(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
09 January 2020 (09.01.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/009572 A1

(51) International Patent Classification:
C25B 11/03 (2006.01) *C25B 9/10* (2006.01)
C25B 13/02 (2006.01) *C25B 9/18* (2006.01)
C25B 1/04 (2006.01)

(21) International Application Number: PCT/NL2019/050409

(22) International Filing Date: 03 July 2019 (03.07.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2021260 06 July 2018 (06.07.2018) NL

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*
— *with amended claims (Art. 19(1))*

(54) Title: ELECTROLYSIS SYSTEM COMPRISING AN ELECTRODE ARRAY

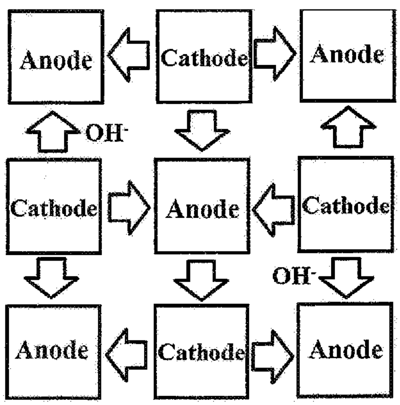

Fig. 3b

(57) Abstract: The present invention is in the field of a system for electrolysis and in particular for electrolysis of water into hydrogen and oxygen, the system comprising an anode, a cathode and electrolyte and an electrical potential/power supplier, as well as an input and output. The produced gas may be stored, such as in a vessel.

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Electrolysis system comprising an Electrode array

FIELD OF THE INVENTION

The present invention is in the field of a system for electrolysis and in particular for electrolysis of water into hydrogen and oxygen, the system comprising an anode, a cathode and electrolyte and an electrical potential/power supplier, as well as an input and output. The produced gas or liquids may be stored, such as in a vessel.

BACKGROUND OF THE INVENTION

Electrolysis is a technique using an electrical potential difference to provide a direct electric current (DC) for driving a chemical reaction. Without the electrical potential difference the reaction would not occur. Electrolysis may be important for separation of elements or splitting of molecules, such as H_2 and O_2 from H_2O, or for separation from naturally occurring sources. The voltage that is needed for electrolysis to occur is called the decomposition potential.

During actual electrolysis a direct electric current is provided through an electrolyte. The current enters in the form of electrons in the cathode where a reduction reaction creates a current carried by ions that travel to the other electrode where an oxidation reaction supplies again electrons. The electrolyte has the function of carrying an ionic current. The reactants/products may form separate phases or they may be dissolved in the electrolyte in case of a liquid electrolyte. By chemical reactions at the electrodes compound may be decomposed. Main components in electrolysis are an electrolyte, an electrical current, and electrodes, and in particular a cathode and anode. The electrolyte conducts ions either through a solid or a liquid. An applied voltage provides for the thermo-dynamical energy that is necessary for the reaction. In the external circuit the electric current is carried by electrons. Further typically two electrodes are present per electrochemical cell, that are electrical conductors. They provide a physical interface between electrolyte and the electrical circuit that provides the energy. Electrodes may be made of various materials, such as metals, graphite, and semiconductor material. Typically in electrolysers many electrochemical cells are electronically connected in parallel, a monopolar configuration, or in series, a bipolar configuration.

The amount of electrical energy that is added is considered to be equal to the change in (thermo-dynamical) Gibbs free energy of the reaction. Due to losses in a system the required energy is always higher and often much higher, for instance due to a release of heat.

Electrolysis of water produces hydrogen according to

$2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g);\ E_0 = +1.229$ V.

The required cell potential at standard conditions is ≥ 1.229 V. It is noted that energy efficiency of water electrolysis may vary widely. The efficiency of an electrolyser is often defined as the enthalpy contained in the hydrogen, compared to electrical energy provided. Heat/enthalpy values for hydrogen are about 144 MJ/kg. Some reports quote water electrolysis efficiencies between 50% and 70% for alkaline electrolysers; higher efficiencies are available, such as 95% efficiency. Production costs for 1 kg of hydrogen are about €5 in the near term and €2 in the long term.

Only a small fraction of hydrogen gas produced worldwide is generated by electrolysis, and normally used onsite. The generated hydrogen may be used for subsequent reaction, such as for forming ammonia.

A disadvantage with prior art systems is that the current density is still rather low. For instance, in alkaline electrolysis (with an aqueous electrolyte containing usually potassium hydroxide to make it more conductive) the current densities are typically of the order of 3000 A/m^2 in industrial electrolysers. In polymer electrolyte membrane (PEM) electrolysers this can be up to an order of magnitude higher. A reason for the lower current densities in alkaline electrolysis are larger Ohmic losses. By Ohms law the losses are proportional to the current density (A/m^2) and the distance over which the current travels. The main focus is therefore on making thinner membranes that reduce the distance between the anode and cathode, such as thinner than 0.5 mm thickness.

A way of reducing Ohmic losses may be reducing the current density. However this directly reduces the amount of gas (hydrogen) produced thus making the electrolyser more expensive per kg of hydrogen produced per unit of time.

Various documents recite electrode systems, such as US 2015/292094 A1), WO 2015/085363 A1), US 2012/222954 A1, US 6,254,741 B1, US2014/284209 A1, US 2015/075977 A1 and WO 2017/170664 A1.

The present invention therefore relates to a system for electrolysis, which solves one or more of the above problems and drawbacks of the prior art, providing reliable results, without jeopardizing functionality and advantages.

SUMMARY OF THE INVENTION

The present invention relates to an electrolysis system, in particular for generation of gaseous species, such as hydrogen and oxygen, and for generation of lower alcohols, such as methanol, and ethanol, for carboxylic acids or ions thereof, such as formic acid and formate, methane, CO, and NH_3. The present invention relates to an innovative geometric electrode array, providing higher current densities (at the same or similar overpotential), such as two times higher than comparable prior art electrolysis systems comprising planar electrodes, with a same Ohmic voltage drop, and thus comparable or less Ohmic losses. In the present system current flows in two substantially independent (such as perpendicular) directions so that for the same current per unit volume a two times lower current density may be applied and thus a two times lower Ohmic voltage drop may be obtained, compared to in a planar configuration. Another advantage is that e.g. gas may be removed through a centre of an electrode rather than at the back (in zero-gap systems, or in front of in traditional systems with a gap between the electrode and the membrane). This avoids a need for separate flow channels (other than just making a hole in the center of the electrode). It is also a better suited configuration for miniaturization than the traditional sandwich model which tends to be bulky. Finally a good prospect for membrane-less operation is provided, i.e. the present array may also be operated without a membrane, with a chimney-like action providing effective separation of e.g. gases being produced, such as hydrogen and oxygen. Buoyant rise of the gaseous species allows for easy collection, whereas if a liquid would be produced a pump may be applied.

The present array comprises elongated, slender, (pillar like, or column like) shaped electrodes, in addition to a an array of said electrodes. The height of the electrodes is preferably at at least two times as large as a cross-sectional dimension thereof. The cross-sectional dimension may relate to a (largest) diameter in case of largely circular electrodes, to a longest diagonal in case of multigonal electrodes, to a longest perpendicular line in case of a triangle, and so on. Typically two or more anodes are present and two or more cathodes, preferably [3-m] anodes (wherein m may be up to 2^{20}), and preferably [3-n] cathodes (wherein n may be up to 2^{20}). The cathodes and anodes are typically alternating, that is a cathode is in at least two direction adjacent to two anodes, and vice versa. A material, typically a fluid material, in between said at least one cathode and at least one anode comprises an electrolyte and is suited for transfer of electrolyte species typically being ions, or precursors thereof, such as a solution comprising a polar solvent, such as water. For performing electrolysis the at least one anode and at least one cathode are at least partly in fluidic contact the material. This contact may be direct or indirect, i.e. a further medium may be provided in between an electrode and fluid material. For performing the electrolysis also an electrical potential/power supplier, typically of a direct current type (DC), is provided. As electrolyte may need to be replenished, or refreshed, or re-supplied, such in a continuous mode, in a semi-continuous mode, in a batch-wise mode, an input and an output are provided, as well as an optional outlet for gaseous species, typically one outlet per gaseous species.

Thereby the present invention provides a solution to one or more of the above mentioned problems and drawbacks.

Advantages of the present description are detailed throughout the description.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates in a first aspect to a system according to claim 1.

In an exemplary embodiment of the present system at least one electrode is made from a metal, such as Pt, Ir, Ni, Cu, Zn, Ru, Ti, Fe, NiFe/NiO, graphite, a semiconductor, or combinations thereof. The Electrode material may be provided on a support.

In an exemplary embodiment of the present system a width of the at least one cathode is 0.9-1.1 times a length thereof.

In an exemplary embodiment of the present system a width of the at least one anode is 0.9-1.1 times a length thereof.

In an exemplary embodiment of the present system a width of the at least one anode is 0.1-5 cm.

In an exemplary embodiment of the present system a width of the at least one cathode is 0.1-5 cm.

In an exemplary embodiment of the present system a height of the cathode may be at least 1 mm, such as at least one cm.

In an exemplary embodiment of the present system a height of the anode is at least 1 mm, such as at least one cm.

In an exemplary embodiment of the present system an electrode may comprise a current collector, typically parallel to the height of the electrodes. The current collector provides an improved conductance and may increase a current applied to the electrodes.

In an exemplary embodiment of the present system the solution may be an aqueous solution or a melt.

In an exemplary embodiment of the present system the solution may comprise anions and cations, preferably selected from at least one of Li^+, Rb^+, K^+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, Mg^{2+}, SO_4^{2-}, HCO_3^-, and OH^-, preferably K^+ and OH^- for water electrolysis and preferably HCO_3^- and K^+ for CO_2 electrolysis.

In an exemplary embodiment of the present system may comprise 2-2^{20} cathodes and 2-2^{20} anodes, preferably 4-2^{15} cathodes and 4-2^{15} anodes, more preferably 10-2^{12} cathodes and 10-2^{12} anodes, even more preferably 16-2^{10} cathodes and 16-2^{10} anodes, such as 32-2^9 cathodes and 32-2^9 anodes, wherein the array comprises at least one symmetry axis, such as a two-fold axis, a three-fold axis, and a four-fold axis.

In an exemplary embodiment the present system may be for electrolysis of water, wherein the voltage supplier in operation provides a potential difference over the electrodes of about 1.23-2.2V, such as 1.48-2 V, and optionally providing an overpotential.

In an exemplary embodiment of the present system a cross section of the at least one anode and at least one cathode may be independently selected from square, rectangular, circular, ellipsoidal, multigonal, such as pentagonal, hexagonal, octagonal, and combinations thereof. As such a large freedom of design is provided by the present system.

In an exemplary embodiment of the present system the solution and/or electrolyte may flow parallel to a height of the anode or cathode.

In an exemplary embodiment of the present system the height of the at least one cathode may be substantially equal to the height of the at least one anode, i.e. both are of equal height or almost equal height.

In an exemplary embodiment of the present system the width of the at least one cathode may be substantially equal to the width of the at least one anode, i.e. an array of electrodes appears to substantially regular in one direction of a top view.

In an exemplary embodiment of the present system the length of the at least one cathode may substantially equal to the length of the at least one anode, i.e. an array of electrodes appears to substantially regular in one direction of a top view. Each individual electrode may be structured as indicated.

In an exemplary embodiment the present system may comprise at least one storage vessel for fluids, such as for replenishing or for storage of gases being produced.

In an exemplary embodiment of the present system at least one electrode may be hollow. In addition thereto also a fluid material may be provided at both an inside and an outside of the electrode. Therewith both an internal and an external surface, as well as the surface in the preferred pores and channels, may be used for electrolysis.

In an exemplary embodiment of the present system at least one electrode may be obtained by 3D-printing. Below an example thereof is given.

In an exemplary embodiment of the present system at least one membrane (M) may be provided in between at least one cathode and at least one anode, preferably in between any cathode and any neighboring anode. The membrane preferably may have a thickness of 0.001-0.1 cm, such as 0.01-0.05 cm.

In an exemplary embodiment of the present system at least one electrode comprises an indention (U-profile), preferably an indentation over a full height thereof, or is hollow (□-profile), or is Y-shaped, or is H-shaped, and combinations thereof.

In an exemplary embodiment of the present system at least one electrode may have a wall thickness of 0.1-3 mm. In case of a hollow electrode the wall thickness of the electrode and pillar like structure may fully coincide, whereas in case of a beam like structure the outer part of the electrode may function as an electrode, and the inner part thereof as a core or support, or the full electrode may be considered to have the wall thickness.

In an exemplary embodiment of the present system at least one cathode and at least one anode may be separated by a membrane or porous substrate, such as a bipolar membrane, and are thus chemically separated from one and another.

The anode may be at an outside of the electrode and a cathode may be at an inside, or wherein the anode may be at an inside of the electrode and a cathode may be at an outside thereof. If a common electrode plate is used the cathode may extend slightly more to a top side (or likewise bottom side), and the anode slightly more to a bottom side (or likewise top side).

In an exemplary embodiment of the present system at least one anode may be in electrical connection to a common anode plate.

In an exemplary embodiment of the present system at least one cathode may be in electrical connection to a common cathode plate.

In an exemplary embodiment of the present system a cathode or a group of cathodes may be in electrical connection to a first common cathode plate and an anode or a group of anodes may be in electrical connection to a first common anode plate, and so on, wherein the first common cathode plate may be electrically connected in series or in parallel to the first common anode plate, which in turn may be connected to a second common cathode plate, and so on.In an exemplary embodiment of the present system in the array anodes and cathodes may be alternating.

In an exemplary embodiment of the present system at least one electrode may comprise pores, such as pores with a diameter of 1 nm-10 mm.

In an exemplary embodiment of the present system pores may have a heterogeneous size, that is very small sized pores may be present, such as of 1-100 nm, slightly larger size pores may be present, such as of 0.1-100 µm, and relatively large pores may be present, such as of 100 µm-1 mm. Therewith gas transport and liquid transport can be controlled well, and a pore size can be adapted to specific species, such as gas species, such as H_2 and O_2, allowing one species to pass, and to block another.

In an exemplary embodiment of the present system a pore density may be 1-10^9 pores/cm^2, such as 100-10^6 pores/cm^2.

In an exemplary embodiment of the present system a porosity (volume open/volume solid) may be from 0.1-0.95, preferably 0.5-0.9. The porosity can be measured in various ways, such as by using a water evaporation method and calculating accordingly (pore volume = (weight of saturated sample - weight of dried sample)/density of water).

In an exemplary embodiment of the present system a distance between an anode and neighboring cathode may be 0.001-5 cm, preferably 0.01-0.3 cm. depending on design and further boundary conditions the distance may vary and may be adapted.

In an exemplary embodiment the present system may comprise at least one of sealing side covers, a support, such as supporting pillars, a first gas outlet for a first gaseous species, such as H_2, a second gas outlet for a second gaseous species, such as O_2, a pump, and a fluid material chamber.

The one or more of the above examples and embodiments may be combined, falling within the scope of the invention.

EXAMPLES

The below relates to examples, which are not limiting in nature.

A conventional- and a matrix electrode were both 3D-printed to produce two similar electrodes in terms of pore structure and material. The reaction studied were

$4H_2O + 4e^- \rightarrow 2H_2O + 4OH^-$ $E_c = -0.826V$

$4OH^- \rightarrow +O_2 + 2H_2O + 4e^-$ $E_a = 0.404V$

The performance of the electrode has been measured in the range of 1.48 to 3.0 V, with minimal step size of the used power source being 0.1 V.

The used electrolyte is KOH dissolved in water. Experiments have been done for 0.1 M, 1 M and 3 M KOH. The material used for the electrode is 316-L stainless steel, which was used for the 3-D print. The material contains about 10 % Nickel ($Fe0.9Ni_{0.1}$) and is used as a cathode material. The material choice for the 3D printed plastic parts is Acrylonitrile Butadiene Styrene (ABS), in view of its strength and that it does not react with high concentrations KOH.

The electrode wall thickness was 2 mm. The porosity of the material was about 50 percent. The current density expected was about 2000 A/m². The pores/channels in this printed structure have a diameter of around 250 µm, which is found sufficient for the bubbles to escape in view of sizes of the gas bubbles in electrolysis. These channels are set under an angle of 45 degrees. Hollow electrodes, reminiscent of chimneys, are designed to be able to remove gas with an almost zero gap between the electrodes and the membrane. The chimney width and length were about 4 mm. For a good comparison a 2 mm gap behind each electrode in the conventional configuration was provided for the removal of bubbles.

The anode plate is connected to 18 electrodes and the cathode plate is connected to 17 electrodes. This systems has 58 surfaces of 8×20 mm, which oppose an electrode of opposite polarity. The 0.5 mm thick membrane (Zirfon Perl, Agfa) is folded in the 0.7 mm gap between the anodes and the cathodes to separate the oxygen gas and hydrogen gas.

For every step in potential, a waiting time of 2 minutes is used in order to have the reaction reach an equilibrium state. The chimneys from the array electrodes produced clouds of bubbles above the electrode. This was most visible on chimneys from the cathode. For every emerging oxygen molecule, 2 hydrogen molecules are produced, which explains the difference in chimney activity.

The main result is shown in Figures 7 and 8. Figure 7 shows that the required overpotential to obtain a certain current per unit external electrode area is similar between the conventional and array configurations. This is expected since similar electrodes and membrane are used. Figure 8 shows a roughly 50% increase in current per unit volume at the same potential compared to the conventional configuration. This is related to the roughly 1.5 times higher surface area per unit volume of the array electrolyser. When upscaling to more anodes and cathodes, this factor can be shown to approach approximately 2 for the used dimensions.

An average performance increase of 27% has been achieved (

Concentration	Conventional	Matrix
3M	700	804

(current densities in A per m^2 of external anode area at 2.2V)). Also the Tafel slope in mV/decade shows a clear improvement (

Concentration	Conventional	Matrix
3M	116	79).

Further the exchange current density in 10^{-6} A/cm^2 shows a clear improvement (

Concentration	Conventional	Matrix
3M	3.5	3.1).

The invention is further detailed by the accompanying figures, which are exemplary and explanatory of nature and are not limiting the scope of the invention. To the person skilled in the art it may be clear that many variants, being obvious or not, may be conceivable falling within the scope of protection, defined by the present claims.

FIGURES

The invention although described in detailed explanatory context may be best understood in conjunction with the accompanying figures.

Fig. 1 shows a conventional alkaline water electrolysis setup.

Fig. 2 shows a traditional (left) and zero gap cell (right) layout.

Fig. 3a and 3c show a prior art layout and fig. 3b and 3d a layout of the present invention.

Figs. 4a-e show a layout of a 3D-printed array.

Fig. 5 shows a chimney design.

Fig. 6 shows a layout with concentric electrodes.

Figs. 7 and 8 show a comparison between current densities of a prior art system and the present system.

DETAILED DESCRIPTION OF THE FIGURES

In the figures:

100 present system

10 electrode array
51 common Anode plate
52 common Cathode plate
A Anode
C Cathode
e electrode
E electrolyte
M membrane
S support
V Voltage

Fig. 1 shows a conventional alkaline water electrolysis setup.

The figures have been detailed throughout the description.

Fig. 2 shows a traditional (left) and zero (right) gap cell layout.

Fig. 3a and 3c show a prior art layout and fig. 3b and 3d a layout of the present invention.

Figs. 4a-e show a layout of a 3D-printed array. Fig. 4a shows a worked open top view of a 7 by 5 array with alternating cathodes (18) and anodes (17) with a membrane m in between the electrodes, each electrode having a chimney layout (see fig. 5). Fig. 4b shows a worked open side view with alternating electrodes producing O_2 and H_2, respectively. Also a common anode plate 51 and common cathode plate 52 are shown, as well as supports S. Gas outlets are provided at a top side. Optionally, by making only outlets in the top plate for the cathodes (or the anodes), the products produced at the anodes (or the cathodes) may be collected from outlets below the top plate (for instance at a location (schematically indicated with an "X"). Fig. 4c shows a top section of fig. 4b. Figs. 4d and 4e show a worked open version of the present system and a closed system thereof, respectively. Also the side covers ssc are shown.

Fig. 5 shows a chimney design of a 3D-printed electrode.

Fig. 6 shows a layout with concentric electrodes.

Fig. 7 shows a comparison between current densities (A per m^2 of external electrode area) of a prior art system and the present system with a 3 M KOH.

Fig. 8 shows a comparison between volumetric current densities (A per m^3 of total electrolyser volume) of a prior art system and the present system with a 3 M KOH.

CLAIMS

1. Electrolysis system comprising

a geometric electrode array (10), the array comprising

at least three pillar shaped anode (A), preferably [3-m] anodes,

at least three pillar shaped cathode (C), preferably [3-n] cathodes,

wherein in the array anodes and cathodes are alternating,

wherein the at least one pillar shaped cathode has a height that is at least two times as large as a cross-sectional dimension, and/or

wherein the at least one pillar shaped anode has a height that is at least two times as large as a cross-sectional dimension, and/or

wherein a width of at least one cathode is 0.9-1.1 times a length thereof, and/or

wherein a width of at least one anode is 0.9-1.1 times a length thereof,

preferably wherein at least one membrane (M) is provided in between at least one cathode and at least one anode,

a material in between said cathode and anode, the material comprising an electrolyte and suited for transfer of ions,

wherein the anodes and cathodes are at least partly in fluidic contact with the material,

an electrical potential/power supplier,

a fluid material input and output, and

an optional outlet for gaseous species.

2. Electrolysis system according to embodiment 1, wherein at least one electrode is made from a metal, such as Pt, Ir, Ni, Cu, Zn, Ru, Ti, and Fe, NiFe/NiO, graphite, a semiconductor, or combinations thereof, and optionally comprises a support.

3. Electrolysis system according to any of claims 1-2, wherein a width of at least one anode is 0.1-5 cm, and/or wherein a width of at least one cathode is 0.1-5 cm, and/or wherein a height of at least one cathode is at least 1 mm, such as at least one cm, and/or wherein a height of at least one anode is at least 1 mm, such as at least one cm.

4. Electrolysis system according to any of claims 1-3, wherein the material is a solution, such as an aqueous solution or a melt.

5. Electrolysis system according to any of claims 1-4, wherein the solution comprises anions and cations, preferably selected from at least one of Li^+, Rb^+, K^+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Na^+, Mg^{2+}, SO_4^{2-}, HCO_3^-, and OH^-, preferably K^+ and OH^- for water electrolysis and preferably HCO_3^- and K^+ for CO_2 electrolysis.

6. Electrolysis system according to any of claims 1-5, comprising $4-2^{20}$ cathodes and $4-2^{20}$ anodes, wherein the array comprises at least one symmetry axis, such as a two-fold axis, a three-fold axis, and a four-fold axis.

7. Electrolysis system according to any of claims 1-6, for electrolysis of water, wherein the voltage supplier is adapted to provide~~s~~ a potential difference over the electrodes of about 1.5-2.2V, and optionally to provide an overpotential.

8. Electrolysis system according to any of claims 1-7, wherein a cross section of ~~the~~ at least one anode and at least one cathode is independently selected from square, rectangular, circular, ellipsoidal, multigonal, such as pentagonal, hexagonal, octagonal, and combinations thereof.

9. Electrolysis system according to any of claims 1-8, wherein the solution and/or electrolyte flows parallel to a height of the anode or cathode.

10. Electrolysis system according to any of claims 1-9, wherein the height of at least one cathode is substantially equal to the height of at least one anode, and/or wherein the width of at least one cathode is substantially equal to the width of at least one anode, and/or wherein the length of at least one cathode is substantially equal to the length of the at least one anode, for each individually.

11. Electrolysis system according to any of claims 1-10, comprising at least one storage vessel for fluids.

12. Electrolysis system according to any of claims 1-11, wherein at least one electrode is hollow.

13. Electrolysis system according to any of claims 1-12 wherein at least one electrode is obtained by 3D-printing.

14. Electrolysis system according to any of claims 1-13, wherein at least one membrane (M) is provided in between any

cathode and any neighboring anode, wherein the membrane preferably has a thickness of 0.001-0.1 cm, such as 0.01-0.05 cm.

15. Electrolysis system according to any of claims 1-14, wherein at least one electrode comprises an indention (U-profile), preferably an indentation over a full height thereof, or is hollow (□-profile), or is Y-shaped, or is H-shaped, and combinations thereof.

16. Electrolysis system according to any of claims 1-15, wherein at least one electrode has a wall thickness of 0.1-3 mm.

17. Electrolysis system according to any of claims 1-16, wherein at least one anode is in electrical connection to at least one common anode plate (51), and/or wherein at least one cathode is in electrical connection to at least one common cathode plate (52), wherein optionally said common plates are in electrical connection.

18. Electrolysis system according to any of the preceding claims 1-17, wherein an electrode comprises a current collector, and/or

wherein at least one cathode and at least one anode are separated by a membrane or porous substrate, such as a bipolar membrane, and are thus chemically separated from one and another..

19. Electrolysis system according to any of claims 1-18, wherein at least one electrode comprises pores, such as pores with a diameter of 1 nm-10 mm, and/or wherein the pores have a heterogeneous size, and/or wherein a pore density is 1-10^9 pores/cm^2, and/or wherein a porosity (volume open/volume solid) is from 0.1-0.95, preferably 0.5-0.9, and combinations thereof.

20. Electrolysis system according to any of claims 1-19, wherein a distance between an anode and neighboring cathode is 0.001-5 cm, preferably 0.01-3 cm.

21. Electrolysis system according to any of claims 1-20, comprising at least one of sealing side covers (ssc), a support (S), such as supporting pillars, a first gas outlet for a first gaseous species, such as H_2, a second gas outlet for a second gaseous species, such as O_2, a pump, and a fluid material chamber.

AMENDED CLAIMS
received by the International Bureau on 11 December 2019 (11.12.2019)

1. Electrolysis system comprising
a geometric electrode array (10), the array comprising
$4-2^{20}$ pillar shaped anodes (A),
$4-2^{20}$ shaped cathodes (C),
wherein in the array anodes and cathodes are alternating,
wherein the at least one pillar shaped cathode has a height that is at least two times as large as a cross-sectional dimension,
wherein the at least one pillar shaped anode has a height that is at least two times as large as a cross-sectional dimension,
wherein a width of at least one cathode is 0.9-1.1 times a length thereof,
wherein a width of at least one anode is 0.9-1.1 times a length thereof,
preferably wherein at least one membrane (M) is provided in between at least one cathode and at least one anode,
a material in between said cathode and anode, the material comprising an electrolyte and suited for transfer of ions,
wherein the anodes and cathodes are at least partly in fluidic contact with the material,
an electrical potential/power supplier,
a fluid material input and output, and
an optional outlet for gaseous species.

2. Electrolysis system according to embodiment 1, wherein at least one electrode is made from a metal, such as Pt, Ir, Ni, Cu, Zn, Ru, Ti, and Fe, from NiFe/NiO, from graphite, from a semiconductor, or combinations thereof.

3. Electrolysis system according to any of claims 1-2, wherein a width of at least one anode is 0.1-5 cm,
wherein a width of at least one cathode is 0.1-5 cm,
wherein a height of at least one cathode is at least 1 mm, and
wherein a height of at least one anode is at least 1 mm.

4. Electrolysis system according to any of claims 1-3, wherein the material is a solution.

5. Electrolysis system according to any of claims 1-4, wherein the solution comprises anions and cations, preferably K^+

and OH^- for water electrolysis and preferably HCO_3^- and K^+ for CO_2 electrolysis.

6. Electrolysis system according to any of claims 1-5, wherein the array comprises at least one symmetry axis.

7. Electrolysis system according to any of claims 1-6, for electrolysis of water, wherein the voltage supplier is adapted to provide~~s~~ a potential difference over the electrodes of about 1.5-2.2V, and to provide an overpotential.

8. Electrolysis system according to any of claims 1-7, wherein a cross section of at least one anode and at least one cathode is independently selected from square, rectangular, circular, ellipsoidal, multigonal, and combinations thereof.

9. Electrolysis system according to any of claims 1-8, wherein the solution and/or electrolyte flows parallel to a height of the anode or cathode.

10. Electrolysis system according to any of claims 1-9, wherein the height of at least one cathode is substantially equal to the height of at least one anode, and wherein the width of at least one cathode is substantially equal to the width of at least one anode, and wherein the length of at least one cathode is substantially equal to the length of the at least one anode, for each individually.

11. Electrolysis system according to any of claims 1-10, comprising at least one storage vessel for fluids.

12. Electrolysis system according to any of claims 1-11, wherein at least one electrode is hollow.

13. Electrolysis system according to any of claims 1-12 wherein at least one electrode is obtained by 3D-printing.

14. Electrolysis system according to any of claims 1-13, wherein at least one membrane (M) is provided in between any cathode and any neighboring anode, wherein the membrane has a thickness of 0.001-0.1 cm.

15. Electrolysis system according to any of claims 1-14, wherein at least one electrode comprises an indention (U-profile), or is hollow (□-profile), or is Y-shaped, or is H-shaped, and combinations thereof.

16. Electrolysis system according to any of claims 1-15, wherein at least one electrode has a wall thickness of 0.1-3 mm.

17. Electrolysis system according to any of claims 1-16,

wherein at least one anode is in electrical connection to at least one common anode plate (51), and wherein at least one cathode is in electrical connection to at least one common cathode plate (52), wherein said common plates are in electrical connection.

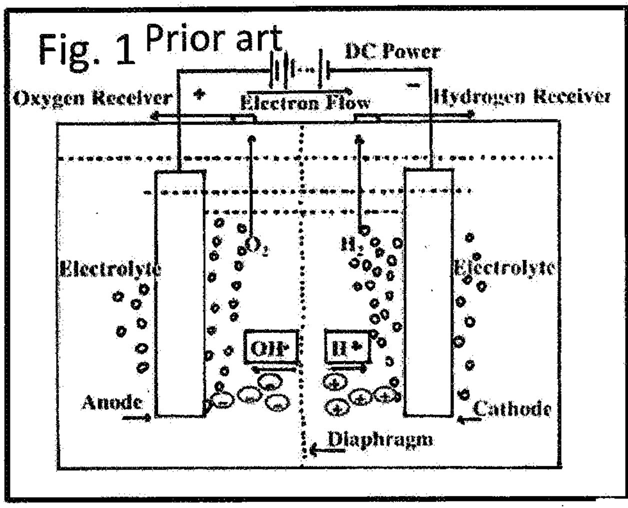
18. Electrolysis system according to any of the preceding claims 1-17, wherein an electrode comprises a current collector, and

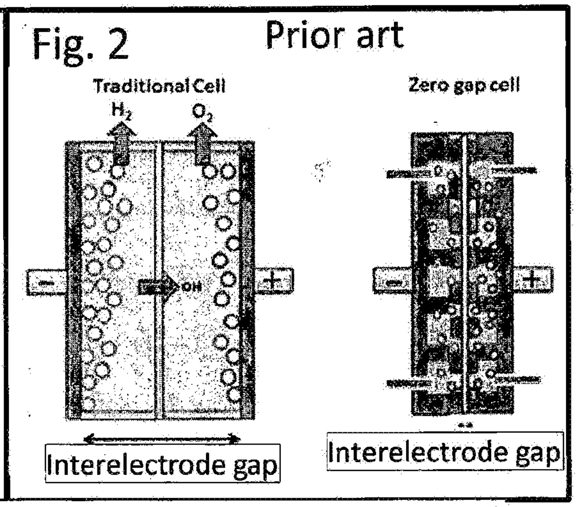
wherein at least one cathode and at least one anode are separated by a membrane or porous substrate, and are thus chemically separated from one and another.

19. Electrolysis system according to any of claims 1-18, wherein at least one electrode comprises pores, and wherein the pores have a heterogeneous size, and wherein a pore density is $1\text{-}10^9$ pores/cm^2, and wherein a porosity (volume open/volume solid) is from 0.1-0.95.

20. Electrolysis system according to any of claims 1-19, wherein a distance between an anode and neighboring cathode is 0.001-5 cm.

21. Electrolysis system according to any of claims 1-20, comprising at least one of sealing side covers (ssc), a support (S), a first gas outlet for a first gaseous species, a second gas outlet for a second gaseous species, a pump, and a fluid material chamber.





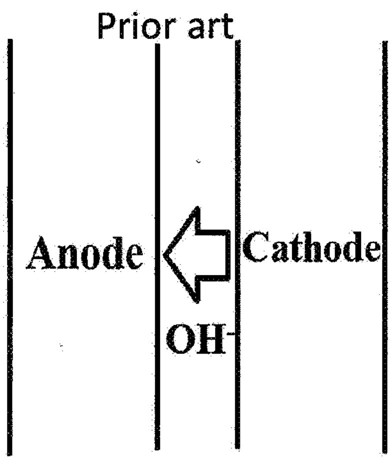


Fig. 3a

Fig. 3b

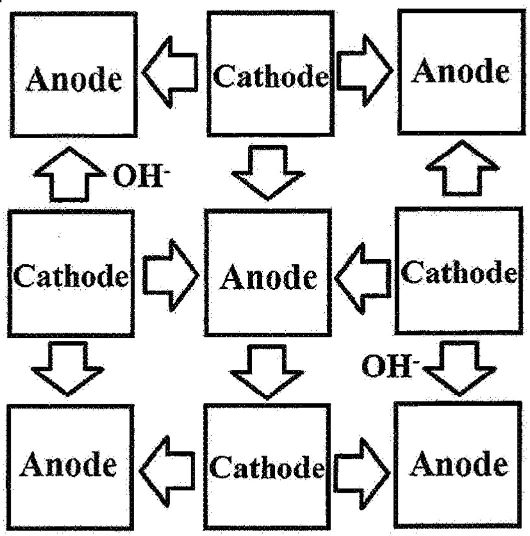
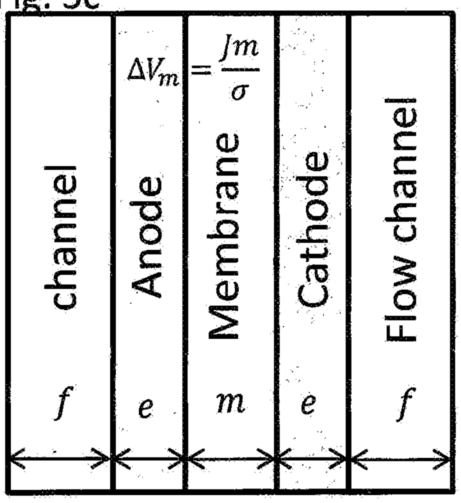


Fig. 3c



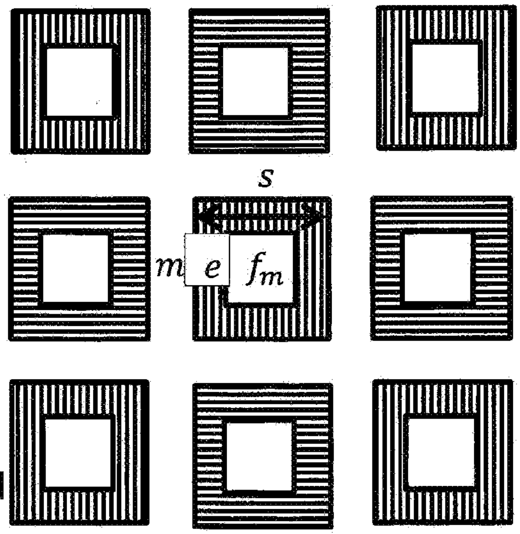
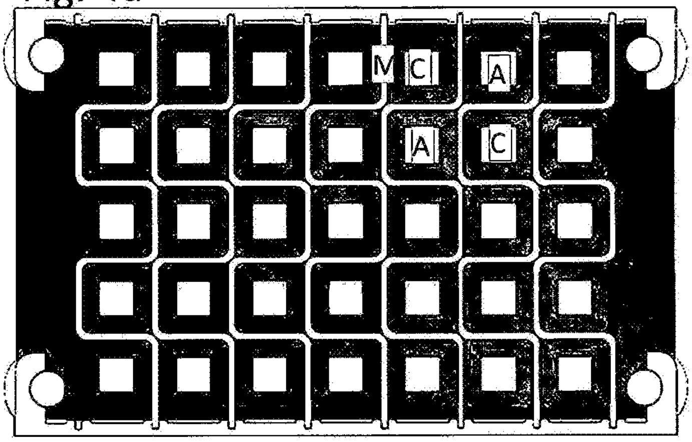


Fig. 3d

Fig. 4a



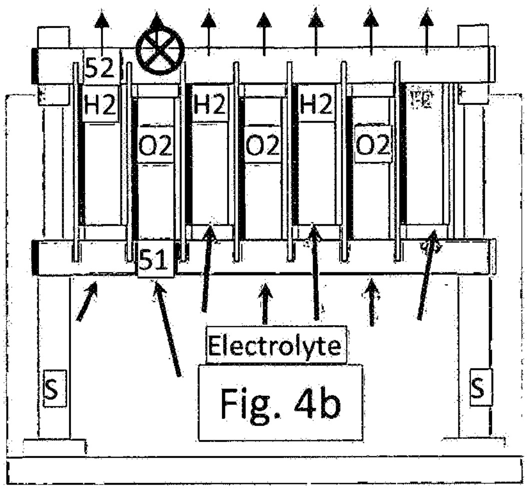


Fig. 4b

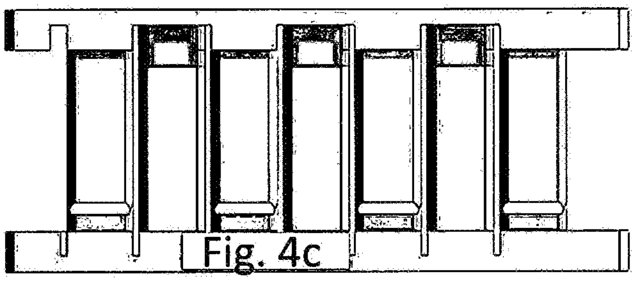


Fig. 4c

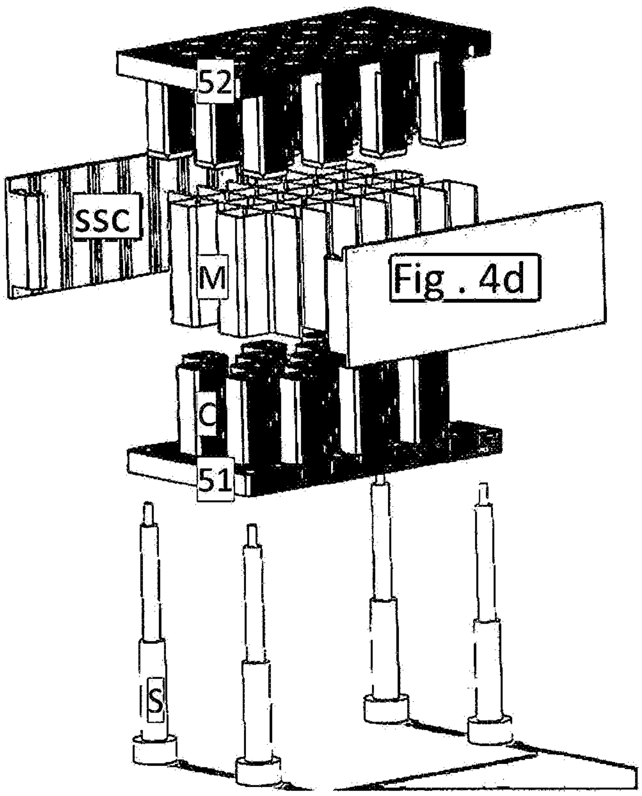


Fig . 4d

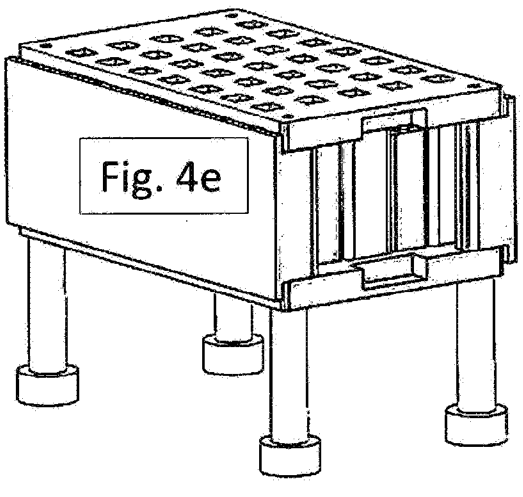


Fig. 4e

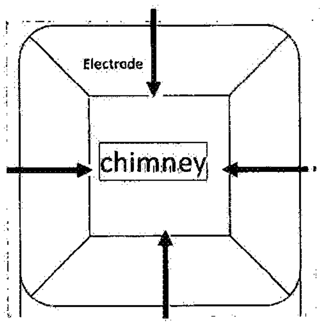


Fig. 5

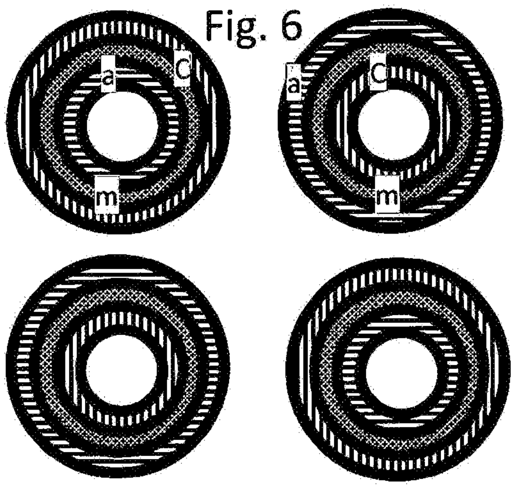


Fig. 6

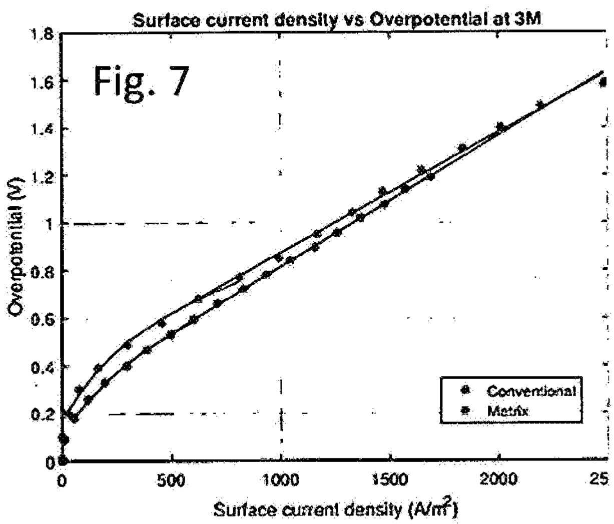


Fig. 7

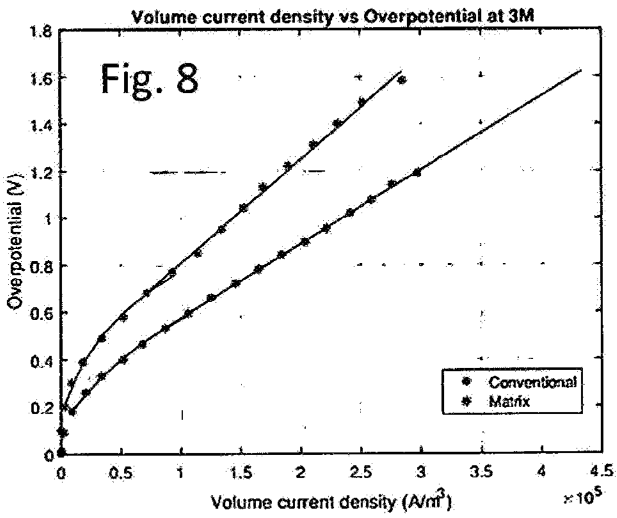


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2019/050409

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B11/03 C25B13/02 C25B1/04 C25B9/10 C25B9/18
ADD.

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)
C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/292094 A1 (SWIEGERS GERHARD FREDERICK [AU] ET AL) 15 October 2015 (2015-10-15) paragraph [0123] - paragraph [0129]; figures 4b, 12, 13; example 3 -----	1-21
X	US 2012/222954 A1 (LOTHRING ADOLF [AT]) 6 September 2012 (2012-09-06) paragraph [0122] - paragraph [0123]; figure 8 abstract -----	1-13, 15-18, 20,21
X	US 6 254 741 B1 (STUART ANDREW T B [CA] ET AL) 3 July 2001 (2001-07-03) column 1, lines 5-25 figures 3, 4 -----	1-11,14, 17,18, 20,21

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 October 2019	18/10/2019

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Desbois, Valérie

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/075977 A1 (ADAM STEFAN KASPRZAK [US] ET AL) 19 March 2015 (2015-03-19) claims 1, 2; figures 1-5 -----	1-11,17, 18,20,21
X	WO 2017/170664 A1 (MITSUBISHI HEAVY IND ENVIRONMENTAL & CHEMICAL ENG CO LTD [JP]) 5 October 2017 (2017-10-05) abstract figures 1, 6 -----	1,2,4, 6-11,18, 21
A	WO 2015/085363 A1 (AQUAHYDREX PTY LTD [AU]) 18 June 2015 (2015-06-18) paragraph [0030] paragraph [0068] claims 1-41; figure 1 -----	1-12,14, 15,19,21
A	US 2017/067170 A1 (HANSEN DON LEE [US]) 9 March 2017 (2017-03-09) claim 29 -----	13
A	US 2014/284209 A1 (GILMAN BRIAN DANIEL [US]) 25 September 2014 (2014-09-25) claim 1; figure 15 -----	1-21

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2019/050409

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015292094 A1	15-10-2015	AU 2013273920 A1	15-01-2015
		BR 112014030994 A2	27-06-2017
		CA 2875882 A1	19-12-2013
		CN 104583459 A	29-04-2015
		EP 2859135 A1	15-04-2015
		JP 6267691 B2	24-01-2018
		JP 2015525297 A	03-09-2015
		JP 2018076596 A	17-05-2018
		KR 20150063347 A	09-06-2015
		RU 2014152260 A	27-07-2016
		US 2015292094 A1	15-10-2015
		US 2019256991 A1	22-08-2019
		WO 2013185170 A1	19-12-2013
US 2012222954 A1	06-09-2012	AT 508813 A1	15-04-2011
		AU 2010302924 A1	24-05-2012
		BR 112012007594 A2	23-08-2016
		CA 2775366 A1	07-04-2011
		CN 102639753 A	15-08-2012
		EA 201270477 A1	30-11-2012
		EP 2483449 A1	08-08-2012
		JP 2013506051 A	21-02-2013
		KR 20120096479 A	30-08-2012
		US 2012222954 A1	06-09-2012
		WO 2011038432 A1	07-04-2011
		ZA 201202419 B	26-06-2013
US 6254741 B1	03-07-2001	AT 232245 T	15-02-2003
		AU 4282700 A	05-03-2001
		BR 0012936 A	30-04-2002
		CA 2379018 A1	15-02-2001
		CN 1399689 A	26-02-2003
		DE 60001369 D1	13-03-2003
		EP 1203111 A1	08-05-2002
		JP 2003506576 A	18-02-2003
		MX PA02001273 A	12-08-2002
		NZ 516761 A	26-11-2002
		US 6254741 B1	03-07-2001
		WO 0111112 A1	15-02-2001
		ZA 200200649 B	08-10-2002
US 2015075977 A1	19-03-2015	NONE	
WO 2017170664 A1	05-10-2017	CN 108431302 A	21-08-2018
		JP 6244599 B2	13-12-2017
		JP 2017186588 A	12-10-2017
		KR 20180079462 A	10-07-2018
		WO 2017170664 A1	05-10-2017
WO 2015085363 A1	18-06-2015	US 2016312370 A1	27-10-2016
		WO 2015085363 A1	18-06-2015
US 2017067170 A1	09-03-2017	CN 108138338 A	08-06-2018
		EA 201890645 A1	31-01-2019
		EP 3347508 A1	18-07-2018
		JP 2018530669 A	18-10-2018
		KR 20180051570 A	16-05-2018
		US 2015068889 A1	12-03-2015

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2019/050409

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 2017067170 A1	09-03-2017
		WO 2017042639 A1	16-03-2017
		ZA 201802121 B	26-06-2019
US 2014284209 A1	25-09-2014	CA 2900853 A1	25-09-2014
		EP 2976446 A1	27-01-2016
		US 2014284209 A1	25-09-2014
		WO 2014153389 A1	25-09-2014