US 20070246370A1

(19) **United States**

(12) **Patent Application Publication**
(10) **Pub. No.: US 2007/0246370 A1**
**Dimroth**
(43) **Pub. Date: Oct. 25, 2007**

(54) **DEVICE AND METHOD FOR PHOTOVOLTAIC GENERATION OF HYDROGEN**

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(21) Appl. No.: **11/576,939**

(22) PCT Filed: **Oct. 7, 2005**

(86) PCT No.: **PCT/EP05/10844**

§ 371(c)(1),
(2), (4) Date: **May 30, 2007**

(30) **Foreign Application Priority Data**

Oct. 18, 2004 (DE) ................................ 102004050638.8

**Publication Classification**

(51) **Int. Cl.**
*C25B 1/00* (2006.01)

(52) **U.S. Cl.** ................................ **205/628**

(57) **ABSTRACT**

The invention relates to a device and a method for the photo-voltaic generation of hydrogen from hydrogen-containing compounds, sunlight being concentrated on solar cells by means of an optical concentrator and the consequently generated voltage being used directly for the electrolysis of a hydrogen-containing compound, in particular deionised water, in order to generate hydrogen.

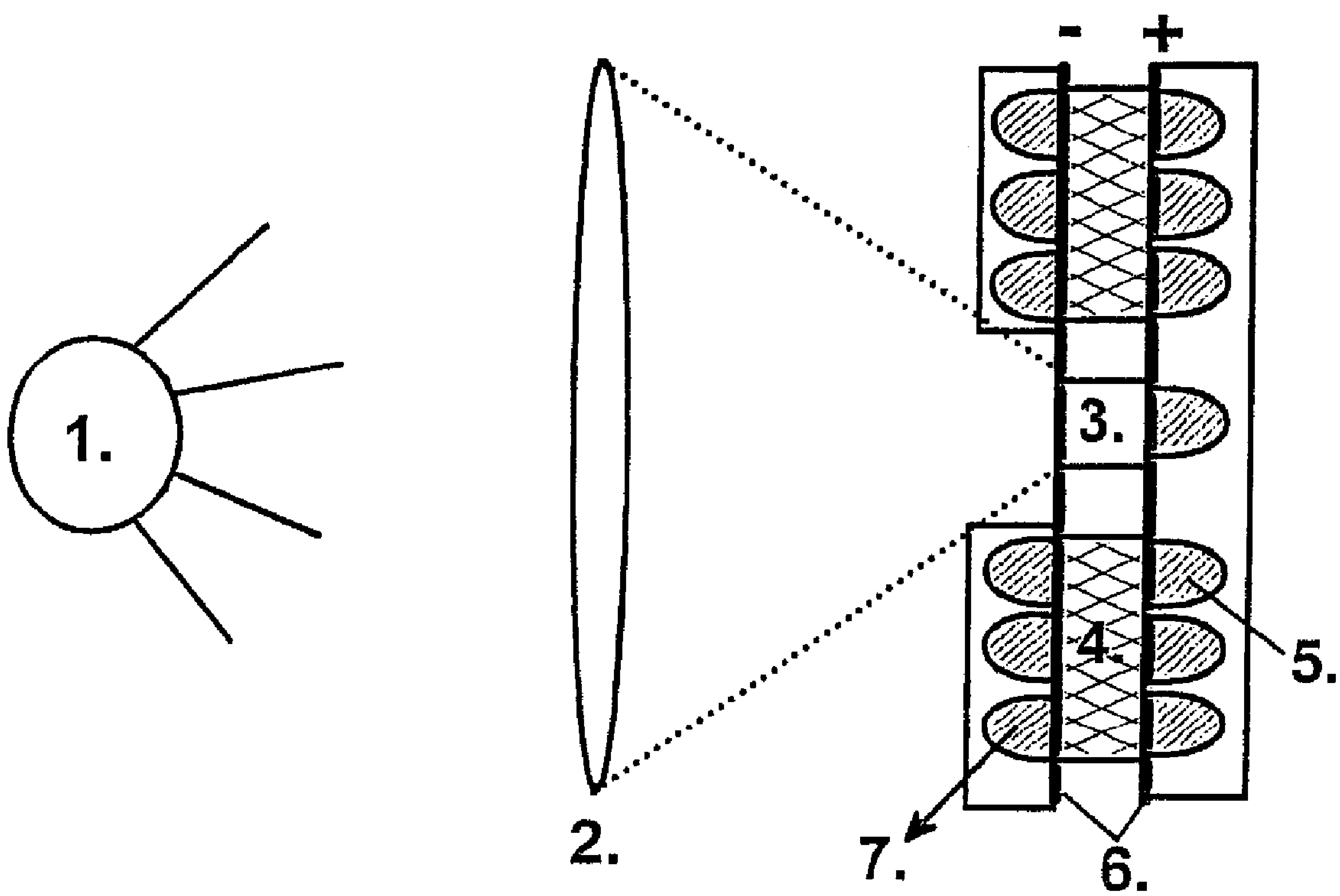


Fig. 1

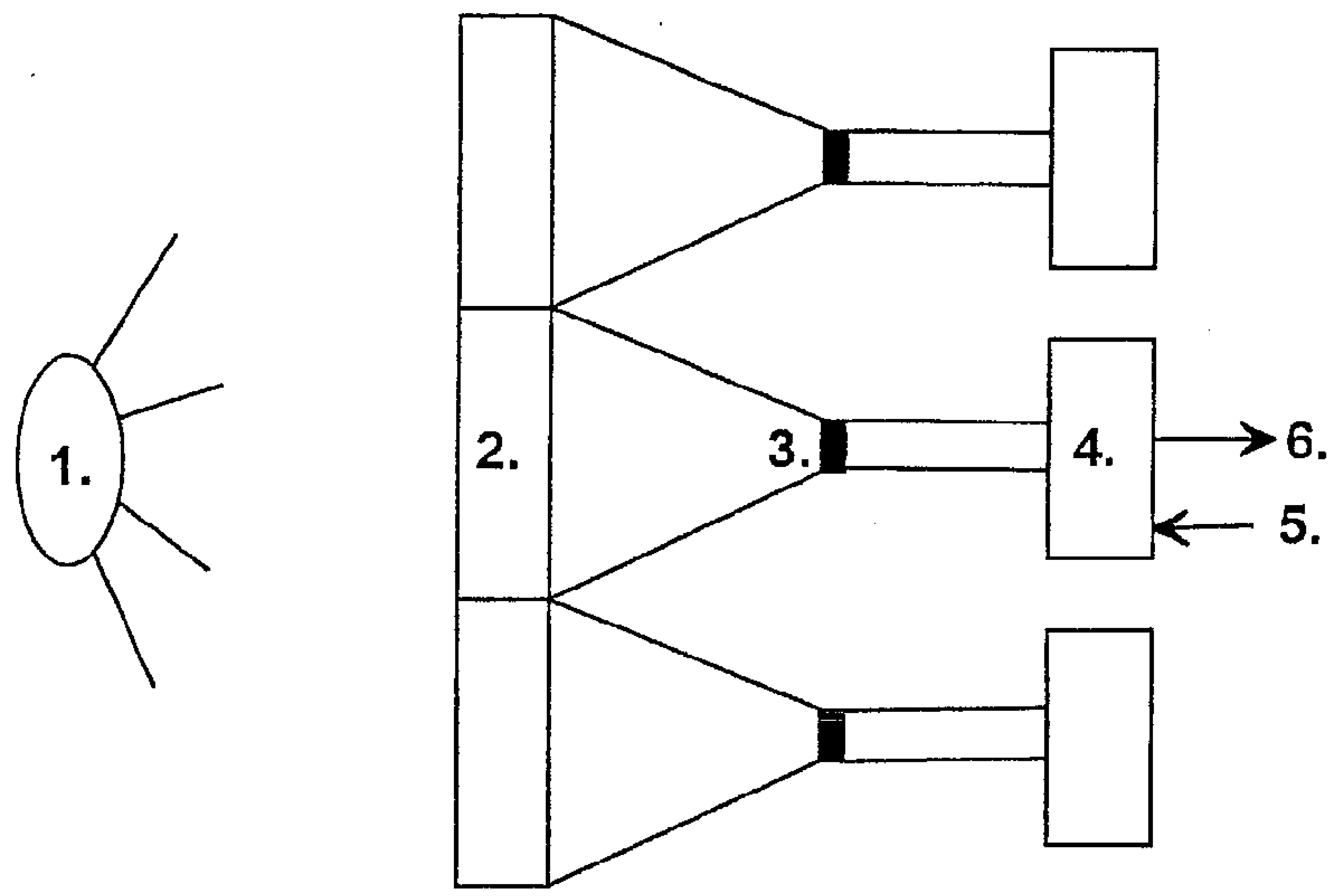



Fig. 2

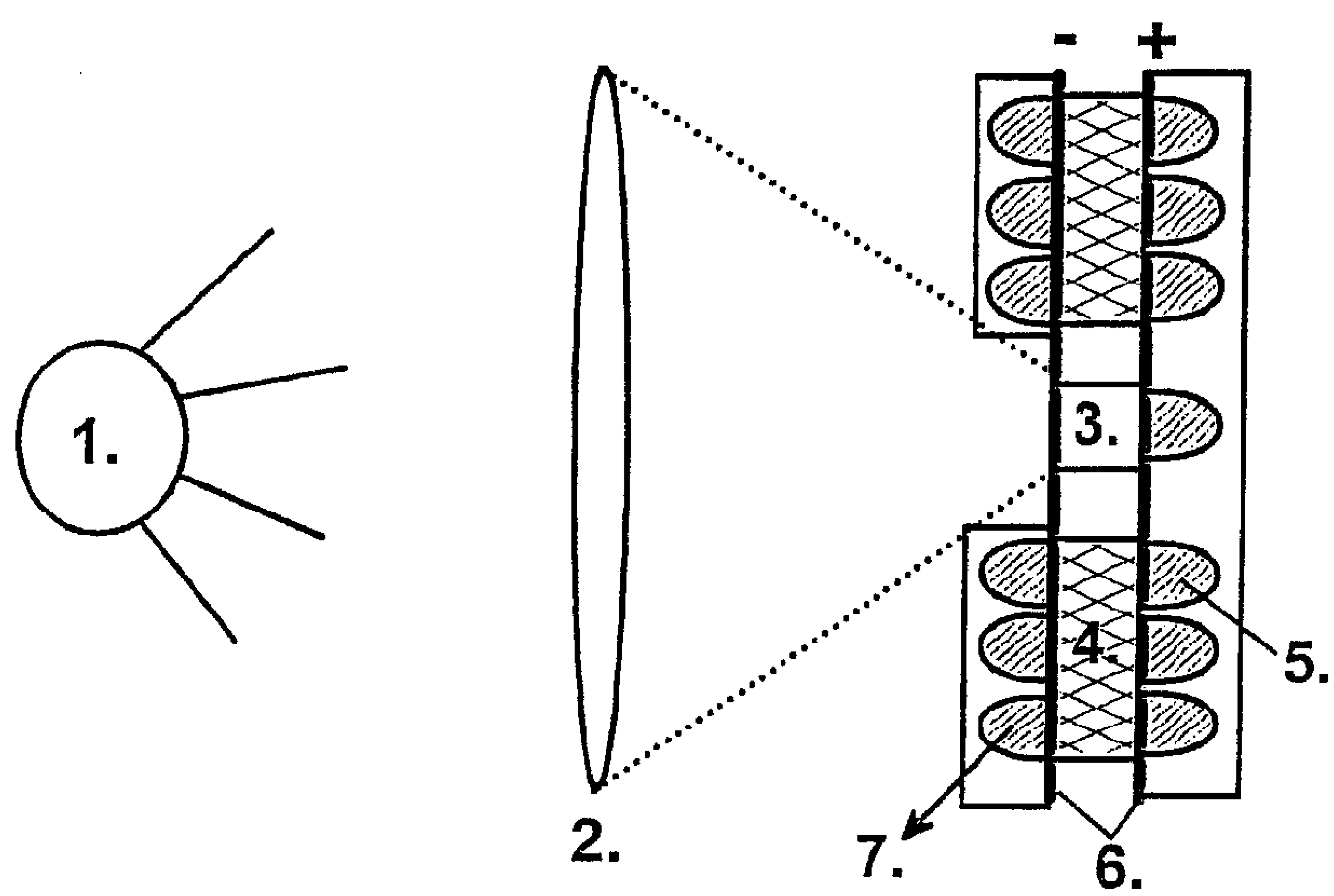


Fig. 3

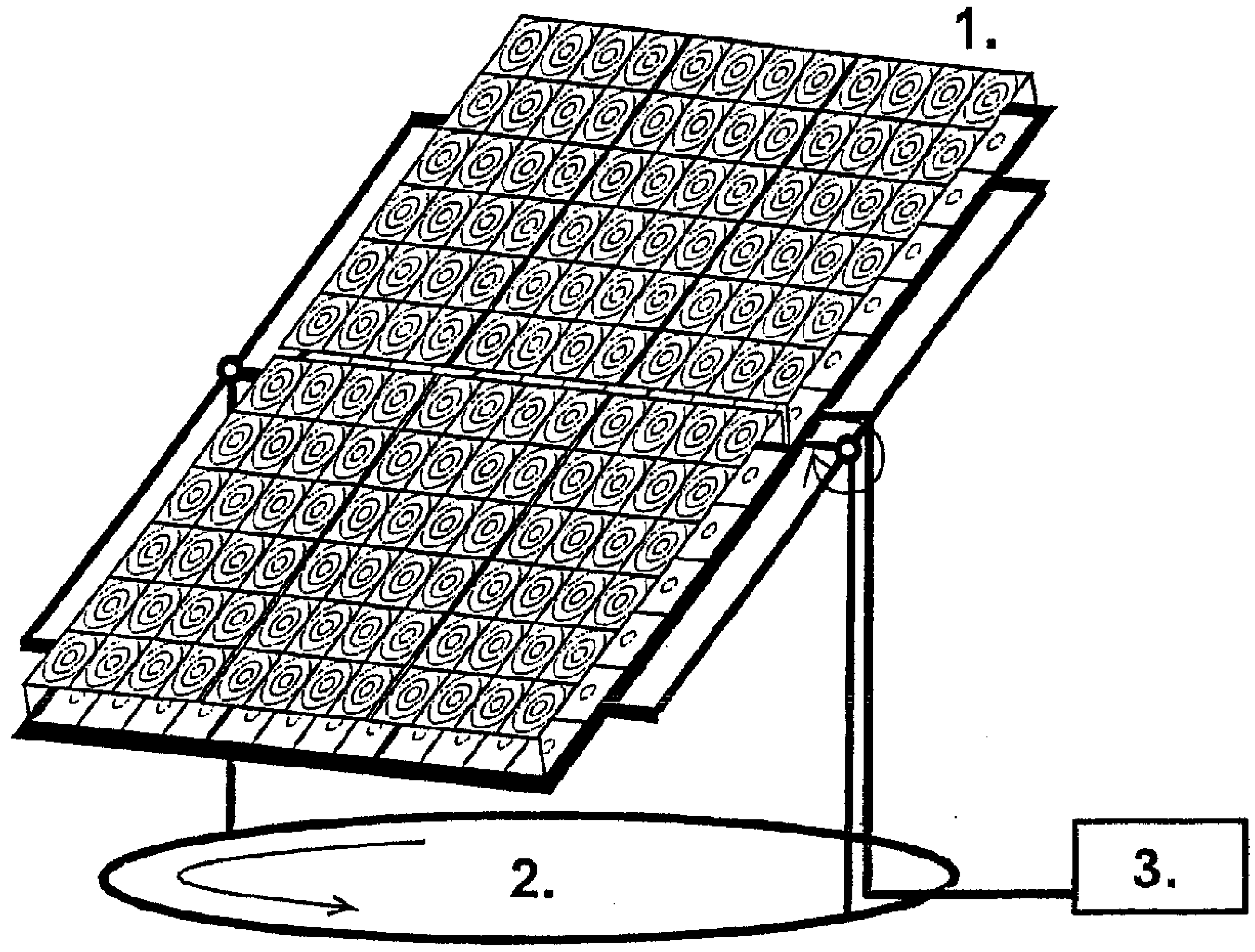

1.
2.
3.

Fig. 4

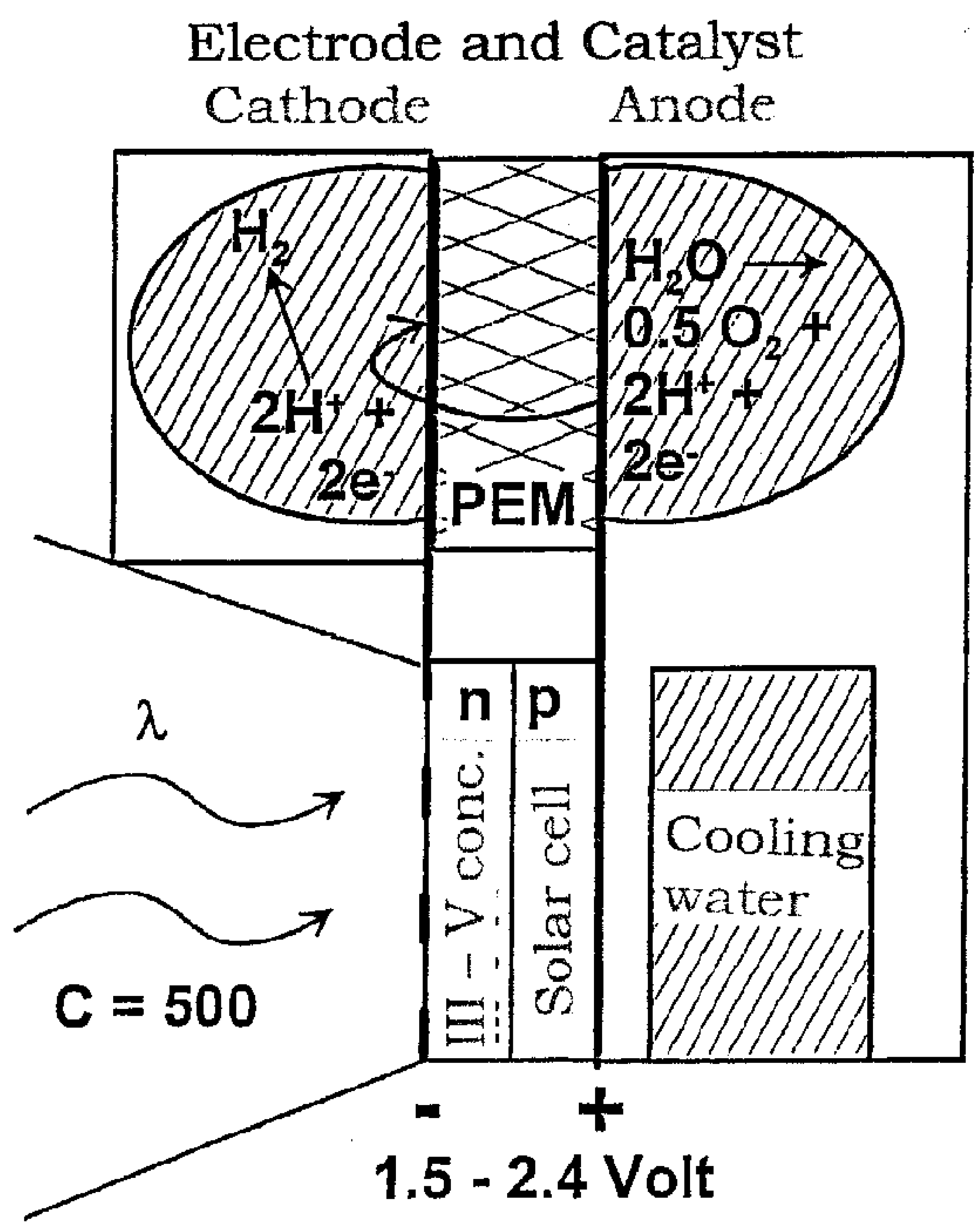

Electrode and Catalyst
Cathode
Anode
H2
2H+ +
2e-
PEM
H2O
0.5 O2 +
2H+ +
2e-
n
p
III - V conc.
Solar cell
Cooling
water
λ
C = 500
-
+
1.5 - 2.4 Volt

Fig. 5

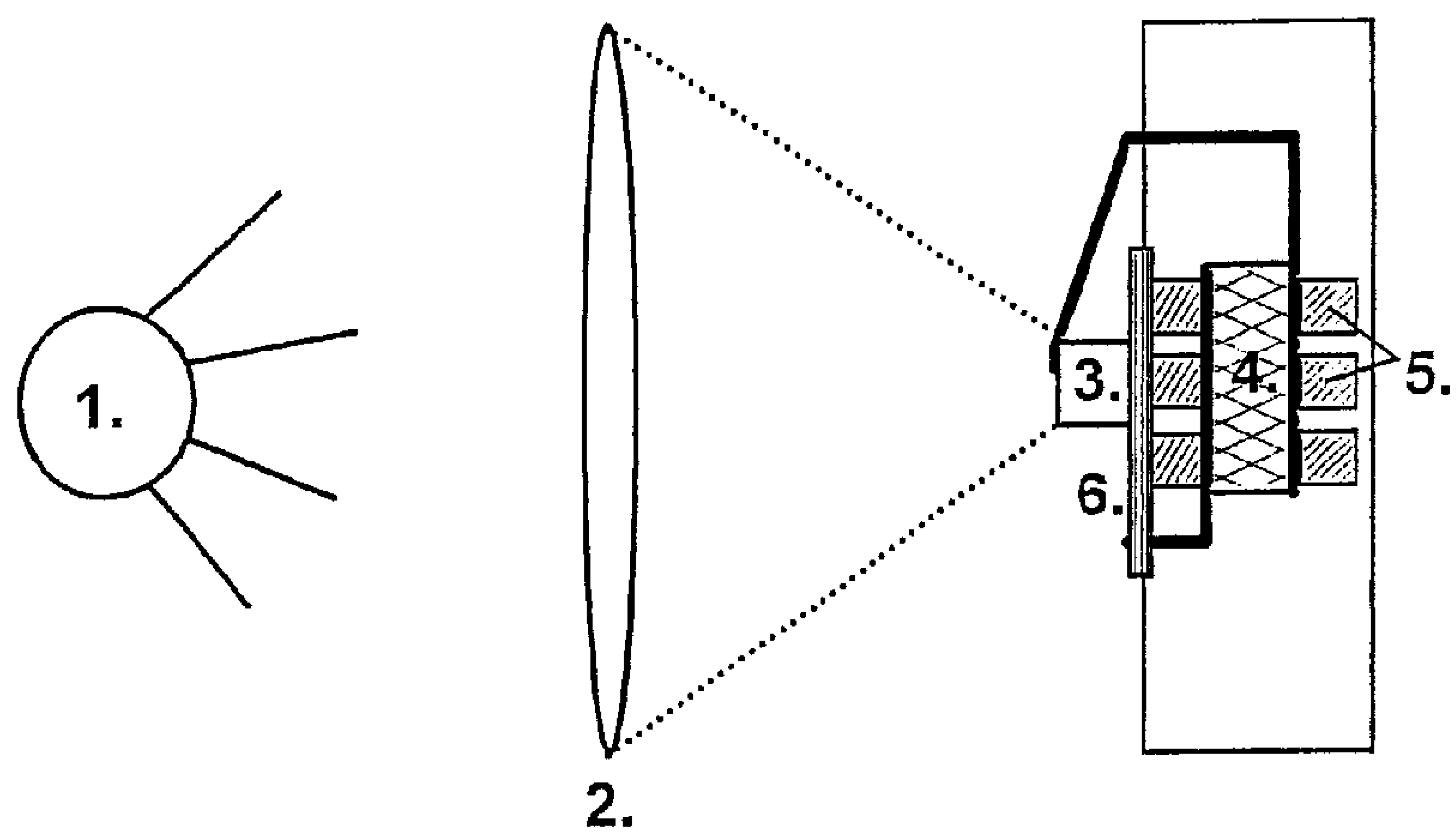



Fig. 6

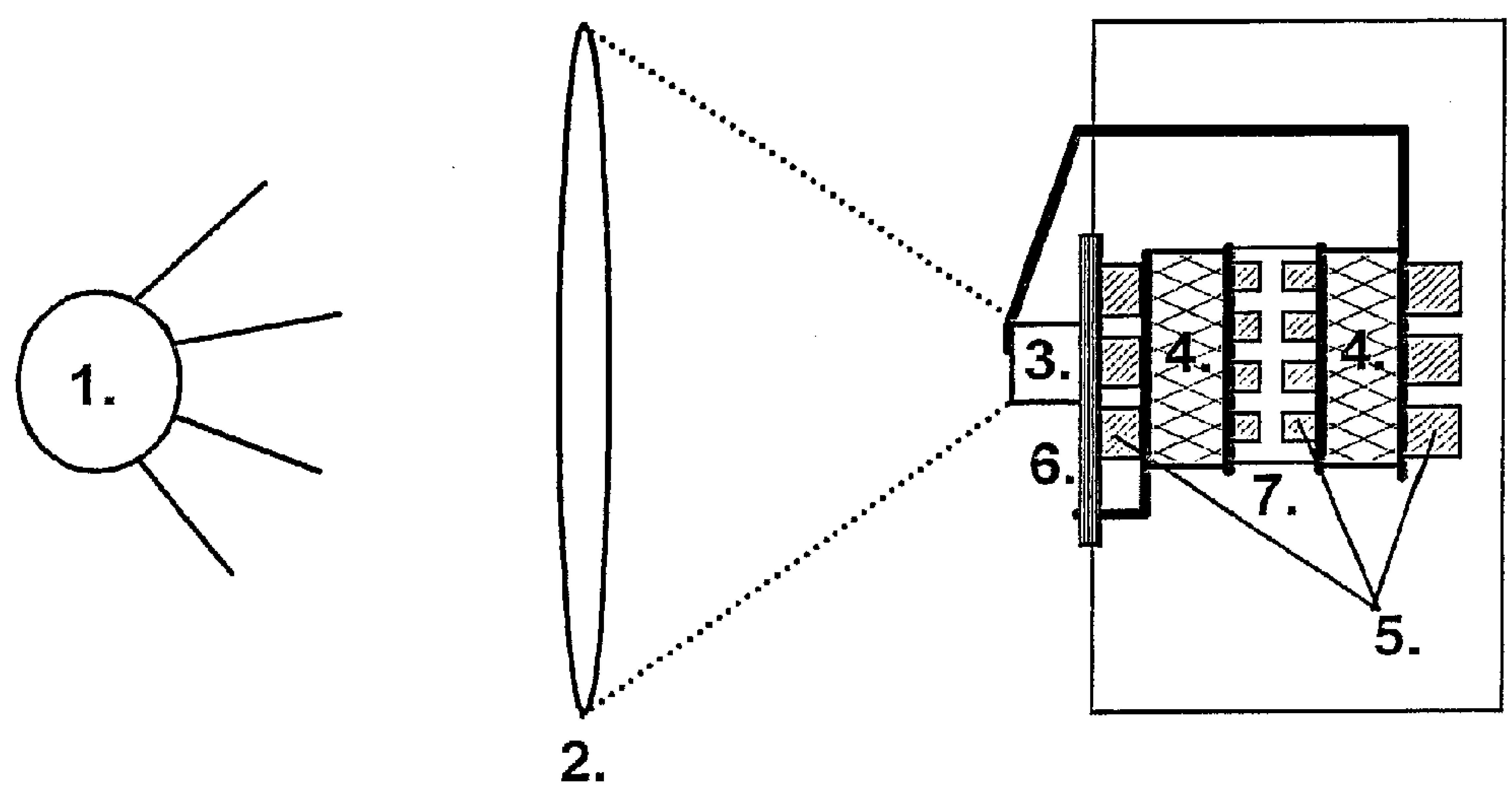
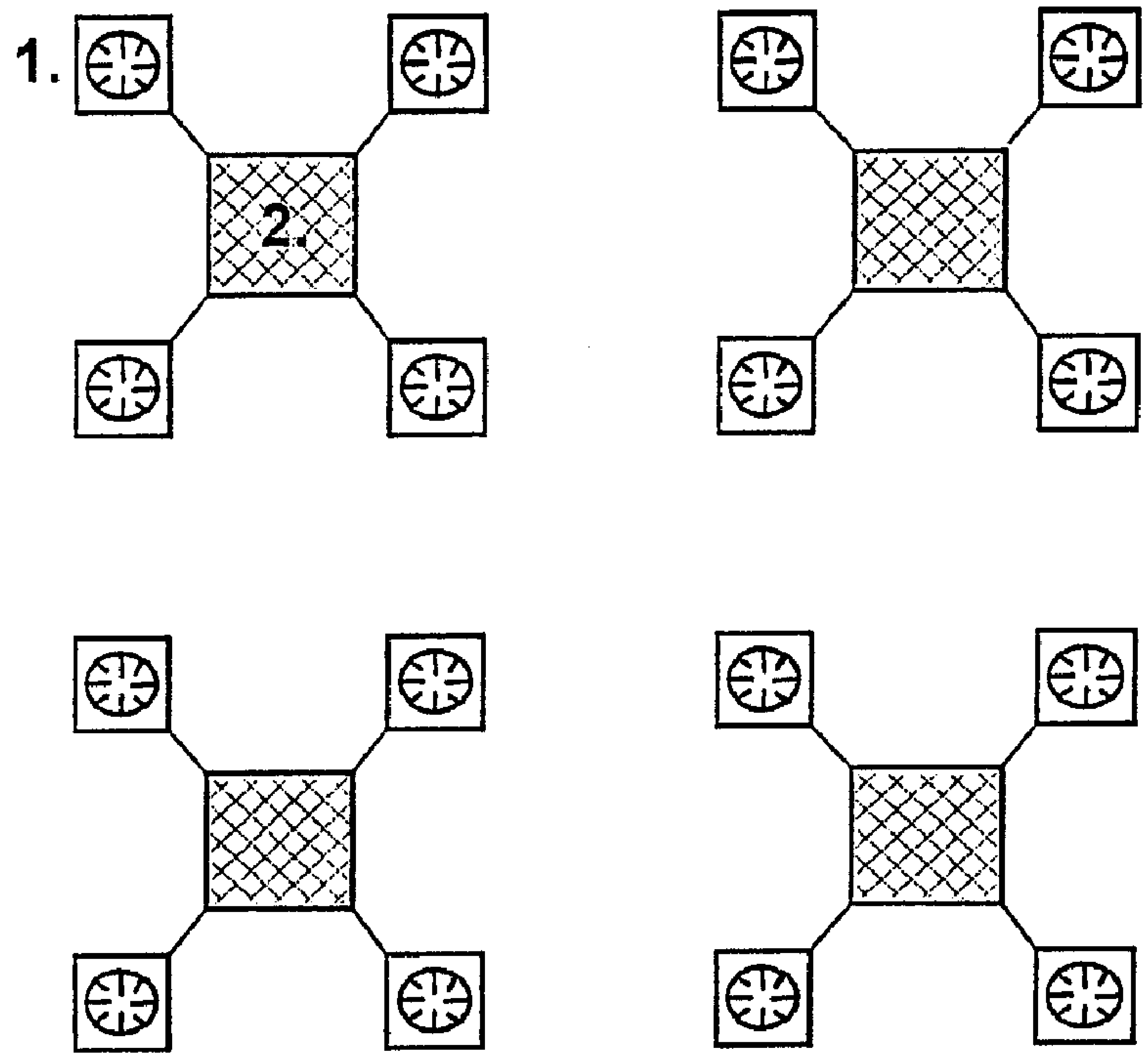


Fig. 7



# DEVICE AND METHOD FOR PHOTOVOLTAIC GENERATION OF HYDROGEN

[0001] The invention relates to a device and a method for the photo-voltaic generation of hydrogen from hydrogen-containing compounds, sunlight being concentrated on solar cells by means of an optical concentrator and the consequently generated voltage being used directly for the electrolysis of a hydrogen-containing compound, in particular of deionised water, in order to generate hydrogen.

[0002] Solar hydrogen can be obtained with the help of biological water splitting by bacteria, photoelectrochemical cells, from biomass reforming or by solar thermal splitting of water at high temperatures.

[0003] The electrolysis of hydrogen by means of photovoltaics has been achieved to date generally by separate, successively connected systems made of solar module and electrolysis unit. The same applies to systems which use wind energy for the electrolysis. Preliminary systems are described for example also in the review paper by M. A. K. Lodhi "A Hybrid System of Solar Photovoltaic, Thermal and Hydrogen: a Future Trend" Int. J. Hydrogen Energy, vol. 20, number 6, pp. 417-484 (1995). This publication also describes the use of concentrating PV systems for current generation and hybrid systems which both use solar-generated electricity and heat for the electrolysis.

[0004] The level of effectiveness of the hydrogen generation is relatively low for all these systems and the method is altogether expensive. In the past, there were also ideas of using solar cells directly for the electrolysis of water or an aqueous solution but the voltage of most solar cells at the operating point is too low to implement the electrolysis.

[0005] The electrolysis of water with the help of a semiconductor electrode was described for the first time in July 1972 in Nature vol. 238 "Electrochemical Photolysis of Water at a Semiconductor Electrode" by Akira Fijishima and Kenichi Honda. This publication shows how hydrogen can be separated from an aqueous solution with the help of sunlight. Water is hereby brought into direct contact with an n conducting semiconductor layer made of $TiO_2$ and a Pt-counter-electrode. In the case of $TiO_2$, the potential difference achieved in sunlight suffices for the splitting of water. It is described how hydrogen and oxygen can be obtained from water with this photoelectrochemical process. Because of the high band gap energy of $TiO_2$ however, only a very small part of the solar spectrum is captured in the electrode and used for the electrolysis. Hence this process is not efficient.

[0006] In a patent by D. I. Tchernev from 1975 (U.S. Pat. No. 3,925,212) "Device for Solar Energy Conversion by Photo-Electrolytic Decomposition of Water", it is shown for the first time that also separated p and n conducting semiconductor layers can be used as electrodes with illumination for splitting water. In this arrangement also there are semiconductor layers in direct contact with the electrolyte.

[0007] A further patent from 1984 "Photolytic production of hydrogen", U.S. Pat. No. 4,466,869 by A. Williams, describes for the first time that the photoelectrode can also consist of a layer structure of a plurality of semiconductor layers which are mounted one above the other and have different band gap energy. Hence the photoelectrode corresponds in principle to a cascade solar cell, as is used also preferably in the invention described here. At the National Renewable Energy Laboratory NREL, work has taken place since 1998 on a system for the generation of hydrogen by means of solar energy. O. Khaselev, J. A. Turner describe in Science; vol. 280, Apr. 17 (1998), p. 425-427 "A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting" a photoelectrochemical method for water splitting. For the first time, a cascade solar cell made of III-V semiconductors was hereby used as one of the photoelectrodes. The counter-electrode consisted of platinum. In addition, the use of concentrated sunlight was mentioned for the first time. The semiconductor layers in all the mentioned arrangements are in direct contact with the electrolyte and themselves represent one of the electrodes for the water splitting. The photovoltaic energy generation and the electrolysis of water are hence not spatially separated.

[0008] It was therefore the object of the present invention to provide a system for the photovoltaic generation of hydrogen which has high efficiency in the hydrogen generation and thereby is simultaneously economical in production.

[0009] This object is solved by the device and the method for photo-voltaic generation of hydrogen according to claim **1** and **17**. The further dependent claims reveal advantageous developments.

[0010] According to the invention, a device for the photovoltaic generation of hydrogen from hydrogen-containing compounds is provided, which consists of a plurality of units which track the position of the sun, which device has an optical concentrator for concentrating sunlight onto a solar cell, at least one solar cell which is not in contact with the hydrogen-containing compounds and is electrically connected to an electrolysis unit which has an anode and a cathode in contact with the hydrogen-containing compounds, the units being disposed on a tracking system following the position of the sun.

[0011] In comparison with systems known from prior art in which two separate systems are used, on the one hand, for photovoltaic current generation and, on the other hand, for electrolysis, the system underlying the present invention is characterised by the integration of solar power generation and hydrogen production in one system and hence by a lower material and spatial requirement, higher efficiency and potentially lower costs for the solar hydrogen. Hence electrical losses which are normally produced by the wiring of solar cells in a module are hence dispensed with. Even if individual cells within a module do not function, the functional capacity of the remaining units is not impaired. A substantial advantage relative to photoelectro-chemical methods is based on the fact that the photovoltaic cell is not in direct contact with the electrolyte. This can otherwise lead to significant problems, such as e.g. the oxidation of semiconductor layers or the removal or deposition of material by the electrolysis. This extends the long term stability of such systems. In addition, optical absorption losses of the sunlight in the hydrogen-containing compound are avoided.

[0012] Preferably each individual unit of the device has an electrical power of 1 to 100 W.

[0013] The electrolysis unit according to the invention preferably has an operating temperature of −10° C. to 200° C., particularly preferred of 30° C. to 100° C.

[0014] A point-focusing lens, such as e.g. a Fresnel lens, is used preferably as optical concentrator. Alternatively, a curved Fresnel lens with a line focus, a parabolic mirror with a line focus or a dished mirror with a point focus can be used.

[0015] The solar cell is preferably constructed from a plurality of layers made of semiconductor materials which are connected to each other in series and have respectively different band gap energy. The semiconductor materials are thereby preferably selected from the group consisting of silicon, germanium and the III-V compounds of aluminium, gallium or indium with nitrogen, phosphorus, arsenic or antimony.

[0016] The polarity of the solar cell is freely selectable so that both an np polarity and a pn polarity is possible. The solar cell, if merely a pn or np transition is present, can have a voltage of more than 1.4 volts, particularly preferred of 1.6 to 2.4 volts. If the solar cell has a plurality of series-connected pn or np transitions, then a voltage in the range of 1.5 to 6 volts can be achieved. The solar cell thereby preferably has an area of 0.01 to 1 cm squared.

[0017] Preferably a proton-permeable polymer membrane (PEM) with two electrodes, the cathode and the anode is used as electrolysis unit.

[0018] Preferably the anode and the cathode consist of noble metals, in particular here platinum, palladium or iridium, the compounds thereof, e.g. iridium oxide, or of metals coated with noble metal, in particular here nickel, iron or copper. These materials also serve as catalyst for the electrolysis. The electrodes can preferably have in addition a distribution structure which is disposed on the electrodes in order to distribute the current. This is preferably a metal grating.

[0019] A further variant of the device according to the invention provides that the anode is connected to a channel system through which the hydrogen-containing compounds flow. The cathode is likewise connected to a channel system or to a gas-permeable material through which the generated hydrogen is discharged.

[0020] A further embodiment of the device according to the invention provides that the electrolysis unit consists of two or more units which are connected to each other in series and have a correspondingly higher operating voltage.

[0021] According to the invention, a method for the generation of hydrogen from hydrogen-containing compounds is also provided, in which sunlight is concentrated on at least one solar cell by means of an optical concentrator and, with the photovoltaically generated voltage, the hydrogen-containing compounds are electrolysed at a temperature preferably in the range of −10° C. to 200° C., particularly preferred of 30° C. to 100° C., the solar cell being contacted electrically with an electrolysis unit with a cathode and/or an anode and the protons formed by the electrolysis being conducted from the anode to the cathode where they are reduced to form molecular hydrogen.

[0022] A preferred embodiment of the method according to the invention provides that the hydrogen-containing compounds are also used for cooling in that the hydrogen-containing compounds are made to flow along the solar cell.

[0023] Preferably the hydrogen-containing compound contains deionised water in substantial parts. In this case, it is then also possible to generate also oxygen in addition to hydrogen.

[0024] The subject according to the invention is intended to be explained in more detail with reference to the subsequent Figures, without wishing to restrict said subject to the embodiments shown herein.

[0025] FIG. **1** shows a schematic representation of the method for generating hydrogen according to the invention.

[0026] FIG. **2** shows a first embodiment of the device according to the invention.

[0027] FIG. **3** shows a device for photovoltaic generation of hydrogen as an overall system according to the invention.

[0028] FIG. **4** shows schematically the principle of energy conversion in the method according to the invention for generating hydrogen.

[0029] FIG. **5** shows a second embodiment of the device according to the invention.

[0030] FIG. **6** shows a third embodiment of the device according to the invention.

[0031] FIG. **7** shows the schematic construction of a device according to the invention in which an electrolysis unit is combined with a plurality of solar cells.

[0032] In FIG. **1**, the system is represented schematically, which can generate hydrogen efficiently by the electrolysis of hydrogen-containing compounds, e.g. aqueous solutions, such as deionised water, with the help of photovoltaically generated energy. This system consists of a concentrator **2** which concentrates the sunlight **1** onto a solar cell **3**. The concentration factor of the sunlight can thereby be in the range of 50 and approx. 1500. Preferably concentrations of sunlight here are in the range of 300 and 1000. A solar cell **3** which converts the sunlight into electrical power is situated at the focal point of the concentrator **2**. Voltages>1.4 volts, as are necessary for the electrolysis, are hereby generated at the operating point of the solar cell. This can be achieved by solar cells made of III-V semiconductors having one or more pn or np transitions. As cascade solar cells, for example those made of GaInP/GaInAs or AlGaInAs/Ge can be used. The band gaps of the solar cells should hereby be chosen such that the current-voltage characteristic line of the cell, with the concentrated solar spectrum, achieves as high as possible an efficiency for the electrolysis of the hydrogen-containing compounds. The polarity of the solar cell can both be p to n and n to p. The voltage applied to the solar cell **3** is used directly for the electrolysis of the hydrogen-containing compounds **5**. The p and n conducting layers of the solar cells are connected directly to the electrodes of the electrolysis unit **4**. The thereby produced hydrogen **6** is discharged and stored. If water is used for the electrolysis, then oxygen can also be obtained as further gas. Each individual solar cell in the system illustrated in FIG. **1** is connected directly to an electrolysis unit. It is however also possible that up to 4 solar cells or even more are connected directly to a single electrolysis unit. Furthermore, it is possible that the electrolysis unit consists of two electrolysis units which are connected in series one behind the other, as a result of which the operating voltage is doubled. The integration of a plurality of separate concentrator-solar cells-electrolysis unit units in an overall system is essential for the invention. These units then can (but need not) be completely separated from each other electrically. They are thereby disposed on a tracking unit and track the sun.

[0033] A first embodiment of a device according to the invention for the photovoltaic generation of hydrogen is illustrated in FIG. 2. This device consists of a Fresnel lens 2 which concentrates the sunlight 1 by a factor 300 or more and directs it onto a cascade solar cell 3 made of III-V semiconductors. The surface area of the solar cell is thereby between 0.01 to 1 $cm^2$. In the solar cell, the concentrated sunlight is converted into electrical energy with high efficiency of more than 30%. The voltage of the solar cell at the operating point is thereby >1.4 volts.

[0034] The III-V materials have not been used for terrestrial energy generation to date since they are too expensive. By using concentrated light, the semiconductor surface is however significantly reduced and use becomes economical. In future, this is intended also to be used for solar power generation on earth. The Fraunhofer ISE has been working in this context for some years on the so-called FLATCON™ concentrator. This system likewise uses cascade solar cells with concentrated sunlight for the generation of electrical power.

[0035] In a cascade solar cell, a plurality of layers made of III-V semi-conductors of different band gap energy are deposited one on the other. These partial cells are monolithically, i.e. on the substrate, connected in series to each other. As a result, operating voltages between 1 volt for a single solar cell and approx. 6 volts for a solar cell with 5-6 series-connected pn transitions can be achieved. Solar cells with 3 pn transitions have achieved efficiencies of up to 37% for the conversion of concentrated sunlight into electrical energy (R. King et al. "Metamorphic III-V Materials" Proc. of 19$^{th}$ European Photovoltaic Solar Energy Conference Paris 2004). The combination of the band gaps and materials for the application described here must be reoptimised with respect to maximisation of the efficiency for the electrolysis of water. Examples of possible material combinations are for example GaInP/GaInAs, GaAs/Ge, AlGaInAs/Ge, AlGaAs/Si, GaInP/GaInAs/Ge, AlGaInP/GaAs/GaInNAs/Ge or AlGaInP/GaIn/AlGaInAs/GaInAsN/Ge. In addition to the lower consumption of materials, a further advantage in the use of concentrated light resides in the fact that the voltage of a solar cell increases logarithmically with the concentration.

[0036] The front and rear contact of the solar cell is connected directly via a metal grating 6 to electrodes (e.g. made of noble metals, such as platinum, palladium, iridium or iridium oxide which serve also as catalyst for the electrolysis, or made of nickel, iron or copper electrodes which are coated with such noble metals) on a proton-permeable polymer membrane (PEM) 4. The surface of the PEM membrane can extend up to the total surface of incidence of the sunlight (apart from the surface of the solar cell). The PEM membrane can however also adopt only a much smaller surface area. The membrane is on the positive side of the anode in direct contact with the hydrogen-containing solution which consists of e.g. deionised water 5. However other solutions can also be used which also need not necessarily be transparent. The solution will firstly flow through below the solar cells in one possible arrangement and contributes there to the cooling. As a result, the efficiency of the solar cells can be increased. Subsequently, the solution is conducted through a channel system to the anode and is split there into oxygen and hydrogen ions. The oxygen molecules produced on the anode side rise within the liquid and can be collected there. The $H^+$ ions migrate through the PEM membrane to the negative cathode where they react with respectively two electrons to form molecular hydrogen. The cathode side is covered in turn with a channel system through which the hydrogen-containing solution flows or with a gas-permeable or porous material through which the hydrogen can be conducted to the store.

[0037] FIG. 3 shows a device 1 according to the invention which is assembled to form an overall system for photovoltaic generation of hydrogen. The gases are collected here at the upper edge of the individual modules and supplied to a store 3. This store can consist of e.g. compressed gas cylinders. The inflow pipe to the modules can be evacuated. The modules are mounted on a 2-axis tracking unit 2 which follows the course of the sun. This is necessary to retain the focus of the lens always precisely on the solar cell. Since PEM electrolysis units achieve degrees of efficiency of 80 to 90%, with the system described here made of III-V cascade solar cells and PEM electrolysis unit, system degrees of efficiency of 27% can be achieved for the generation of hydrogen by means of sunlight.

[0038] The principle of energy conversion is represented schematically in FIG. 4. A hydrogen-containing compound is guided along the anode for example through a channel. The result hereby is then splitting of water into oxygen and protons. The protons can in turn pass through the proton-permeable polymer membrane (PEM) and thus reach the cathode. The result here is reduction of the protons to form molecular hydrogen. In the present example, the polymer membrane is disposed adjacent to the solar cell. In addition, the solar cell can be cooled from the rear by a channel through which cooling water flows.

[0039] FIG. 5 shows a further embodiment of the invention in which the PEM electrolysis unit 4 is disposed under the solar cell 3. The water flows here directly through channels 5 below the solar cell which are soldered on a Cu plate 6. The Cu plate can thereby be separated electrically by an insulator from the water. Good thermal contact between the water for the electrolysis and the solar cell is produced. Hydrogen and oxygen are conveyed in this case as gas bubbles in the liquid.

[0040] In a further embodiment of the invention described here, two electrolysis units are connected in series. This is sensible if the voltage of the concentrator solar cell at the operating point achieves twice the voltage necessary for the electrolysis, i.e. approx. 3 volts. Such high voltages can be achieved with a single highly efficient cascade solar cell made of III-V semiconductors. A possible construction for the series connection of two PEM electrolysis units is shown in FIG. 6. The following meanings apply in this Figure:

[0041] 1 Sun

[0042] 2 Point-focusing lens

[0043] 3 III to V cascade solar cell

[0044] 4 PEM membrane with electrodes

[0045] 5 Water or hydrogen-containing solution for the electrolysis for cooling the solar cell

[0046] 6 Metal plate made of Cu as carrier for the solar cell

[0047] 7 Structured, conductive separator between the two PEM membranes with water channels, e.g. made of titanium

[0048] In a further embodiment of the invention, respectively two to four concentrator solar cells are connected to only one electrolysis unit (see FIG. 7). This arrangement is suitable if the current generated by one concentrator solar cell does not suffice to operate the electrolysis unit efficiently. The arrangements of FIG. 2 and FIG. 7 or FIG. 5 and FIG. 7 can also be combined together.

1. A device for the generation of hydrogen from hydrogen-containing compounds, comprising.

a plurality of units made of respectively at least one optical concentrator for concentrating sunlight onto at least one solar cell, and

at least one solar cell which is not in contact with the hydrogen-containing compounds and is electrically connected to an electrolysis unit which has an anode and a cathode in contact with the hydrogen-containing compounds,

wherein the units are disposed on a tracking system following the position of the sun.

2. The device according to claim 1, wherein each unit has an electrical power of less than 100 watts.

3. The device according to claim 1, wherein the electrolysis unit has an operating temperature of −10° C. to 200° C., in particular of 30° C. to 100° C.

4. The device according to claim 1, wherein the optical concentrator is a point-focusing lens, Fresnel lens or a line-focusing lens.

5. The device according to claim 1, wherein the optical concentrator is a parabolic mirror with a line focus.

6. The device according to claim 1, wherein the optical concentrator is a dished mirror with a point focus.

7. The device according to claim 1, wherein the solar cell consists of a plurality of layers of semiconductor materials which are connected to each other in series and have respectively different band gap energy.

8. The device according to claim 7, wherein the semiconductor materials are selected from the group consisting of silicon, germanium and ITT-V compounds of aluminium, gallium, indium, nitrogen, phosphorus, arsenic and antimony.

9. The device according to claim 8, wherein the solar cell has an np polarity.

10. The device according to claim 1, wherein the solar cell has a pn polarity.

11. The device according to claim 1, wherein the solar cell has a pn or np transition and a voltage of more than one of: 1.4 V, and 1.6 to 2.4 V.

12. The device according to claim 1, wherein the solar cell has a plurality of series-connected pn or np transitions and has a voltage in the range of 1.5 to 6 V.

13. The device according to claim 1, wherein the solar cell has an area of 0.01 to 1 $cm^2$.

14. The device according to claim 1, wherein the electrolysis unit contains a proton-permeable polymer membrane (PEM) which is in direct contact with the cathode and the anode.

15. The device according to claims 1, wherein the anode and the cathode to includes at least one of:

noble metals, taken from the group consisting of: palladium and iridium, the compounds thereof, iridium oxide, and

metals coated with noble metals, taken from the group consisting of: iron or copper.

16. The device according to claim 1, wherein a distribution structure, having a metal grating, is disposed on the electrodes in order to distribute the current.

17. The device according to claim 1, wherein at least one channel or a gas-permeable material is disposed at the cathode in order to discharge the generated hydrogen.

18. The device according to claim 17, wherein the channel and/or the coating on a side orientated towards the light is light-impermeable or metal-coated.

19. The device according to claim 1, wherein the hydrogen-containing compound is of deionised water in substantial parts.

20. The device according to claim 1, wherein the electrolysis unit consists of a plurality of series-connected units consisting of electrodes and proton-permeable membranes.

21. A method for the generation of hydrogen from hydrogen-containing compounds, in which sunlight is concentrated on at least one solar cell by means of an optical concentrator and, with the photovoltaically generated voltage, the hydrogen-containing compounds are electrolysed and the protons formed by the electrolysis are conducted from the anode to the cathode where they are reduced to form molecular hydrogen, a plurality of units being used which track the position of the sun and consist of at least one concentrator and at least one solar cell which is not in contact with the hydrogen-containing compounds and is contacted electrically with an electrolysis unit with a cathode and an anode.

22. The method according to claim 21, wherein solar cells consisting of a plurality of pn or np transitions which are connected to each other in series and consist of semiconductor materials which have respectively different band gap energy are used.

23. The method according to claim 21, wherein the semiconductor materials are selected from the group consisting of silicon, germanium and ITT-V compounds of aluminium, gallium, indium, nitrogen, phosphorus, arsenic and antimony.

24. The method according to claim 21, wherein the number of pn or np transitions of the solar cell is chosen such that the solar cell has a voltage in the range of 1.5 to 6 V.

25. The method according to claim 21, wherein the light is concentrated by the factor of one of: 50 to 1500, and 300 to 1000.

26. The method according to claim 21, wherein the light is concentrated with a point-focusing Fresnel lens, a point-focusing dished mirror, a line-focusing optical lens or a parabolic mirror.

27. The method according to claim 21, wherein a proton-permeable polymer membrane is used as electrolysis unit.

28. The method according to claim 21, wherein the hydrogen from the units is assembled and collected.

29. The method according to claim 21, wherein the generated hydrogen is discharged via a channel system.

30. The method according to claim 21, wherein the hydrogen-containing compounds are used for cooling in that the hydrogen-containing compounds are made to flow along the solar cells.

31. The method according to claim 21, wherein molecular oxygen is generated as by-product.

32. The method according to claim 21, wherein the hydrogen-containing compound consists of deionised water in substantial parts.

* * * * *