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(54) **APPARATUS FOR THE ELECTRICAL PRODUCTION OF HYDROGEN**

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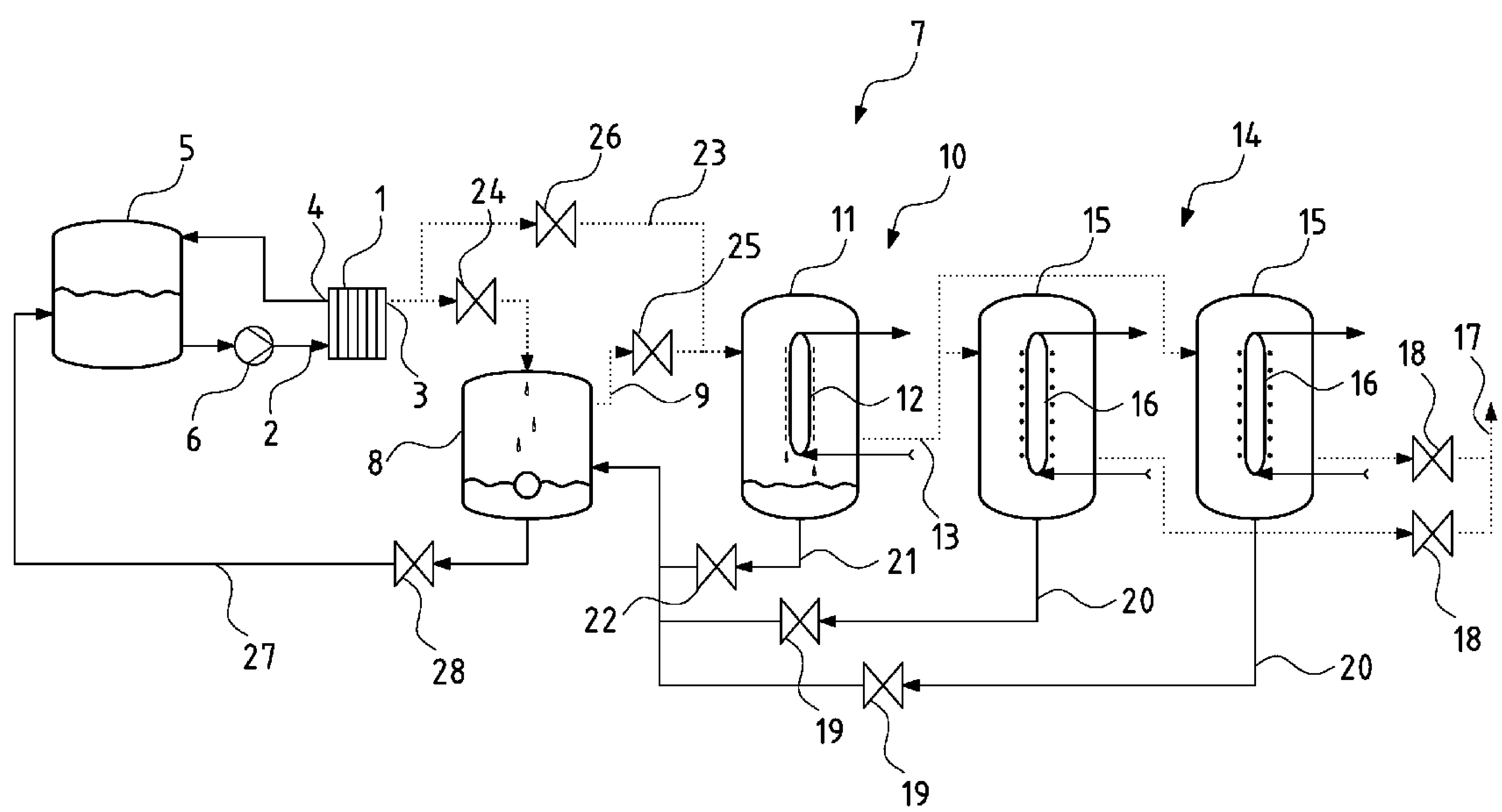
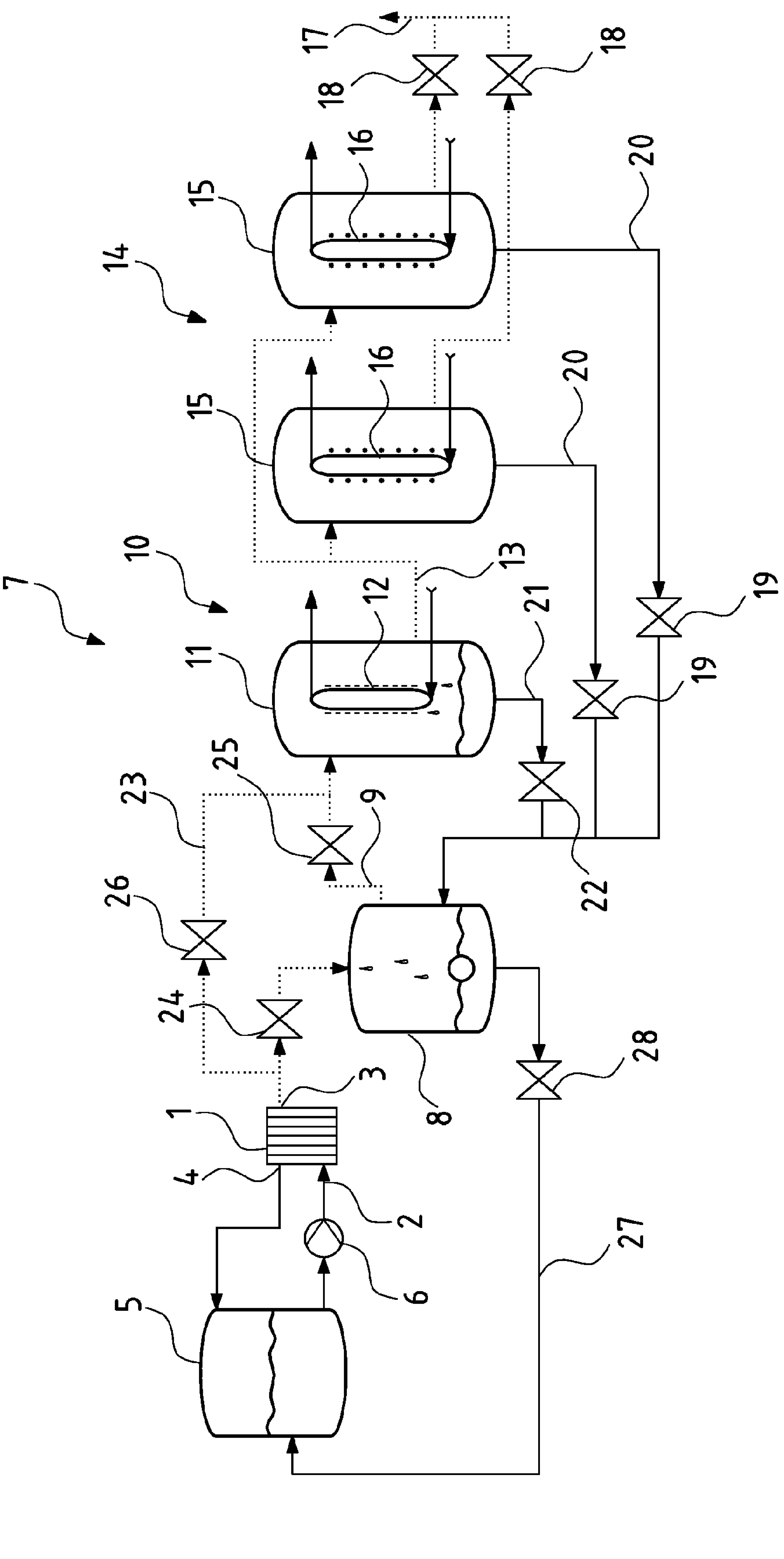
(57) **ABSTRACT**

An apparatus for the electrical production of hydrogen from water includes an electrolyzer (**1**) of the PEM type. The electrolyzer (**1**) has an inlet (**2**) for the introduction of water and a first outlet (**3**) for the hydrogen which is enriched with water and/or water vapor and is produced in the electrolyzer (**1**) and also a second outlet (**4**) for oxygen. A water separation device (**7**) which has at least a thermal separation stage (**10**) adjoins the electrolyzer (**1**).





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APPARATUS FOR THE ELECTRICAL PRODUCTION OF HYDROGEN

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a United States National Phase application of International Application PCT/EP2011/001899 and claims the benefit of priority under 35 U.S.C. §119 of European Patent Application EP 10 004114.4-1227 filed Apr. 19, 2010, the entire contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention pertains to an apparatus for the electrical production of hydrogen from water.

BACKGROUND OF THE INVENTION

[0003] The use of electrolyzers for producing hydrogen from water by means of electric energy belongs to the state of the art. Such electrolyzers exist in various designs. The present invention pertains to an apparatus with an electrolyzer of the PEM type (Polymer Electrolyte membrane), i.e., an electrolyzer that operates with a proton-permeable polymer membrane. Such electrolyzers are typically built in so-called stacks in order to achieve the highest possible gas yield in the smallest possible space. Water is fed on one side here to each membrane, and splitting into hydrogen and oxygen takes place by the electrodes, which are arranged on both sides of the membrane and are supplied with the electrolysis voltage, and hydrogen is produced on one side of the membrane and oxygen on the other side, on which the water is fed.

[0004] To guarantee the permeability to protons of the polymer electrolyte membrane, it is necessary to keep the membrane moist at all times, which does, however, cause the hydrogen produced to be also typically provided with water vapor and/or water in the form of droplets. This water burden being entrained in the hydrogen is undesired in many industrial applications, and it is therefore to be removed. For example, the water burden being entrained is thus to be removed before storage in case of storage of the hydrogen in the metal hydride storage means commonly used now. Mechanical water separators are usually insufficient here, because they are unable to sufficiently free the hydrogen stream of water.

[0005] Arranging a water separation device, which operates according to the principle of pressure swing adsorption, downstream of the electrolyzer on the outlet side for drying the hydrogen therefore belongs to the state of the art. The hydrogen stream, which leaves the electrolyzer and is enriched with water and water vapor, is sent now via one or more molecular sieve beds, which bind the water. However, such binding takes place only as long as the molecular sieve beds are not saturated. The molecular sieve beds must therefore be regenerated at regular intervals. Two molecular sieve beds are therefore provided in practice, and flow takes place through them alternatingly, and the non-active bed is being regenerated by being flushed with dried hydrogen in counterflow. This method is comparatively complicated and impairs especially the efficiency of the apparatus, because the hydrogen used for the backwash usually escapes unused. The method reaches its limits especially with increasing water load in the hydrogen stream, and these apparatuses, which are known from the state of the art, are therefore rather ineffective.

SUMMARY OF THE INVENTION

[0006] Against this background, a basic object of the present invention is to provide an apparatus of this type for the electrical production of hydrogen from water such that it operates with the highest possible efficiency for generated dried hydrogen, i.e., hydrogen freed of a majority of the water.

[0007] The apparatus according to the present invention for the electrical production of hydrogen from water has an electrolyzer of the PEM type, i.e., one that operates with a proton-permeable polymer membrane. This electrolyzer is provided with an inlet for introducing water and with a first outlet for the hydrogen, which is enriched with water and/or water vapor and is produced in the electrolyzer, as well as with a second outlet for oxygen and water. The apparatus has, moreover, a water separation device, whose inlet is connected by a line with the first outlet of the electrolyzer and whose gas-carrying outlet leads to a hydrogen removal port in or at the apparatus, wherein the water separation device has at least one thermal separation stage.

[0008] Thus, the basic idea of the present invention is to provide an electrolyzer with water separation device within the apparatus, wherein the water separation device has at least one first thermal separation stage. It is apparent that a mechanical separation apparatus may be provided as a separator, for example, a cyclone separator or a gravitational separator, in principle, as part of the separation apparatus or arranged upstream of the latter. Such a separation apparatus is not a separation stage in the sense of the present invention. The water separation device is typically of a two- or more than two-stage design, the first stage being a thermal separation stage, in which water is removed from the hydrogen stream by cooling.

[0009] A hydrogen removal port in the sense of the present invention is defined not only as a port in the actual sense of the word but also as a line within or outside the apparatus, which sends the dried hydrogen to a user or to a storage means. Thus, such a hydrogen removal port in the apparatus can send hydrogen to a metal hydride storage means likewise provided in the apparatus via a line.

[0010] The solution according to the present invention is especially advantageous because the electrolyzer can be operated at comparatively high temperature and hence with high efficiency. The gas losses occurring during pressure swing adsorption are completely avoided.

[0011] Since the temperature should be as high as possible for effective operation of the electrolyzer, but, on the other hand, the proton exchange membrane must always be kept wet, favorable operating conditions are obtained in terms of efficiency if the electrolyzer is operated in ranges of 70° C. to 80° C. or higher. The operating temperature is limited upwardly by the boiling point of water, which must not be reached under any circumstances. However, the water load being entrained doubles with every 11° C. or so. Consequently, if the operating temperature is increased from 60° C. to 70° C., the quantity of water to be removed approximately doubles. Such a quantity of water is unproblematic with the solution according to the present invention, namely, with a first thermal separation stage, especially entirely without loss of hydrogen. The electrolyzer of the apparatus according to the present invention can thus be operated substantially more effectively, because it is operated at a higher temperature, without having to accept the losses known from pressure swing adsorption. By contrast, the energy to be used for cooling is markedly lower.

[0012] The water is advantageously separated in two stages, but more than two stages may be provided as well. The second separation stage is advantageously likewise a thermal separation stage. As an alternative, the second separation stage may also be formed by a pressure swing adsorption apparatus. A pressure swing adsorption apparatus is considered for use as the second stage because only a small quantity of water is to be removed from the hydrogen here, but it is important to remove the water as completely as possible. Since the hydrogen is loaded with small quantities of water only, the molecular sieve beds can be used for a comparatively long time before backwash is necessary.

[0013] According to a variant of the present invention, a water-carrying outlet of at least the first separation stage is advantageously connected to the inlet of the electrolyzer by means of a line for returning the water. The connection by means of a line is brought about at least from time to time, i.e., corresponding valves, which can be actuated correspondingly as needed in order to return the water collected in the first thermal separation stage to the inlet of the electrolyzer, are provided in the line. The line pressure occurring in the system within the apparatus, i.e., the hydrogen pressure, can be used to transport this water. A bypass line with valve is advantageously to be provided for this, namely, between the first outlet of the electrolyzer, i.e., the hydrogen-carrying outlet, and the separator to be emptied, bypassing the separator or separators located in between.

[0014] An inlet of the electrolyzer is defined in the sense of the present invention as any water-carrying line leading thereto, which is fed, for example, from a reservoir within or outside the apparatus. This water can consequently be returned either into this line or advantageously into the reservoir.

[0015] A mechanical preseparator, for example, a gravitational water separator or a cyclone type water separator, is advantageously arranged between the electrolyzer and the first thermal separation stage. Part of the water load being entrained can be separated nearly without loss in such a preseparator. It is especially advantageous in this connection to integrate the preseparator in terms of the lines such that it can also be used at the same time to receive the water returned from the separation stages. The preseparator can be advantageously shut off for this both on the inlet side and the outlet side of its gas-carrying lines by means of valves and can be bypassed via a bypass line, which can likewise be shut off by means of a valve. When the return lines of the separation stages, which can likewise be shut off by means of valves, open again into the preseparator, the water to be returned can be pressed by means of the pressure present anyway in the hydrogen line into the preseparator by shutting off the gas-carrying lines of the preseparator and opening the bypass line when the valves in the return lines are opened. It is unproblematic here if the gas enters the preseparator in the form of hydrogen through the return lines, because this gas can again be fed later into the separation stages.

[0016] The preseparator likewise has a return line, which can be shut off by means of a valve and via which the water collected in the preseparator can be fed to the inlet of the electrolyzer or to the water tank arranged upstream of it. By using a float valve at the bottom of the preseparator, the return of the water can take place quasi automatically insofar as the shut-off valve in the return line leading to the water tank is opened.

[0017] The thermal separation stage or thermal separation stages is/are advantageously provided with an electrically operated, common cooling apparatus. Such cooling apparatuses are available relatively cost-effectively and in a compact form. A compressor type cooling apparatus is advantageously used in case of larger apparatuses. An absorber cooling device or a cooling device operating with Peltier elements may also be used as an alternative, especially in case of smaller apparatuses. It is especially advantageous if the first thermally operating separation stage is designed such that the hydrogen arriving from the electrolyzer that is enriched with water and/or water vapor is cooled to a temperature just slightly above the freezing point, i.e., preferably between 0° C. and 5° C. A majority of the water being entrained in the hydrogen stream condenses in this temperature range. The residual water load in the hydrogen is comparatively small. Since cooling takes place above the freezing point, no special precautionary measures are to be taken in respect to ice formation concerning the removal of the condensed water.

[0018] Cooling to below 0° C. and preferably to below −35° C. advantageously takes place only in the second separation stage of the hydrogen stream. The water being entrained in the hydrogen is crystallized in the form of ice, typically on the heat exchanger walls, in this temperature range. These walls must therefore be deiced from time to time, which can be guaranteed by intermittent operation. Since such apparatuses are never operated typically for longer than 12 hours at a stretch, it is not usually necessary to interrupt the operation in case of suitable design of the cooling surfaces for the purpose of deicing, and it is sufficient, instead, for the apparatus to thaw by itself after being switched off during the pause between operations, for example, during the night. If, by contrast, the apparatus is to be designed for a quasi continuous, 24-hour operation, it is either necessary to provide for a thawing cycle for the second thermal separation stage, which may optionally be supported by an electric heater, or to provide two thermal separation stages in parallel operation, which are operated alternatingly.

[0019] The apparatus according to the present invention operates especially effectively if the electrolyzer, the water separation device as well as any auxiliary units, connection lines, valves and the like that may be present are designed such that the hydrogen is generated and maintained under a pressure of 20 bar or higher, preferably about 30 bar. Operation of the apparatus with this pressure is especially advantageous because no special pressure increase is necessary in this case for storing the hydrogen in metal hydride storage means. The apparatus releases the dry hydrogen with the necessary pressure.

[0020] The present invention will be explained in more detail below on the basis of the exemplary embodiment shown in the drawings. The various features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this disclosure. For a better understanding of the invention, its operating advantages and specific objects attained by its uses, reference is made to the accompanying drawings and descriptive matter in which preferred embodiments of the invention are illustrated.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The only FIGURE shows a diagram of an embodiment variant of the apparatus according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0022] Referring to the drawings in particular, the apparatus shown in the FIGURE is arranged in an essentially closed housing, not shown, but it does not necessarily have to be so designed, but, especially if it is integrated in an instillation, its components may be integrated in the instillation.

[0023] The apparatus has an electrolyzer **1** of the PEM type, which is usually designed as a stack, but it may be designed in any other suitable form as well. The electrolyzer has an inlet **2** for the introduction of water. A first outlet **3** of the electrolyzer **1** is provided for removing the hydrogen produced in electrolyzer **1**, which typically contains water and water vapor. Furthermore, electrolyzer **1** has a second outlet **4**, which is provided for removing the oxygen formed in electrolyzer **1**.

[0024] In the embodiment shown, the apparatus has a reservoir **5** in the form of a water tank, which is connected to the inlet **2** of the electrolyzer via a pump **6** by means of a water line. The second outlet **4** opens via a line in the upper area of the water tank **5**. The first outlet **3**, i.e., the water-carrying outlet **3**, of electrolyzer **1** is connected by means of a line to a water separation device **7**.

[0025] The water separation device **7** has a gravitational water separator **8**, whose gas-carrying line **9** with connected to a first thermal separation stage **10** by means of a line. In this first thermal separation stage **10**, which is formed from a closed container **11** with a coolant line **12** integrated therein, the water-containing hydrogen stream arriving from the gravitational water separator **8** is cooled to a temperature of about 4° C. The coolant line **12** is designed as an evaporator in the area of container **11**. A condenser is provided outside the container. These components are connected to form a cooling circuit in the manner known per se via a throttling site and a compressor. The water condensed at the evaporator **12** collects at the bottom of container **11**.

[0026] The gas leaving the first thermal separation stage **10** enters via a line **13** a second thermal separation stage **14** via a line **13**. The second thermal separation stage **14** is provided with two containers **15** with provided as evaporators **16** in the form of coolant lines arranged in the two containers **15**. The coolant lines of the evaporators **16** have the same design as described for the first thermal separation stage **10** and are connected to a condenser. The cooling circuits have a compressor and a condenser each for all evaporators **16** together and a throttling site and are intended for alternating operation. The separation stages **10** and **14** may be advantageously fed via a common cooling circuit, so that only one compressor is necessary, and the different temperatures are set each by means of the associated throttling sites.

[0027] The hydrogen with the residual water still being entrained with it is cooled to −36° C. in this second thermal separation stage **14**. The remaining residual water resublimes or solidifies now on the evaporator **16**. The hydrogen leaving the second thermal separation stage **14** is available at the hydrogen removal port **17** and is dry, i.e., practically water-free. The containers **15** can be operating alternatingly via outlet-side valves **18**, i.e., one of the containers is used for cooling while the other container is thawed and the water collecting at the bottom of the container is sent into the gravitational water separator **8** via a line **20**, which can likewise be shut off by means of a valve **19**. Valve **19** in a return line **20** is opened only briefly each time, and valve **18** belonging to the container **15** on the outlet side is actuated for shutting off until the thawed water is returned from container **15** into the gravitational water separator **8**.

[0028] A corresponding means is provided for container **11**, and the water can be transferred from container **11** into the gravitational water separator **8** via the line **21** connected there on the bottom side and the downstream shut-off valve **22**. The gravitational water separator **8** is to be bypassed for this via a bypass line **23** and to be shut off by means of the valves **24** and **25**, so that after opening a valve **26** in bypass line **23**, pressure is admitted to container **11** and the water present on the bottom is pressed via line **21** into the gravitational water separator **8**. As an alternative, this return line may also open directly into water tank **5**.

[0029] A water return line **27**, which can be connected to water tank **5** via a valve **28**, adjoins the bottom of the gravitational water separator **8** in this exemplary embodiment. The water separated in the water separation device **7** is consequently returned completely into the water tank **5**. The apparatus is typically operated such that the hydrogen is available with a pressure of 20-30 bar on the outlet side of the electrolyzer. The electrolyzer is operated now at a temperature between 70° C. and 80° C.

[0030] While specific embodiments of the invention have been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that the invention may be embodied otherwise without departing from such principles.

1. An apparatus for the electrical production of hydrogen from water, the apparatus comprising:

an electrolyzer of the PEM type, which has an inlet for introducing water and a first outlet for the hydrogen enriched with water and/or water vapor and produced in the electrolyzer, as well as a second outlet for oxygen and water; and

a water separation device with an inlet connected to the first outlet of the electrolyzer by means of a line and with a gas-carrying outlet leading to a hydrogen removal port in or at the apparatus, wherein the water separation device comprises a thermal separation stage.

2. An apparatus in accordance with claim **1**, wherein the water separation stage further comprises a second separation stage wherein the thermal separation stage is followed by the second separation stage.

3. An apparatus in accordance with claim **2**, wherein the second separation stage is also a thermal separation stage such that there are first and second thermal separation stages.

4. An apparatus in accordance with claim **3**, further comprising a common cooling circuit wherein the first and second thermal separation stages are connected to the common cooling circuit.

5. An apparatus in accordance with claim **2**, wherein the second separation stage has a pressure swing adsorption apparatus.

6. An apparatus in accordance with claim **1**, further comprising a mechanical preseparator between the first outlet of the electrolyzer and the inlet of the thermal separation stage.

7. An apparatus in accordance with claim **6**, wherein the water separated in the separation stage is introduced into the preseparator via return lines.

8. An apparatus in accordance with claim **7**, wherein the return lines are provided with shut-off valves and a bypass line, which bypasses the preseparator and can be shut off by means of a valve, and wherein gas-carrying inlet and outlet lines of the preseparator can be shut off by means of valves.

9. An apparatus in accordance with claim **7**, wherein the preseparator is connected to the inlet for introducing water by means of a line in the form of a return line that can be shut off by means of a valve.

10. An apparatus in accordance with claim **1**, wherein the water separation device has a water-carrying outlet of at least the first separation stage, which said outlet is connected to the inlet of the electrolyzer for returning the water by means of a line at least from time to time.

11. An apparatus in accordance with claim **1**, wherein the thermal separation stage has an electrically operated cooling apparatus.

12. An apparatus in accordance with claim **11**, wherein the cooling apparatus comprises an absorber cooling apparatus, a compressor cooling apparatus or a cooling apparatus operated with Peltier elements.

13. An apparatus in accordance with claim **1**, wherein the separation stage is designed such that hydrogen arriving from the electrolyzer and enriched with water and/or hydrogen is cooled to a temperature below 5° C. and above the freezing point.

14. An apparatus in accordance with claim **2**, wherein the second separation stage is a thermal separation stage, which is designed such that the hydrogen discharged from the first separation stage and enriched with water and/or water vapor is cooled to below 0° C.

15. An apparatus in accordance with claim **2**, wherein the second separation stage is a thermal separation stage and is operated intermittently.

16. An apparatus in accordance with claim **1**, wherein hydrogen that is produced is maintained under a pressure of 20 bar or more.

17. An electrical hydrogen from water production apparatus comprising:

a polymer electrolyte membrane electrolyzer comprising an electrolyzer body with an electrolyzer inlet for introducing water, an electrolyzer first outlet for hydrogen enriched with water and/or water vapor and a second electrolyzer outlet for oxygen and water;

an electrolyzer outlet line; and

a water separator with a separator inlet connected to the electrolyzer first outlet via said electrolyzer outlet line and with a gas-carrying outlet leading to a hydrogen removal port, the water separator comprising a thermal separation stage.

18. An apparatus in accordance with claim **17**, wherein said water separator further comprises another separation stage wherein the thermal separation stage is followed by the another separation stage.

19. An apparatus in accordance with claim **18**, wherein the another separation stage is also a thermal separation stage such that there are first and second thermal separation stages.

20. An apparatus in accordance with claim **19**, further comprising a cooling apparatus cooling the first and second thermal separation stages.

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