyst arrangement (22, 24), an exhaust products outlet (32) exiting from the reaction chamber and a gas outlet (34) for extracting the gaseous products and a flow conduit (6) connecting the container with the reaction chamber, characterized in that the container (1) for containing the aqueous solution (2), besides a first outlet (3) communication with the flow conduit (6) for liquid output to the reaction chamber (7), comprises a second outlet (12) for gaseous output, the second outlet being connected to a valve (13).
8. The hydrogen generator according to claim 7, characterized in that at least one of the gas outlet (34) of the reaction chamber (7) and the second outlet (12) of the container (1) are connected to a respective fuel cell.
9. The hydrogen generator according to claim 7, characterized in that the second outlet (12) of the container (1) is coupled with the gas outlet (34) of the reaction chamber (7).
10. The hydrogen generator according to claim 7, characterized in that the second outlet (12) of the container (7) opens into the surrounding.
11. A method of operating a hydrogen generator comprising a container (1) for containing an aqueous solution (2) of at least one metal hydride, a reaction chamber (7) containing a catalyst arrangement (22, 24), an exhaust products outlet (32) exiting from the reaction chamber and a gas outlet (34) for extracting the gaseous products and a flow conduit (6) connecting the container with the reaction chamber, preferably according to any of claims 1 to 10, characterized in that the aqueous solution (2) of the at least one metal hydride used in the container (1) has a pH value of between 5.5 and 7.

12. The method according to claim 11, characterized in that the aqueous solution (2) of the at least one metal hydride used in the container (1) has a pH value of between 6.2 and 7.
- 5 13. The method according to claim 11 or 12, of operating a hydrogen generator according to any of claims 1 to 6, characterized in that the ratio of the time of stay of the aqueous solution (2) of the at least one metal hydride in the first volume (21) to the time of stay of the aqueous solution (2) of the at least one metal hydride in the second volume (23) is larger than 1 to 4.
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14. The method according to claim 13, characterized in that the ratio of the time of stay of the aqueous solution (2) of the at least one metal hydride in the first volume (21) to the time of stay of the aqueous solution (2) of the at least one metal hydride in the second volume (23) is larger than 1 to 10.
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15. The method according to claim 14, characterized in that the ratio of the time of stay of the aqueous solution (2) of the at least one metal hydride in the first volume (21) to the time of stay of the aqueous solution (2) of the at least one metal hydride in the second volume (23) is larger than 1 to 30.
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