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(54) Title: A PHOTOELECTROCHEMICAL DEVICE SUITABLE FOR PRODUCTION OF ELECTRICITY AND SEAWATER DESALINIZATION

(57) Abstract: The present invention relates to a photoelectrochemical system for energy production and seawater desalinization characterized by the presence of an inorganic photoanode and a biocathode comprising an enzyme immobilized on a carbon based cathode. The invention allows for direct conversion of sunlight into energy and for production offresh water, thus can be used for water desalinization or in combination with water desalinization systems.

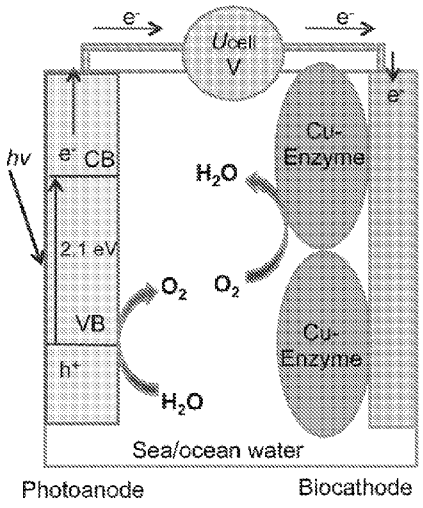


FIG. 1

A PHOTOELECTROCHEMICAL DEVICE SUITABLE FOR PRODUCTION OF ELECTRICITY AND SEAWATER DESALINIZATION

FIELD OF THE INVENTION

The present invention relates to a photoelectrochemical device for energy production and seawater desalinization comprising an inorganic photoanode and a biocathode comprising an enzyme immobilized on a carbon based cathode.
The invention allows for direct conversion of sunlight into energy, producing at the same time fresh water from seawater and thus it can be used for seawater desalinization or in combination with water desalinization systems, and does not need any supply of fuel except of sunlight and seawater

BACKGROUND OF THE INVENTION

Modern energy services are crucial to human well-being and to a country's economic development. Access to energy is essential for the provision of clean water, sanitation and healthcare and for the provision of reliable and efficient lighting, heating, cooking, mechanical power, transport and telecommunications services. It is an alarming fact that today billions of people lack access to the most basic energy services. Indeed the World Energy Outlook 2014 shows that nearly 1.3 billion people are without access to electricity.
Furthermore, according to the World Health Organization and UNICEF Joint Monitoring Programme in 2015 more than 80 countries have water shortages and 1 billion people around the world lacked access to safe water making water crisis the most relevant global risk based on impact to society, as a measure of devastation as announced by the World Economic Forum in 2015. Therewith approximately 1338×10^{15} m^3 of water (96.5% of all Earth's water) are stored in ocean/sea, a part of which can be actually used for production of fresh water. Therefore, there is a need for smarter solutions leading to sustainable production of energy from environmental resources as well as production of fresh water for drinking, cooking and sanitary use.
The current invention addresses both these issues and provides in one device a common solution for both problems.

Currently, most of solar energy transformation devices are represented by photovoltaic solar cells directly transforming solar light into electrical power with

over 80% of the solar market dominated by the crystalline silicon-based solar cell technology, partially due to the well-developed silicon industry. These solutions are quite expensive and both sustainability of solar cell production and solar cell panel recycling or scrapping become vital reasons for looking for new solutions.

For several years, biological photosynthesis principles for energy extraction has been explored providing numerous examples of biological photosystem II wired to electrodes for water oxidation. However, these systems have the disadvantage of being complicated, unstable, particularly in alkaline environment, and with low efficiency (less than 1%) and low perspectives of improvement. Generally, the bioelectrochemical systems include redox mediators having the drawback of increased toxicity, complexity and cost, which may lead to operational failures. Among possible solutions, artificial photosynthetic systems have been explored for electrocatalytic production of H_2 "solar fuel" (at Pt cathode) by water splitting to O_2 and H^+ at a sunlight-illuminated semiconductor anode (e.g. TiO_2) at potentials less positive (more negative) than the standard potential of water decomposition (1.23 V) or H_2 evolution. Water photoelectrochemical splitting have been optimized using several different relatively expensive approaches, with varying extent of effectiveness. Hitherto, artificial photosynthesis devices have been considered solely for H_2 production at Pt cathodes in strongly alkaline solutions, and never were shown to operate in such environmental media as seawater, where underlying reactions are thermodynamically unfavourable.

Hence, an improved system able to efficiently produce energy, such as electrical energy, as well as fresh water at low costs from environmental resources would be advantageous.

OBJECT OF THE INVENTION

It is an object of the invention to provide a system that is able to produce electricity sustainably and at low cost and at the same time produce fresh water from seawater.

It is a further objection of the invention to produce a seawater desalinization device or a device that can improve the efficiency of current desalinization systems.

It may be seen as an object of the current invention to provide a device and a method for converting solar energy into electrical energy sustainably and at low cost.

It may be seen as an object of the current invention to provide a system and a method for converting seawater into fresh water sustainably and at low cost.
It is a further object of the present invention to provide an alternative to the prior art.
In particular, it may be seen as an object of the present invention to provide a photoelectrochemical device that solves the above-mentioned problems of the prior art by converting sun light irradiation into electrical energy by using seawater and oceanwater to produce fresh water.

SUMMARY OF THE INVENTION

The invention solves the above problems and reach the above mentioned objects through a photoelectrochemical device that couples photoelectrooxidation of water induced by sunlight irradiation and biocatalytic electroreduction of oxygen gas achieved by employing the electrical energy produced by the photoelectrooxidation of the water.

One of the great advantages of the photoelectrochemical device of the invention is that it can convert solar energy into electricity employing sustainable and low cost materials as well as aqueous solutions at ambient and environmental friendly conditions, such as physiological/environmental pH, high chloride content, ambient pressure and temperature.
A second advantage of the photoelectrochemical device of the invention is the ability of producing fresh water from water solutions, such as environmental water solutions comprising salts, i.e. saline water, and being neutral/alkaline (pH 7-8). When in operation, saline water is oxidized at the photoanode and fresh water is produced at the biocathode. In that way the photoelectrochemical device may be used in combination or may support water desalinization systems.

In this invention, artificial photosynthetic systems with enzymatic cathodes operating with no mediators to directly convert solar energy in electricity that can be used both as a power source, for water desalination, and for production of fresh water from seawater are constructed. Two reactions underlie the system operation: photoelectrocatalytic oxidation of H_2O to O_2 and H^+ at the semiconductor anodes and bioelectrocatalytic O_2 reduction to water at the biocathodes comprising an O_2 reducing enzyme immobilized on inexpensive carbon materials.

Thus, the above described object and several other objects are intended to be obtained in a first aspect of the invention by providing a photoelectrochemical device comprising: a semiconductor photoanode; a biocathode comprising copper proteins immobilized on the high-surface area cathode with no mediators, wherein the cathode is a carbon based electrode, and wherein the cathode is electrically connected to the photoanode.

The photoanode, such as a photoanode comprising iron oxide, such as hematite, for example doped hematite, or comprising titanium oxide or titania, such as doped titania, employed by the photoelectrochemical device of the invention has an optimal valence band potential so as to achieve a catalytic photoelectrooxidation of water to oxygen gas.
In some embodiments, the photoanode comprises iron oxide such as hematite.
In some other embodiments, the photoanode comprises titanium dioxide.

In some further embodiments, the photoanode may comprises a co-catalyst.
For example, the photoanode may be coated firstly with the catalyst followed by the co-catalyst. In some embodiments, both catalyst and co-catalyst are co-deposited.
Examples of co-catalysts that can be used are based on transition metals, such as Zn or Ti. The co-catalysts may also be referred to as doping elements.
Thus, the photoanode comprises iron oxide, such as hematite or doped hematite.
For example, doped hematite may be Zinc doped or Titanium doped or Ti and Zn doped hematite.
One of the advantages of the use of a co-catalyst is the reduction of the water oxidation overpotentials.
Thus, in some embodiments, the photoanode comprises metal doped-hematite, such as Zn, Ni or Co doped hematite.

Due to the band gap of the semiconductors comprised in the photoelectrode or photoanode, such as Iron oxide/ Fe_2O_3 or doped hematite, upon light irradiation ($h\nu$) electrons can be promoted from the valence band into the conduction band thus leaving holes (h^+) in the valence band. This, in turn, causes oxidation of the water of an aqueous solution in contact with the photoanode.

Hematite or doped hematite has the advantage of being a very stable at neutral and alkaline pH and a relatively low cost photocatalyst with suitable band edges positions.

Furthermore, hematite can be supported on a transparent double face glass substrate coated with a transparent conducting oxide (TCO) layer, for example fluorine doped tin oxide (FTO) or indium doped tin oxide (ITO), thus allowing for transmittance of the incident light.

In some embodiments, the doped hematite is produced by co-deposition, e.g. electrochemical co-deposition, of a doping metal and hematite on a transparent conductive substrate, such as transparent conducting oxide.

The photoanode may have different morphologies. For example, the photoanode may comprise a thin layer of oxide deposited on a surface. In some other embodiments, the photoanode may be a semiconductor applied over a three dimensional structure. For example, the photoanode may be formed by a coating of Fe_2O_3, e.g. applied via atomic layer deposition (ALD), on a porous glass coated with FTO.

In some embodiments, the photoanode may be a nanostructured surface thereby a surface with an increased surface area available for the reaction of photoelectrooxidation of water into oxygen gas and other improved reaction characteristics.

In some embodiments, the photoanode is or comprise a semiconductor, such as a wide-band gap semiconductor, for example titania or doped titania.

The Cathode may comprise macromolecular biological catalysts, such as enzymes, e.g. copper proteins that when the photoelectrochemical device according to the invention is in operation, the cathode catalyzes a reduction reaction at the cathode surface. In that, the cathode may also be referred to as biocathode.

Macromolecular biological catalysts, such as enzymes are immobilized onto the carbon based electrode external surface, thus being available for the direct electronic communication with the electrode and the reduction reaction.

Thus, in some embodiments, the copper proteins are immobilized on the cathode.

Copper proteins are generally not immobilized directly on the cathode. In these cases, the copper proteins may be deposited on a redox mediator that is located on the electrode or vice versa.

In these cases the copper proteins on the cathode are electronically connected to the electrode by means of redox mediators and/or redox relays. Examples of mediators are soluble redox active species with appropriate potentials which may be 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) and ferrocene derivatives, and immobilized on the electrode redox active species and polymer films that may be conductive polymers and redox active polymers and gels.

In general, the presence of a mediator facilitates the electron transfer to the enzyme from the electrode, thus improving the device performance.

The invention allows for good electrical and bioelectrocatalytic performance of biocathodes without the need of redox mediators.

Thus, in some embodiments, no redox mediators are present at the cathode

This is of great advantage as it simplifies the structure of the device and, at the same time, provides good current density. Furthermore, the absence of redox mediator reduces the toxicity of the system as redox mediators may be toxic towards the environment.

In some embodiments, the copper proteins are or comprise oxidoreductases exhibiting bioelectrocatalytic activity in seawater or oceanwater at pH between 7 and 9

Generally, most of the oxygen-reducing oxidoreductases are not active or low active in alkaline and chloride-rich environment such as seawater or oceanwater. One of the advantage of the photoelectrochemical device of the invention is that both photoanode and biocathode are active in seawater or oceanwater at pH between 7 and 9.

In some embodiments, the copper proteins are oxidoreductases, such as bilirubin oxidases.

In some further embodiments, the copper proteins are oxidoreductases, such as laccases.

For example, oxidoreductases may be bacterial recombinant laccase enzymes and fungal bilirubin oxidases.
In some other embodiments, oxidoreductases may not be recombinant.
Oxidoreductases being in use exhibit bioelectrocatalytic activity in oxygen reduction reaction at sufficiently high potentials in neutral and alkaline media and in the presence of NaCl.

The cathode comprises at its core a carbon based electrode, e.g. an electrically conducting surface comprising or consisting of a material selected from the group consisting of spectroscopic graphite, highly oriented pyrolytic graphite, graphite felt, graphene oxide, reduced graphene, mesoporous carbon, carbon microfiber, carbon fibre, carbon paste, carbon cloth, screen-printed carbon, carbon nanomaterials, carbon paper and carbon felt.

The combination of the specific copper proteins, such as bilirubin oxidases on carbon based electrode, such as high-surface area carbon based electrode, for example carbon nanomaterials, has the advantage of ensuring good current density, thus not requiring the presence of mediators, and at the same time allowing for use in seawater or oceanwater, i.e. alkaline environment with a pH between 7 and 9 and at high salt concentration such as with a salinity between 3% and 4%.

When the photoelectrochemical device according to the first aspect of the invention is in operation, the electrolyte environment surrounding the photoanode and the cathode may be the same.
In some embodiments, the electrolyte environment surrounding the photoanode and the cathode may be different.

When in operation, the cathode may be surrounded by electrolyte.
When not in operation, the cathode may also be surrounded by electrolyte.
For example, the electrolyte may be a water immiscible electrolyte.

When in operation, the electrolyte surrounding the photoanode is an aqueous electrolyte as the photoanode catalyses the oxidation of water into oxygen gas.

Thus having an electrolyte surrounding the cathode, which is water immiscible, has the advantage of separating the photoanode environment from the one of the cathode avoiding mixing the fresh water produced at the cathode with the saline water present at the photoanode.

The electrolyte may be an ionic liquid electrolyte.

In some embodiments, the electrolyte may be a hydrogel.

In some further embodiments, the electrolyte surrounds and is in contact with the cathode, thus the cathode may comprise the electrolyte.

Hydrogel and ionic liquid electrolyte have a high viscosity, may be of a quasi-solid consistency, and thus may be part of the cathode.

In some embodiments, the photoelectrochemical device is membraneless, thus it may operate without any membrane separation between the photoanode and the cathode.

Photoanode and biocathode may be located in close vicinity, e.g. in a radius range between 0.1 mm and 2 mm.

Close vicinity between photoanode and biocathode may be an advantage as increasing the device performance due to an increase in the production of electricity.

Electrically connected is defined as connected via an electrical connection allowing electrodes produced via an oxidation reaction at the photoanode to travel towards the cathode where a reduction reaction occurs.

In some embodiments, the photoelectrochemical device may further comprise a solution having a pH between 7 and 9.

One of the advantage of the photoelectrochemical device of the invention is that both photoanode and biocathode are active in alkaline environment. This is generally not the case for cathode comprising macromolecular biological catalysts.

This solution having a pH between 7 and 9 may be an electrolyte solution.

In some embodiments, the solution may be an aqueous solution comprising salts, such as sodium, lithium, magnesium, calcium or potassium chloride or bromide. For example, the solution may be seawater or oceanwater.

Several configurations are possible for the photoelectrochemical device of the invention.

In some embodiments, both the electrically connected photoanode comprising doped hematite and biocathode having copper proteins immobilized onto the cathode surface may be operated by being submerged into an aqueous solution, for example an electrolyte solution. The aqueous solution may be saline water, such as seawater and oceanwater.

The photoanode submerged in seawater upon light irradiation produces electrons that collected through the external circuit, i.e. the electrical connection between the electrodes, flow towards the cathode. The oxygen gas produced at the photoanode by oxidation of water diffuses towards the cathode where it is reduced to water.

In some embodiments, the electrolyte solution in contact with the photoanode, e.g. seawater, will also be in contact with the cathode in an open system aiming at electricity production.

Thus, in some embodiments, the photoelectrochemical device is membraneless.

In some other embodiments, the electrolyte solution in contact with the photoanode is different from the one in contact with the cathode.

Indeed, in some further embodiments the cathode is surrounded by a water immiscible electrolyte. The surface of the cathode where copper proteins are immobilized is thus not in contact with the aqueous solution or seawater as surrounded by a water immiscible electrolyte. However, oxygen gas may diffuse from the seawater towards the cathode through the water immiscible electrolyte. In this way, the oxygen gas produced at the photoanode upon light irradiation may reach the surface of the cathode and thus of the copper protein and in turn is oxidized to fresh water.

A separation system may be coupled to the cathode surrounded by the water immiscible electrolyte so that fresh water produced at the cathode may be removed and collected from the surface of cathode and stored separately.

The separation system may comprise a separation membrane at the interface between the water immiscible electrolyte and the surrounding environment.

The separation system may also comprise means for storing the fresh water produced at the cathode.

Water immiscible electrolytes may be gels and ionic liquids, e.g. ionic conductors. Importantly, water immiscible electrolytes should be oxygen permeable so as to allow for diffusion of oxygen gas towards the cathode. Furthermore, water immiscible electrolytes should have a low solubility for salts so as to avoid salt penetration, e.g. NaCl diffusion into the water immiscible electrolyte.

In some other embodiments, a membrane is present between the photoanode and the cathode.

For example, the photoelectrochemical device may further comprise a membrane located between the photoanode and the cathode, thereby separating the photoelectrochemical device at least into two chambers, a photoanode chamber and a cathode chamber by the membrane.

The photoelectrochemical device of the invention may comprise a case where the electrodes are inserted separated by the presence of a membrane. The case comprises at least the photoanode chamber and the cathode chamber.

In some embodiments when the photoelectrochemical device according to the first aspect of the invention is in operation, the oxygen gas produced at the photoanode diffuses at the cathode where is reduced to water.

The membrane may allow for oxygen gas diffusion from the photoanode chamber to the cathode chamber, thus allowing for the reduction reaction to occur at the cathode using as a reactant the oxygen gas produced at the photoanode.

The membrane may be an ion-exchange membrane, such as a cation exchange membrane.

In some other embodiments, the ion-exchange membrane may be an anion exchange membrane.

In some embodiments, the membrane is a semipermeable membrane, such as an osmotic membrane.

In some embodiments, the membrane is an oxygen permeable membrane, thereby allowing for oxygen to diffuses from the photoanode chamber to the cathode chamber.

In some embodiments, the photoelectrochemical device according to the first aspect of the invention further comprises an inlet for a gas comprising oxygen, such as air.

The inlet is suitable for oxygen gas insertion at the biocathode. In this way, oxygen gas can be directly provided at the biocathode for reduction to water.

In some embodiments, the inlet is located in the proximity of the cathode.

When a membrane separates the device into a photoanode chamber and a cathode chamber, the inlet maybe located within the cathode chamber.

When in use, the inlet is submerged in the electrolyte solution.

When an inlet for oxygen gas is not present, the oxygen at the biocathode is provided by simple diffusion from the photoanode.

In some embodiments, the photoelectrochemical device further comprises an outlet for oxygen gas.

In some embodiments, the outlet is located in the proximity of the photoanode. Proximity is defined between 1 and 1000 mm from the surface of the cathode, such as between 5 and 500 mm.

When a membrane separates the device into a photoanode chamber and a cathode chamber, the outlet may be located within the photoanode chamber.

The outlet may be connected to the inlet, thereby when in operation oxygen gas produced at the photoanode may flow towards the inlet and thus be injected into the cathode chamber.

The oxygen gas produced at the photoanode is thus recycled and used to produce fresh water at the cathode.

The photoelectrochemical device converting light irradiation, such as sun light, into energy, such as electrical energy, may be considered a device for producing electricity.

The photoelectrochemical device may also be considered a desalinization device as producing fresh water from a feed of saline water.
Thus, in some embodiments, the photoelectrochemical device is a desalinization device.

In a second aspect, the invention relates to the use of a photoelectrochemical device according to the first aspect of the invention for water desalinization.

In a third aspect, the invention relates to a desalinization system comprising the photoelectrochemical device according to the first aspect of the invention.

In a fourth aspect, the invention relates to a method for producing fresh water through a photoelectrochemical device according to first aspect of the invention, the method comprising:

- oxidizing water at the photoanode upon light irradiation;
- reducing oxygen gas at the cathode, thereby producing fresh water at the cathode.

In a fifth aspect, the invention relates to a method of operating the photoelectrochemical device according to first aspect of the invention, the method comprising: light irradiating the photoanode in contact with a first aqueous solution, thereby producing a charge separation causing oxidation of the first aqueous solution and producing oxygen gas; injecting gas containing oxygen into a second aqueous solution in the proximity of the cathode; reducing the injected gas to water at the cathode, thereby producing fresh water at the cathode.

An advantage of the invention is thus that the photoelectrochemical device according to the first aspect of the invention can be used to produce fresh water from sea and oceanwater.

In a further aspect, the invention relates to the use of the photoelectrochemical device according to the first aspect of the invention in producing fresh water. As the the photoelectrochemical device according to the first aspect of the invention can be used to reduce the salt content in seawater, the photoelectrochemical device can be used in desalinization process for example in combination with a semipermeable membrane, such as an osmotic membrane. In this specific case, when in operation a pressure may be applied to the electrolyte solution present in the photoanode chamber equal to the osmotic pressure needed to prevent inward flow of water across a semipermeable membrane. In this way, the cathode chamber can be used as a mean for storing, i.e. a storage chamber, for the fresh water produced.

The first, second and third and other aspects and embodiments of the present invention may each be combined with any of the other aspects and embodiments. These and other aspects and embodiments of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

BRIEF DESCRIPTION OF THE FIGURES

The photoelectrochemical device according to some embodiments of the invention will now be described in more detail with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

Figure 1 shows a schematic representation of a photoelectrochemical device comprising a Zn-doped hematite photoanode and blue-copper enzymes according to some embodiments of the invention for electricity production.

Figure 2 shows schematic representation of a photoelectrochemical device comprising a Zn-doped hematite photoanode and blue-copper enzymes immobilized on a cathode surrounded by a water immiscible electrolyte according to some embodiments of the invention.

Figure 3A shows a voltammogram comparing hematite photoanodes (1) and Zn-doped hematite photoanodes (2) under illumination and in the absence of light (1') and (2'), at pH 8.

Figure 3B shows voltammetric curves obtained at bilirubin oxidase (BOD) biocathode comprising BOD cross-linked by BS^3 immobilized on a carbon cloth electrode (4) in the presence of O_2 and (3) in the absence of bioelectrocatalysis inhibited by cyanide are presented, at pH 8.

Figure 3C shows representative linear sweep voltammograms recorded with a Zn-doped hematite electrode in different media, under illumination and without.

Figure 3D shows representative linear sweep voltammograms recorded with a TiO_2 nanopartilces–modified electrode in different media, under illumination and without.

Figure 3E shows representative linear sweep voltammograms recorded with the bilirubin oxidase-modified carbon cloth electrode in different media in air-saturated and deaerated solutions.

Figure 4 shows a cyclic voltammogram of the bioelectrocatalytic reduction of oxygen at pH 8 by a biocathode comprising bilirubin oxidase (BOD) cross-linked by BS^3 immobilized on a carbon cloth electrode,(5) in the absence and (6) in the presence of 0.6 M NaCl.

Figure 5A shows a graph comparing of the power produced by a photoelectrochemical devices comprising BOD biocathodes according to some embodiments of the invention, (7) at pH 8 and (8) at pH 8 in the presence of 0.6 M NaCl.

Figure 5B shows current-power (42, 44) and current-cell voltage (41,43) dependences for a photovoltaic biofuel cell comprising bilirubin oxidase-modified carbon cloth electrode as a biocathode and titanium oxide as a photoanode in different media, pH 8.

Figure 5C shows current-power (46, 48) and current-cell voltage (45, 47) dependences for a photovoltaic biofuel cell comprising bilirubin oxidase-modfied carbon cloth electrode as a biocathode and Zn-doped hematite as a photoanode in different media, pH 8.

Figure 5D shows the current-power (50) and current-cell voltage (49) dependences for a photovoltaic biofuel cell comprising bacterial laccase/carbon nanotube-modified graphite electrode as a biocathode and titanium oxide as a photoanode in buffer solution at pH 8.

Figure 5E shows the current-power (52) and current-cell voltage (51) dependences for a photovoltaic biofuel cell comprising bacterial laccase/carbon nanotube-modified graphite electrode as a biocathode and titanium oxide as a photoanode in sea water, pH 8.

Figure 6A shows cyclic voltammograms of dioxygen (O_2) bioelectrocatalytic reduction performed by laccase-modified graphite electrodes according to some embodiments of the invention, (9) to (12) pH varying from 5 to 8..

Figure 6B shows cyclic voltammograms of dioxygen (O_2) bioelectrocatalytic reduction laccase-modified graphite electrodes performed in different electrolytes with (a)-(c) NaCl content increasing from 0 to 0.6 M.

Figure 7A shows the current-power dependences for a photoelectrochemical device according to some embodiments of the invention comprising the laccase/CNT-modified graphite electrode as biocathode, at (13) pH 8 and (14) in the seawater.

Figure 7B shows the device voltage of the photoelectrochemical device operating under illumination vs time.

Figure 8 shows the current-power dependences for the photoelectrochemical device according to some embodiments of the invention comprising the laccase-modified graphite biocathode and the Pt cathode in combination with the Zn-doped hematite photoanode.

Figure 9 is a flow-chart of a method according to some embodiments of the invention.

DETAILED DESCRIPTION OF AN EMBODIMENT

Figure 1 is a schematic representation of the working principle in a photoelectrochemical device according to some embodiments of the invention Figure 1 shows a photoanode electrically connected to a biocathode submerged into an aqueous solution.

The reactions involved in the operation of the photoelectrochemical device are:

- Water oxidation
    - Reaction at the photoanode

$$2H_2O \rightarrow O_2 + 4\mathrm{H}^+ 4\mathrm{e}^- \quad (1)$$

    - Reaction at the cathode

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

The acqueous solution may be seawater and oceanwater, the photoanode may be a Zn-doped hematite (α-Fe_2O_3) photoanode thus a photoanode that catalyse the photoelectrooxidation of H_2O to O_2. The oxygen gas produced at the photoanode diffuses towards the biocathode through the seawater. The biocathode comprises blue-copper enzymes, e.g. fungal bilirubin oxidase or bacterial laccase, which catalyze the electroreduction of O_2 to H_2O. The photoelectrochemical device of figure 1 produces electricity upon light irradiation when submersed in seawater.

Figure 2 is a schematic representation of the working principle in a photoelectrochemical device according to some other embodiments of the invention.

The device of figure 2 comprises the same photanode and biocathode as in figure 1. However, the biocathode of the device of figure 2 is surrounded by a water immiscible electrolyte. The water immiscible electrolyte is in contact with the blue-copper enzymes of the biocathode and creates a separation between the seawater surrounding the photoanode and the biocathode.

The water immiscible electrolyte used is oxygen gas permeable. Oxygen gas produced at the photoanode can diffuse towards and to the biocathode, while seawater cannot come in contact with the biocathode. The fresh water produced by the biocathode may be further collected and stored. The device is thus suitable for water desalination as producing fresh water from a feed of seawater.

In both embodiments, the device may operate in neutral or alkaline media.

Photoanodes were prepared by electrodeposition of hematite-doped films onto of 1.4 cm × 2.2 cm fluorine-doped tin oxide (SnO_2:F, FTO) conducting transparent glass (Nippon Sheet glass, resistance of 20-30 Ω), on one side. The electrodeposition bath consisted of an aqueous solution of $FeCl_3 \cdot 6H_2O$ (5 mM), KF (5 mM), KCl (0.1 M), H_2O_2 (1 M) and $ZnCl_2$ (0.6 mM) at 50°C with N_2 flushed through the solution prior experiments and maintained over the solution during the electrodeposition process. The electrochemical growth of iron oxide film was achieved by a potential cycling procedure (CV), at a scan rate of 0.1 V s^{-1}, from -0.52 to +0.41 V (vs. Ag/AgCl, KCl 3 M) for a whole of 100 cycles. A ratio of

10 % (with respect to Zn+Fe) was found optimal, offering the best photocurrent density. The obtained iron oxide films were annealed at 800 °C for 30 min in air atmosphere. TiO_2–modified electrodes were prepared by blading 4 mg ml^{-1} dispersion of titanium (IV) oxide powder (TiO_2, P25) in either water or ethanol onto FTO electrode and dried at room temperature. An optical system - solar simulator (LS0108) with an integrated filter holder shutter 90°C beam turner from LOT Quantum Design (Darmstadt, Germany) was used for generation of photoelectrochemical currents. A controlled surface area (0.11 cm^2) of the photoanode was directly exposed to the simulated sunlight, initiated from a Xe lamp (L5B521U).

Figure 3A is a voltammogram comparing hematite photoanodes (1) and Zn-doped hematite photoanodes (2) under illumination and in the absence of light (1') and (2') respectively.

The voltammogram in figure 3A was recorded in 50 mM phosphate-buffered saline (PBS) solution, pH 8, with potential scan rate 100 mV s^{-1}. In figure 3B bilirubin oxidase biocathode volammetric curves recorded at a potential scan rate: 5 mV s^{-1} were recorded (4) in the presence of air oxygen and (3) under conditions of cyanide-inhibited enzyme activity.

Biocathodes were prepared by placing 5 µl of 0.5-3 mg mL^{-1} of the enzyme solution (50 mM phosphate buffer (PBS), pH 7.4, for *Bacillus licheniformis* laccase and 0.1 M HEPES, pH 7.2, for bilirubin oxidase (BOD) from *Myrothecium verrucaria*) either onto bare or carbon nanotubes (CNT)-modified electrode surface or on unmodified carbon cloth electrodes. For CNT modification, 4 µl CNT (2 mg ml^{-1} in DMF) were placed on the electrode surface and either incubated at room temperature for 2 h or left overnight at 4 °C under a plastic lid. Alternatively, the enzyme layer was cross-linked either in vapours of 25% glutaraldehyde or by adding 10 µl of freshly prepared 0.1-0.3 mg mL^{-1} of BS[3].

Figure 3C shows linear sweep voltammograms recorded with a Zn-doped hematite electrode in (33, 31) 1M Tris-HCl buffer solution (pH 8.0), (33, 32) seawater (pH 8.0) and (33, 30) in 1 M NaOH; without (33) and under illumination (30,31,32), light intensity: AM 1.5G, 100 mW cm^{-2}; scan rate: 5 mV s^{-1}

Figure 3D shows linear sweep voltammograms recorded with the TiO_2 nanopartilces–modified electrode in (37,34) 1M Tris-HCl buffer solution (pH 8.0), (37,35) seawater (pH 8.0) and (37, 36) in 1 M NaOH; (37) without and (34, 35, 36) under illumination, light intensity: AM 1.5G, 100 mW cm^{-2}; scan rate: 5 mV s^{-1}.

Figure 3E shows linear sweep voltammograms recorded with the bilirubin oxidase-modified carbon cloth electrode, in (38) N_2-saturated and (40, 39) air-saturated (38, 40) 1M Tris-HCl buffer solution (pH 8.0) and (38, 39) seawater (pH 8.0); scan rate: 5 mV s^{-1}.

Figure 4 is a cyclic voltammogram showing bioelectrocatalytic reduction of oxygen by a bio cathode comprising BOD (cross-linked by BS^3) immobilized on a carbon cloth electrode. The cyclic voltammetry of figure 4 was recorded in 0.1 M PBS (5) and 0.1 M PBS containing 0.6 M NaCl (6), at pH 8. The potential scan rate was 5 mV s^{-1}. The curves were corrected for the CV signals in deaerated solutions.

Figure 5A is a graph showing a comparison of the power produced by a photoelectrochemical device according to some embodiments of the invention. The photoelectrochemical device of figure 5A comprises a carbon cloth cathode modified by the immobilization of BOD(cross-linked by BS^3) and Zn-doped photoanode. The power was recorded upon sunlight illumination in 0.1 M PBS (7), and 0.1 M PBS containing 0.6 M NaCl (8) at pH 8.

Figure 5B shows current-power (42, 44) and current-cell voltage (41,43) dependences for a photovoltaic biofuel cell comprising bilirubin oxidase-modified carbon cloth electrode as a biocathode and titanium oxide as a photoanode. recorded in (41, 42) 1 M Tris-HCl buffer solution (pH 8.0) and (43, 44) seawater (pH 8.0). Light intensity: AM 1.5G, 100 mW cm^{-2}; scan rate: 5 mV s^{-1}

Figure 5C shows current-power (46, 48) and current-cell voltage (45, 47) dependences for a photovoltaic biofuel cell comprising bilirubin oxidase-modfied carbon cloth electrode as a biocathode and Zn-doped hematite as a photoanode, recorded in (45, 46) 1 M Tris-HCl buffer solution (pH 8.0) and (47, 48) seawater (pH 8.0); Light intensity: AM 1.5G, 100 mW cm^{-2}; scan rate: 5 mV s^{-1}.

Figure 5D shows the current-power (50) and current-cell voltage (49) dependences for a photovoltaic biofuel cell comprising bacterial laccase/carbon nanotube-modified graphite electrode as a biocathode and titanium oxide as a photoanode, recorded in 1 M Tris-HCl buffer solution (pH 8.0); light intensity: AM 1.5G, 100 mW cm^{-2}; scan rate: 5 mV s^{-1}.

Figure 5E shows the current-power (52) and current-cell voltage (51) dependences for a photovoltaic biofuel cell comprising bacterial laccase/carbon nanotube-modified graphite electrode as a biocathode and titanium oxide as a photoanode, recorded in seawater (pH 8.0); light intensity: AM 1.5G, 100 mW cm^{-2}; scan rate: 5 mV s^{-1}.

Figure 6A shows background-corrected cyclic voltammograms of dioxygen (O_2) bioelectrocatalytic reduction perfomed by a laccase-modified graphite electrodes in 50 mM PBS at pH: 5 (9); 6 (10), 7 (11), and 8 (12). The data are corrected for the signals in deaerated solutions. In the figure 6B a comparison between different electrolytes is shown. In figure 6B the background-corrected cyclic voltammetry showing of dioxygen reduction in the presence of 0 mM (a), 150 mM (b) and 600 mM of NaCl (c), in 50 mM PBS at pH 7 is shown. The potential scan rate was 5 mV s^{-1}.

Figure 7A shows the current-power dependences for a photoelectrochemical device according to some embodiments of the invention. The biocathode of the photoelectrochemical device shown in figure 7A comprises laccase/short thin multiwall carbon nanotubes (STWCNT)-modified graphite electrode as biocathode, while the photoanode comprises Zn-doped hematite.
IV measurements have been recorded in seawater (13) or in PBS buffer pH 8 (14), under simulated sunlight illumination. In figure 7B, the time dependence of the device voltage for the photoelectrochemical device operating under illumination is shown.

Figure 8 shows the current-power dependences for the photoelectrochemical device according to some other embodiments of the invention. The devices shown in figure 8 comprises laccase-modified graphite biocathode (15) in combination

with Zn-doped hematite photoanode or Pt cathode (16) in combination with Zn-doped hematite photoanode

IV measurements have been recorded under the simulated sunlight illumination in 50 mM PBS, pH 8.

Photoelectrocatalytic oxidation of water at the hematite photoanode.

The photoanode operation relies on charge separation in a α-Fe_2O_3 semiconductor film, excited by visible light. The electrons collected at the FTO conductive glass are transported to the biocathode by an external circuit a shown in Figure 1. The Zn-modified hematite photoanode exhibited a 300 mV lower onset potential for water oxidation (around -0.015 V vs. Ag/AgCl) compared to the unmodified hematite, and reaching current densities at of 0.6 mA cm^{-2}, at 1 V, under illumination in alkaline media as shown in Figure 3A. The effect of Zn was ascribed to the Zn contribution to the surface states and acceleration of charge transfer kinetics, possibly by decreasing the rate of surface-mediated electron-hole recombination, by this making Zn-doped hematite an actual water oxidation catalyst. In particular, the contribution of Zn to the surface-associated catalysis of water oxidation is exhibited via the apparent Tafel slopes for the photoelectrocatalytic oxidation of water at the Zn-doped hematite electrodes that approach 120 mV per decade characteristic of a metallised semiconductor with a high concentration of surface states, while for pristine hematite they were close to 59 mV/decade characteristic of a semiconductor with a low concentration of surface states. Similar effects of Co and Al, reflected in the decreased overpotential of the reaction but quite small change in the photocurrent density, can be also discussed in the context of the contribution to surface states. The shift in the photoelectrocatalysis onset potential in the presence of Zn improves the surface electrocatalytic process, and that allows application of hematite for immediate production of electricity when coupled to the oxygen cathode with appropriate potential for catalytic electroreduction of dioxygen. TiO_2-modified photoanodes provide the potential for water oxidation (-1 V) much lower than Zn-doped hematite though their operation in sea-water operation is depressed to a larger extent; nevertherless, their application for production of electricity when coupled to an enzyme biocathode is even more efficient due to the higher voltages of constructed cells.

Bioelectrocatalysis of O_2 reduction by biocathodes

At BOD-modified electrodes bioelectrocatalysis of O_2 reduction, at pH 8, started at 0.47 V vs. Ag/AgCl (Figure 3B), with a 30% drop in the apparent bioelectrocatalytic activity when 0.6 M NaCl was added as shown in (Figure 4). The bioelectrocataytic current was limited by the O_2 diffusion to the electrode and is in the range 100 - 60 μA cm^{-2}. The maximal power density extracted from the photoelectrochemical device with the BOD–cathode and Zn-doped hematite photanode was 32 μW cm^{-2}, at pH 8, being also limited by the oxygen diffusion to the electrode, and 23 μW cm^{-2} in solution containing 0.6 M NaCl, mimicking the seawater conditions as shown in figure 5A, and approaching 4 μW cm^{-2} in sea water as shown in figure 5C. With Titanium oxide photoanodes the maximal power density extracted from the photoelectrochemical device with the BOD–cathode was 225 μW cm^{-2}, in Tris-HCl, at pH 8, and 34 μW cm^{-2} in sea water as shown in figure 5B.

At laccase-modified electrodes the bioelectrocatalytic reduction of O_2 started, depending on pH, from 0.53, 0.48, 0.42 and 0.37 V for pH 5, 6, 7 and 8, respectively, as shown in figure 6A. In the presence of Cl^- anions, laccase electrodes still exhibited an essential activity in O_2 reduction reaction (Figure 6B). At pH 8, the onset of the bioelectrocatalytic reduction of O_2 at the laccase-graphite electrode was around 0.4 V, see figure 6A, and that of e.g. Pt cathode – at 0.265 V The open-circuit voltage U_{oc}, dictated by the difference in the potentials of the biocathode and photoanode reactions, was 500 mV when using the laccase modified-graphite and ca. 350 mV when a more expensive noble metal catalyst, Pt cathode. At room temperature and in alkaline media, 50 mM PBS (pH 8) and seawater, the maximum extracted power density of the photoelectrochemical laccase-biocathode device at 0.5 V was 1.3 μW cm^{-2} and 1 μW cm^{-2}, under illumination, respectively, see figure 7A. With titanium oxide photoanode the performance of the cells was further improved, providing the maximal power density extracted from the photoelectrochemical device with the laccase–cathode of 235 μW cm^{-2}, in Tris-HCl, at pH 8, and 28 μW cm^{-2} in sea water as shown in figures 5D and 5E. The performance of the biofuel cell with the worst charctersitics was superior to the one using the Pt cathode, i.e. 0.4 μW cm^{-2} see figure 8, not mentioning much better performing configurations (figure 7A and figure 5A, laccase immobilised on carbon nanotube-modified graphite electrodes

and BOD coupled to carbon cloth electrodes) Along with this, a quite stable operation was obtained at a cell voltage approaching the U_{oc} for more than 4 hours under simulated sun light.

Figure 9 is a flow-chart of a method according to some embodiments of the invention.

The method 20 of operating a photoelectrochemical device according to first aspect of the invention comprises:

- (S1) light irradiating said photoanode in contact with a first aqueous solution, thereby producing a charge separation causing oxidation of said first aqueous solution and producing oxygen gas;
- (S2) injecting gas containing oxygen into a second aqueous solution in the proximity of the cathode;
- (S3) reducing the injected gas to water at said cathode, thereby producing fresh water at the cathode.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

CLAIMS

1. A photoelectrochemical device comprising:
- a photoanode,
- a cathode comprising copper proteins, wherein said cathode is a carbon based electrode, and wherein said cathode is electrically connected to said photoanode.

2. A photoelectrochemical device according to claim 1, wherein said copper proteins are oxidoreductases exhibiting bioelectrocatalytic activity in seawater or oceanwater at pH between 7 and 9.

3. A photoelectrochemical device according to claim 1 or claim 2, with the proviso that no redox mediators are present at said cathode

4. A photoelectrochemical device according to claim 1 wherein said photoanode comprises metal doped-hematite, such as Zn, Ni or Co doped hematite.

5. A photoelectrochemical device according to claim 4, wherein said doped hematite is produced by co-deposition of a doping metal and hematite on a transparent conductive substrate, such as fluorine doped tin oxide (FTO) glass.

6. A photoelectrochemical device according to claim 1 or claim 2, wherein said photoanode comprises titanium dioxide.

7. A photoelectrochemical device according to any of the claims 1-6, wherein said copper proteins are immobilized on said cathode.

8. A photoelectrochemical device according to any of the claims 1-7, wherein said copper proteins are oxidoreductases, such as bilirubin oxidases.

9. A photoelectrochemical device according to any of the claims 1-7, wherein said copper proteins are oxidoreductases, such as laccases.

10. A photoelectrochemical device according to any of the claims 1-9, wherein said cathode is surrounded by electrolyte.

11. A photoelectrochemical device according to claim 10, wherein said electrolyte is a water immiscible electrolyte.

12. A photoelectrochemical device according to any of the claims 1-11, further comprising an aqueous solution comprising salts, said acqueous solution having a pH between 7 and 9.

13. A photoelectrochemical device according to claim 12, wherein said aqueous solution is an electrolyte solution.

14. A photoelectrochemical device according to any of the claims 12-13, wherein said solution may be an aqueous solution comprising salts, such as sodium chloride or potassium chloride.

15. A photoelectrochemical device according to any of the claims 1-14, said photoelectrochemical device being membraneless.

16. A photoelectrochemical device according to any of the claims 1-14, further comprising a membrane located between said photoanode and said cathode, thereby separating the photoelectrochemical device at least into two chambers, a photoanode chamber and a cathode chamber separated by said membrane.

17. A photoelectrochemical device according to claim 16, wherein said membrane is an ion-exchange membrane, such as a cation exchange membrane.

18. A photoelectrochemical device according to claim 16, wherein said membrane is a semipermeable membrane, such as an osmotic membrane.

19. A photoelectrochemical device according to any of the claims 1-18, wherein when in operation oxygen gas produced at the photoanode diffuse at the cathode where is reduced to water.

20. A photoelectrochemical device according to any of the claims 1-19, further comprising an inlet for a gas comprising oxygen.

21. A photoelectrochemical device according to claim 20, wherein said inlet is located in the proximity of the cathode.

22. A photoelectrochemical device according to any of the claims 20-21, wherein said inlet is located within the cathode chamber.

23. A photoelectrochemical device according to any of the claims 20-22, wherein when in use said inlet is submerged in said electrolyte solution.

24. A photoelectrochemical device according to any of the claims 1-22, further comprising an outlet for oxygen gas.

25. A photoelectrochemical device according to claim 24, wherein said outlet is located in the proximity of the photoanode.

26. A photoelectrochemical device according to any of the claims 24-25, wherein said outlet is located within the photoanode chamber.

27. A photoelectrochemical device according to any of the claims 24-26, wherein said outlet is connected to said inlet, thereby when in operation oxygen gas produced at the photoanode may flow towards the inlet and thus be injected into said cathode chamber.

28. A photoelectrochemical device according to any of the claims 1-27, wherein said photoelectrochemical device is a desalinization device.

29. Use of said photoelectrochemical device according to any of the claims 1-28 for water desalinization.

30. A desalinization system comprising said photoelectrochemical device according to any of the claims 1-28.

31. A method for producing fresh water through a photoelectrochemical device according to any of the claims 1-28, said method comprising:

- oxidizing seawater at said photoanode upon light irradiation;
- reducing oxygen gas at said cathode, thereby producing fresh water at said cathode.

32. A method of operating a photoelectrochemical device according to any of the claims 1-28, said method comprising:

- light irradiating said photoanode in contact with a first aqueous solution, thereby producing a charge separation causing oxidation of said first aqueous solution and producing oxygen gas;
- injecting gas containing oxygen into a second aqueous solution in the proximity of the cathode;
- reducing said injected gas to water at said cathode, thereby producing fresh water at said cathode.

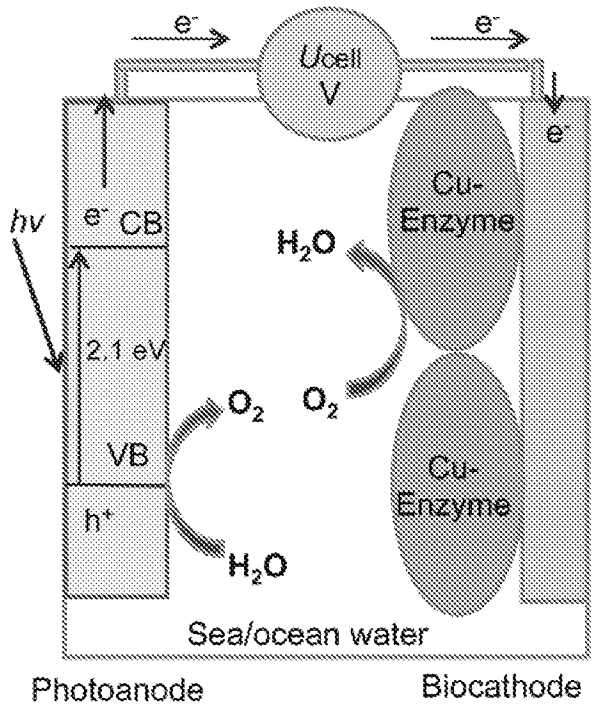

e⁻
Ucell
V
e⁻
e⁻
hv
e⁻ CB
2.1 eV
VB
h⁺
H2O
O2
O2
H2O
Cu-
Enzyme
Cu-
Enzyme
Sea/ocean water
Photoanode
Biocathode

FIG. 1

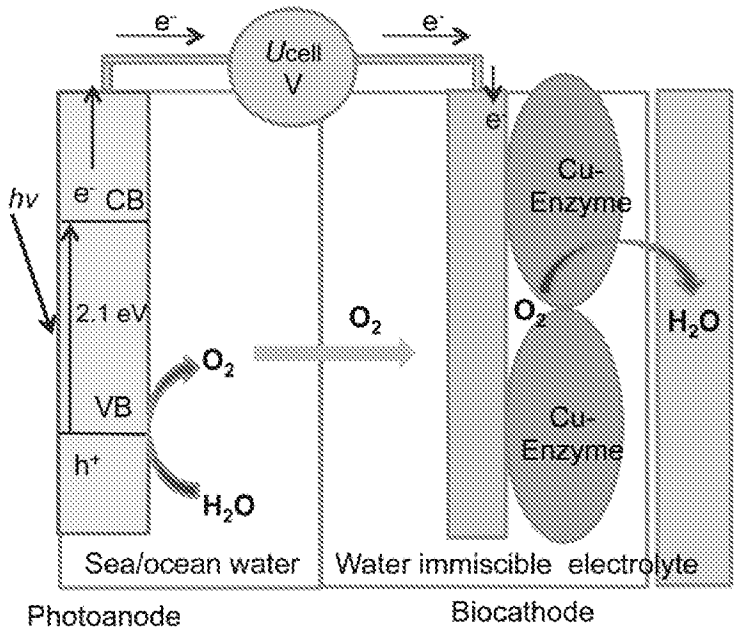

e⁻
Ucell
V
e⁻
e⁻
hv
e⁻ CB
2.1 eV
VB
h⁺
O2
O2
H2O
H2O
Cu-
Enzyme
Cu-
Enzyme
Sea/ocean water
Water immiscible electrolyte
Photoanode
Biocathode

FIG. 2

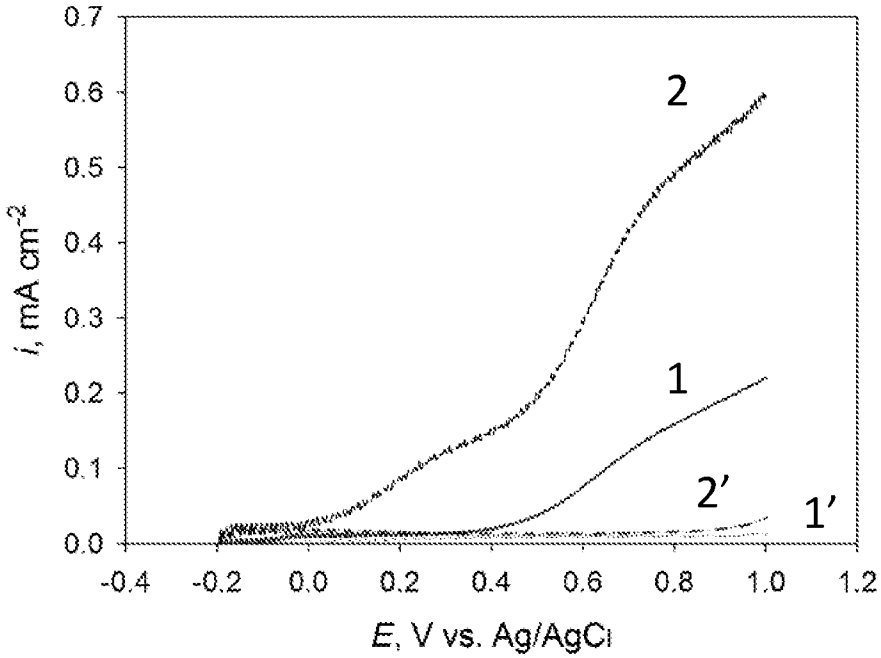

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
i, mA cm-2
2
1
2'
1'
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
E, V vs. Ag/AgCl

FIG. 3A

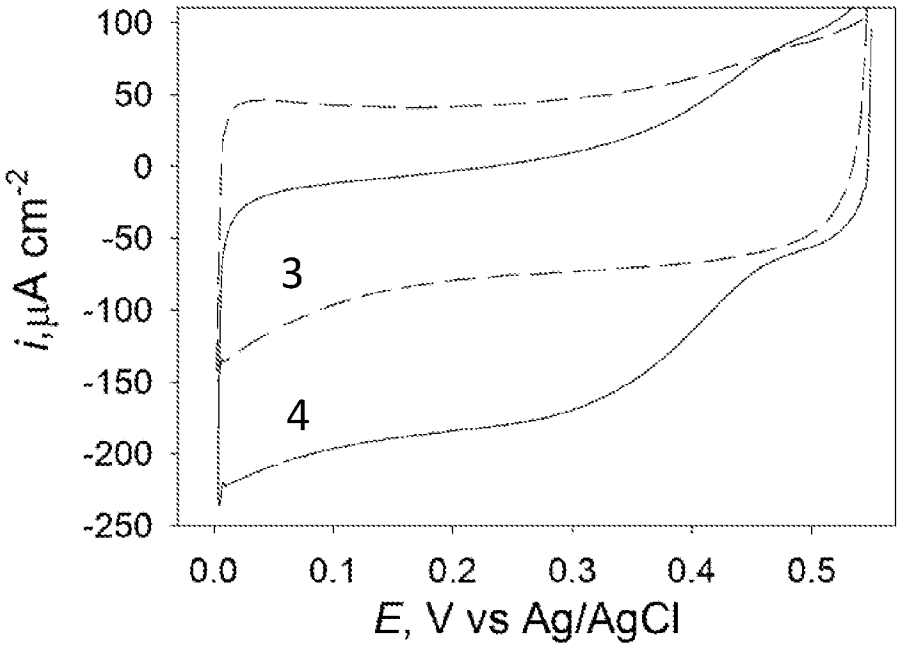

100
50
0
-50
-100
-150
-200
-250
i, µA cm-2
3
4
0.0
0.1
0.2
0.3
0.4
0.5
E, V vs Ag/AgCl

FIG. 3B

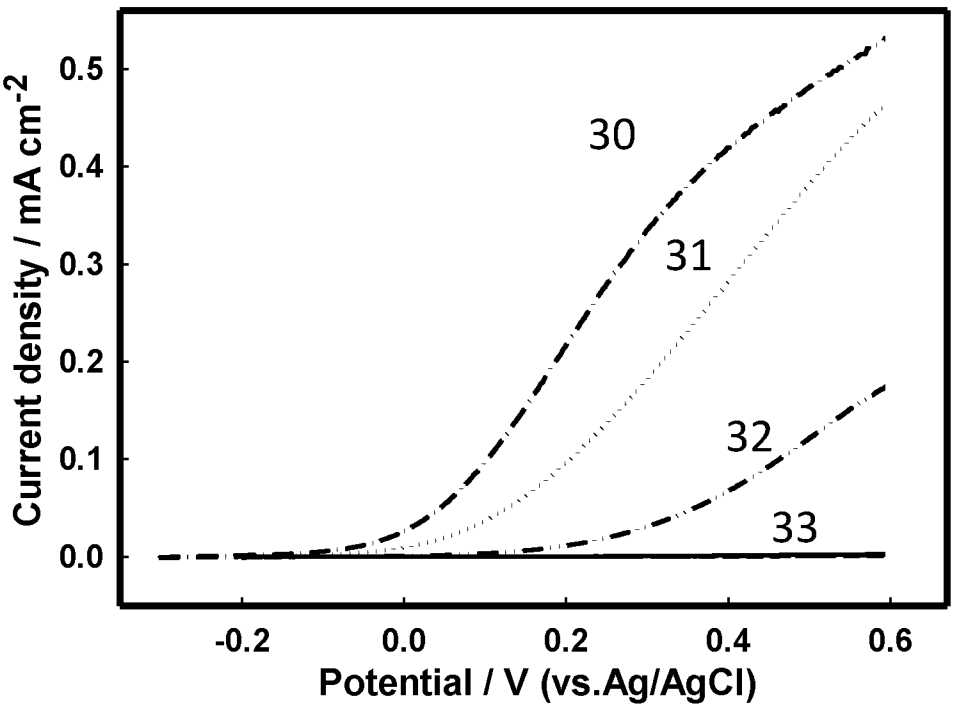

Current density / mA cm-2
0.5
0.4
0.3
0.2
0.1
0.0
30
31
32
33
-0.2
0.0
0.2
0.4
0.6
Potential / V (vs.Ag/AgCl)

FIG. 3C

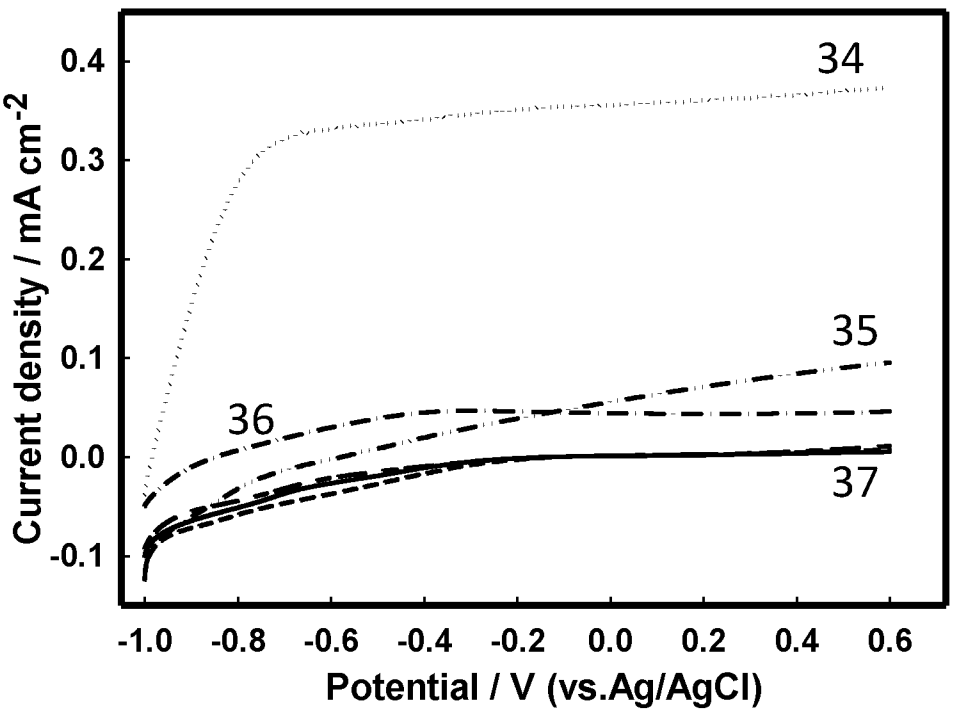

Current density / mA cm-2
0.4
0.3
0.2
0.1
0.0
-0.1
34
35
36
37
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
Potential / V (vs.Ag/AgCl)

FIG. 3D

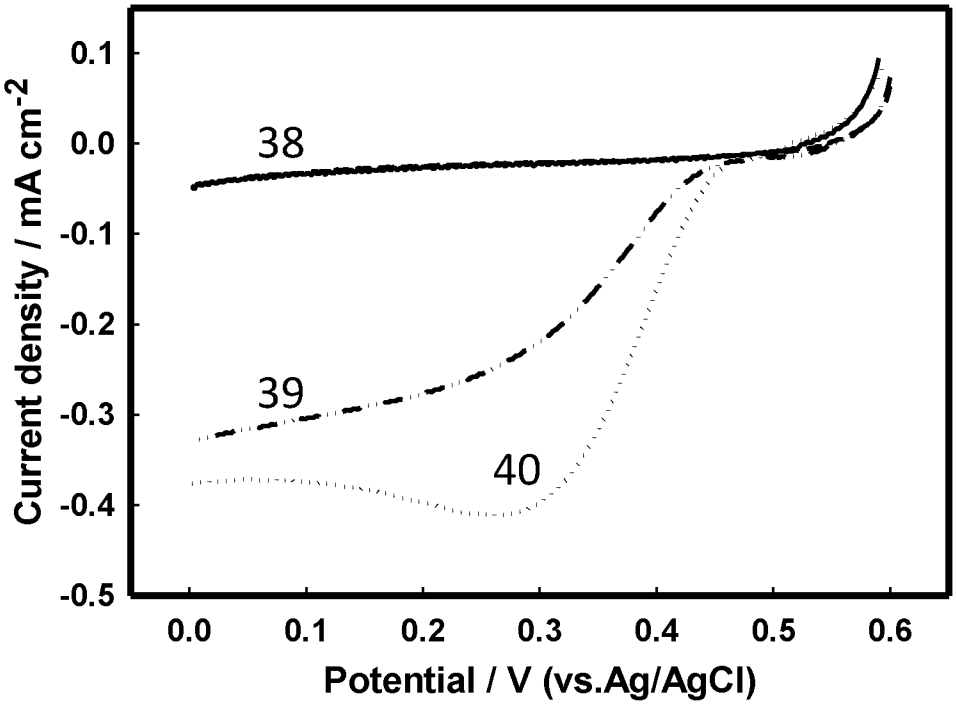

0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
Current density / mA cm-2
38
39
40
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Potential / V (vs.Ag/AgCl)

FIG. 3E

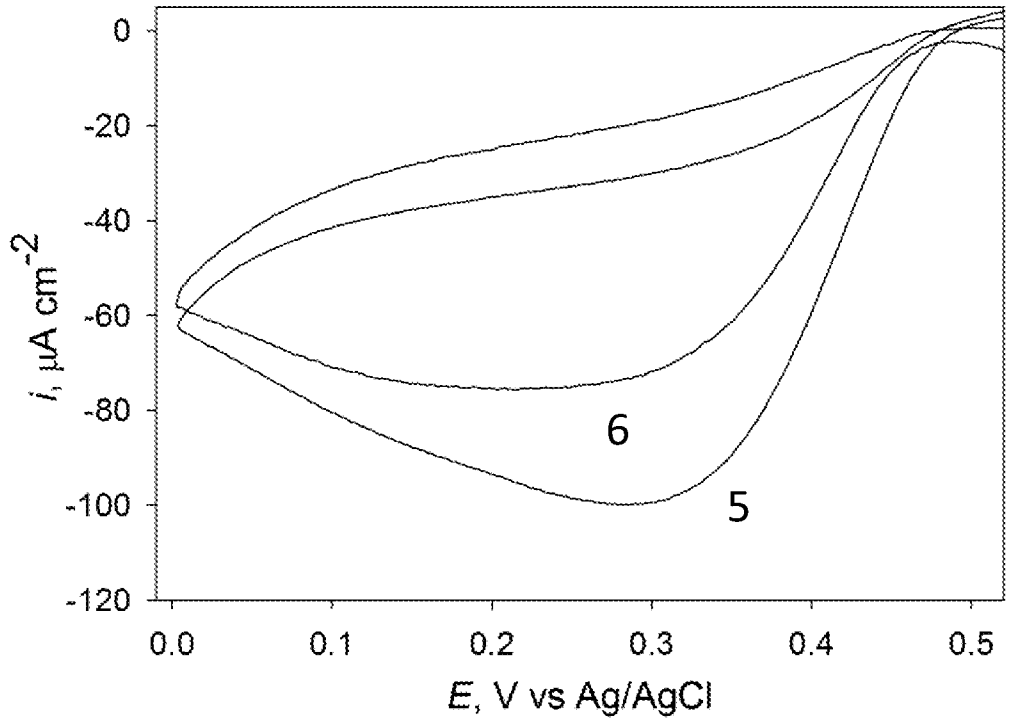

0
-20
-40
-60
-80
-100
-120
i, µA cm-2
6
5
0.0
0.1
0.2
0.3
0.4
0.5
E, V vs Ag/AgCl

FIG. 4

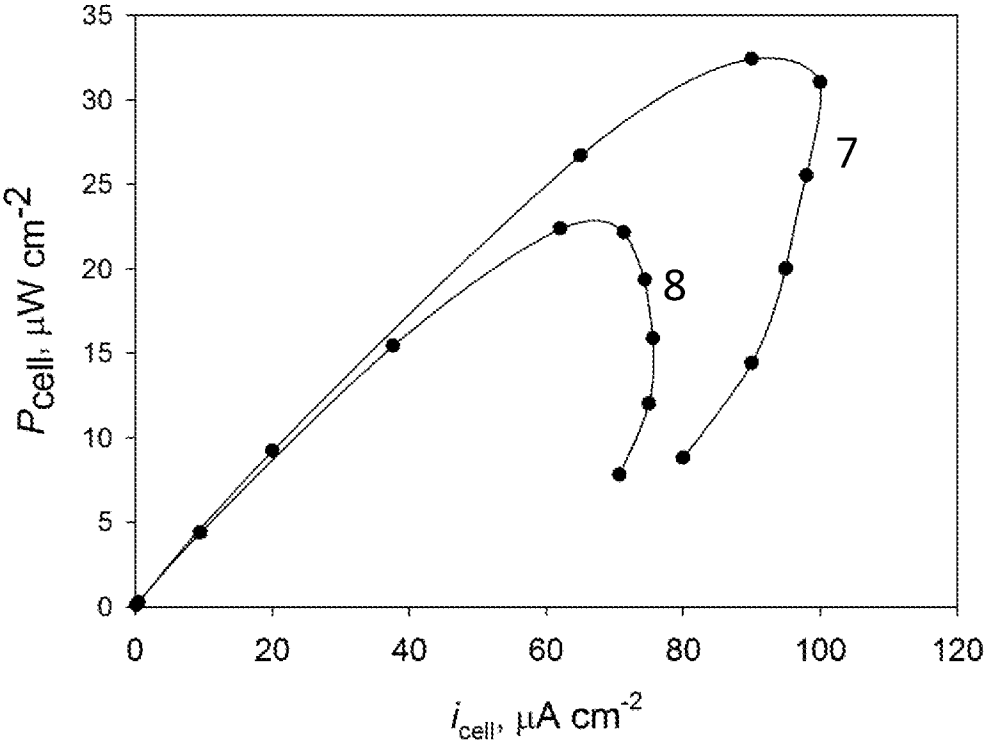

35
30
25
20
15
10
5
0
0
20
40
60
80
100
120
P_{cell}, µW cm^{-2}
i_{cell}, µA cm^{-2}
7
8

FIG. 5A

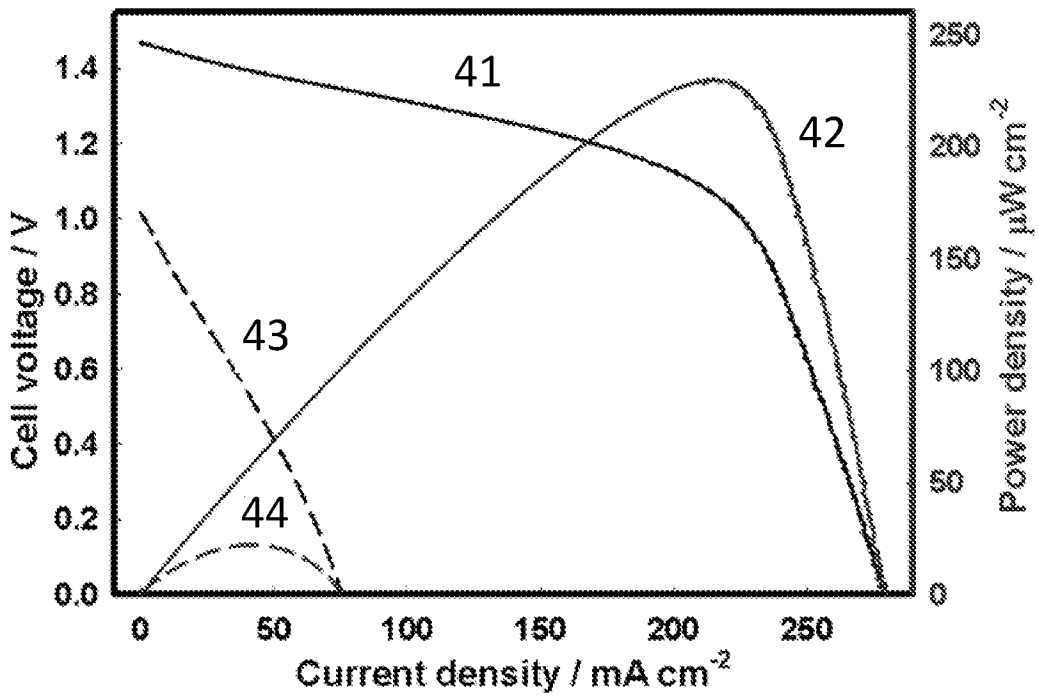

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
Cell voltage / V
Power density / µW cm^{-2}
Current density / mA cm^{-2}
41
42
43
44

FIG. 5B

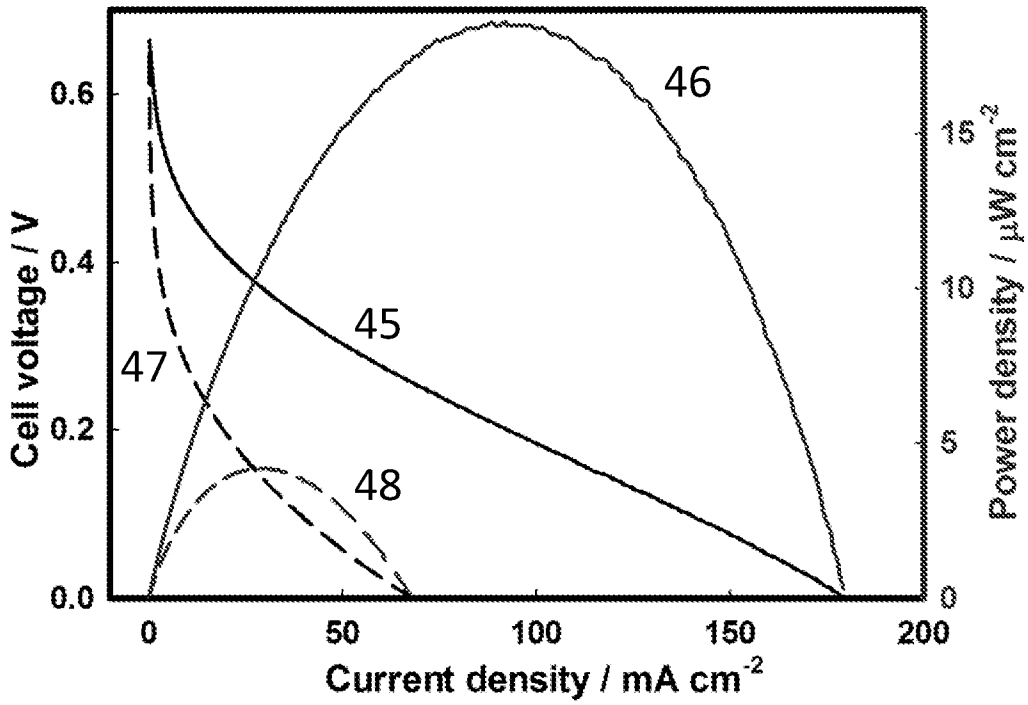

Cell voltage / V
Power density / μW cm-2
Current density / mA cm-2
0.0
0.2
0.4
0.6
0
50
100
150
200
0
5
10
15
45
46
47
48

FIG. 5C

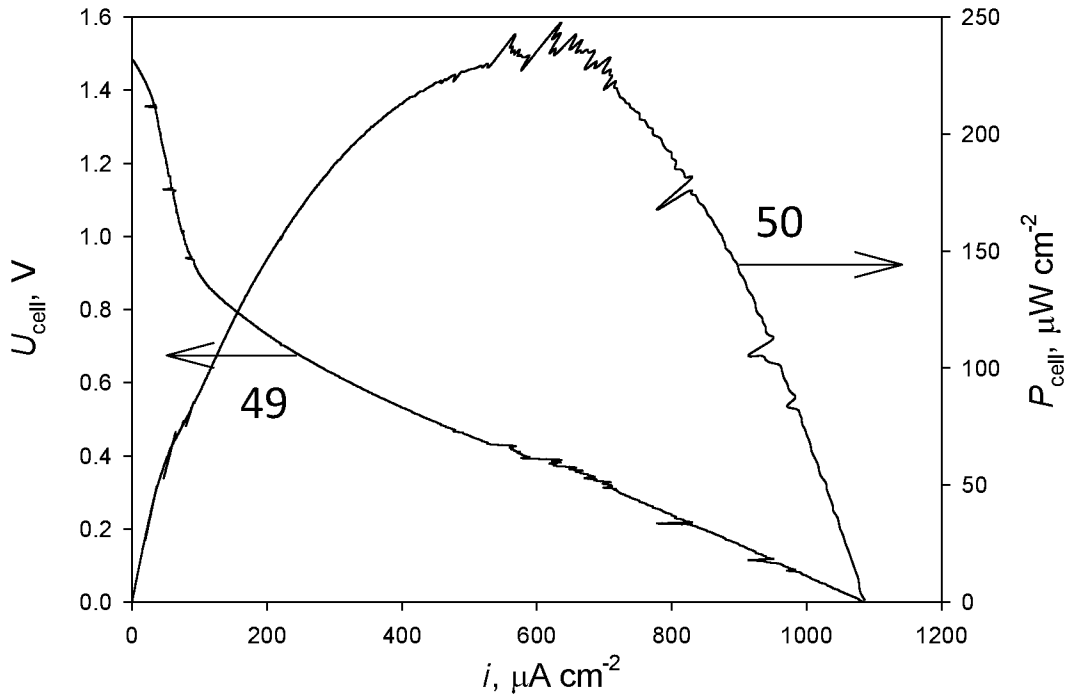

Ucell, V
Pcell, μW cm-2
i, μA cm-2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0
50
100
150
200
250
0
200
400
600
800
1000
1200
49
50

FIG. 5D

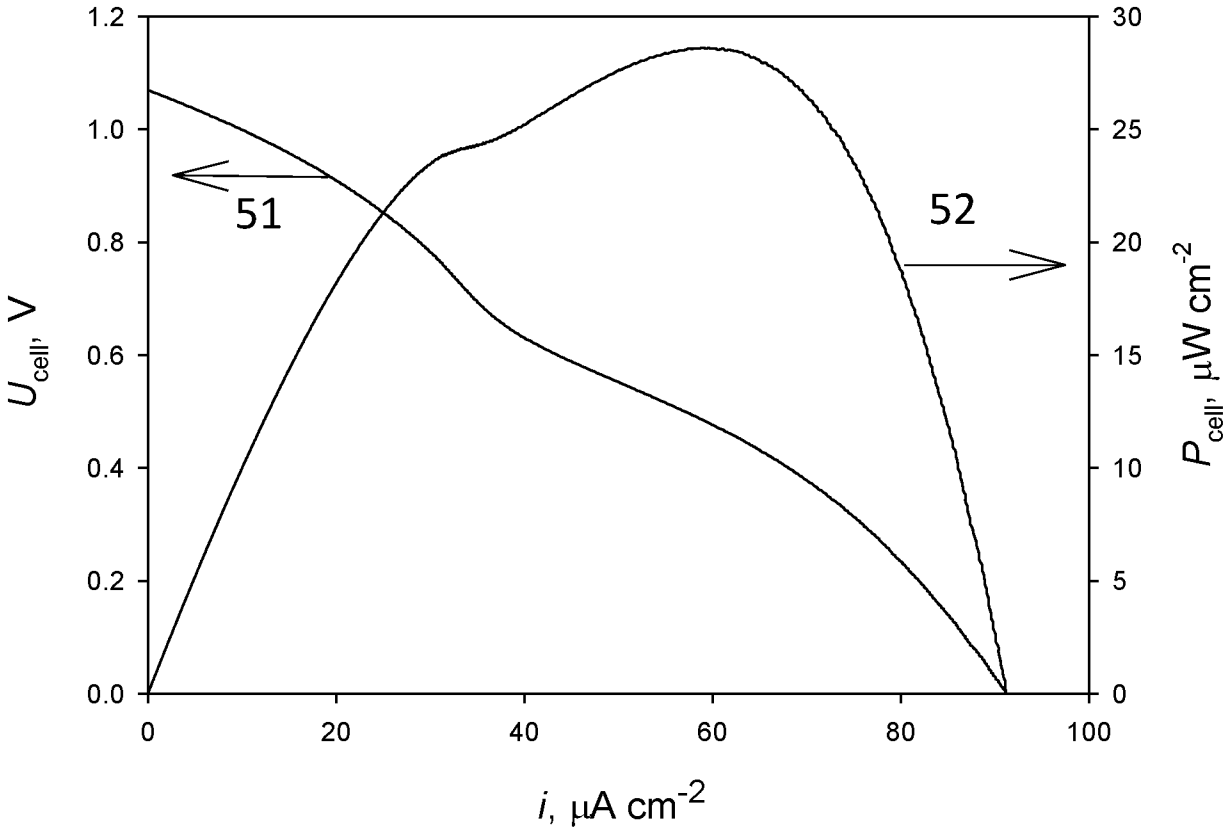

1.2
1.0
0.8
0.6
0.4
0.2
0.0
U_{cell}, V
0
20
40
60
80
100
i, μA cm^{-2}
30
25
20
15
10
5
0
P_{cell}, μW cm^{-2}
51
52

FIG. 5E

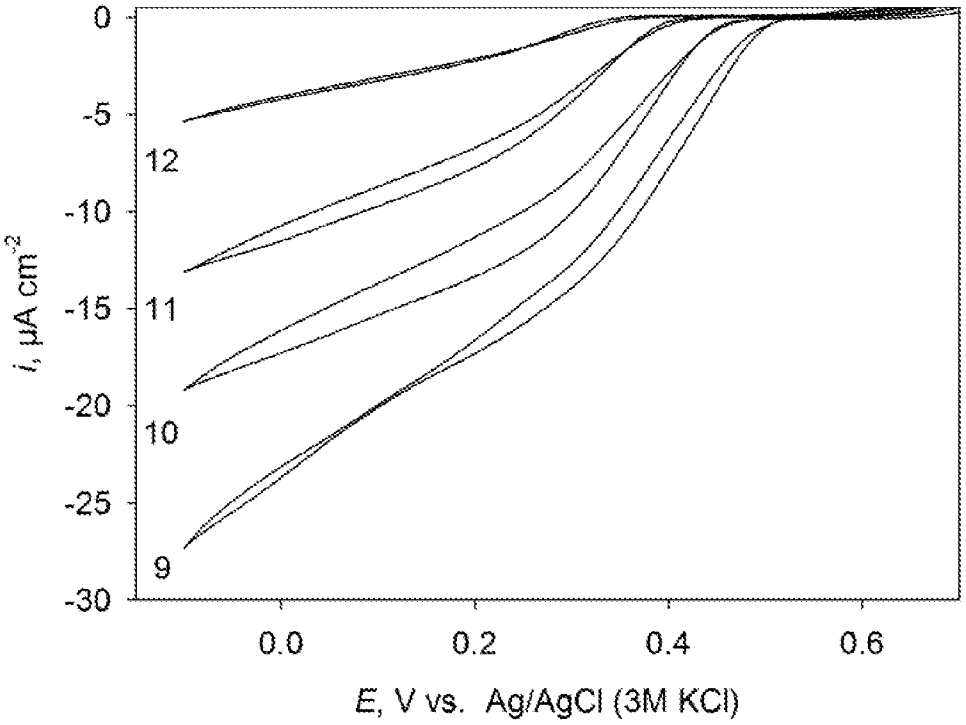

0
-5
-10
-15
-20
-25
-30
12
11
10
9
i, µA cm-2
0.0
0.2
0.4
0.6
E, V vs. Ag/AgCl (3M KCl)

FIG. 6A

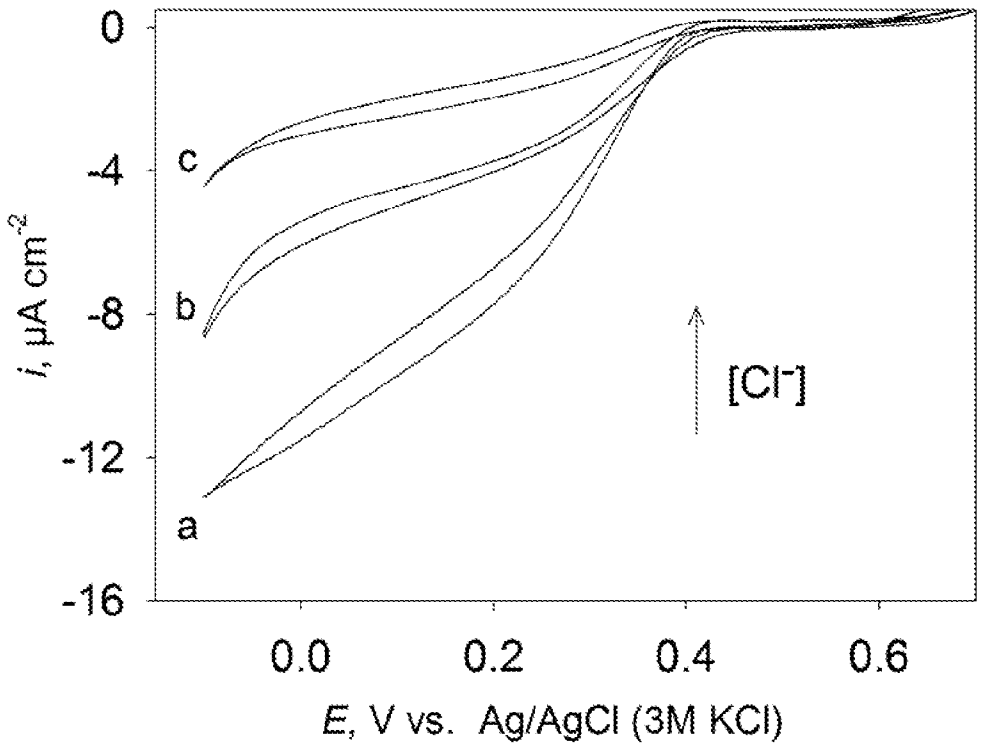

0
-4
-8
-12
-16
c
b
a
[Cl-]
i, µA cm-2
0.0
0.2
0.4
0.6
E, V vs. Ag/AgCl (3M KCl)

FIG. 6B

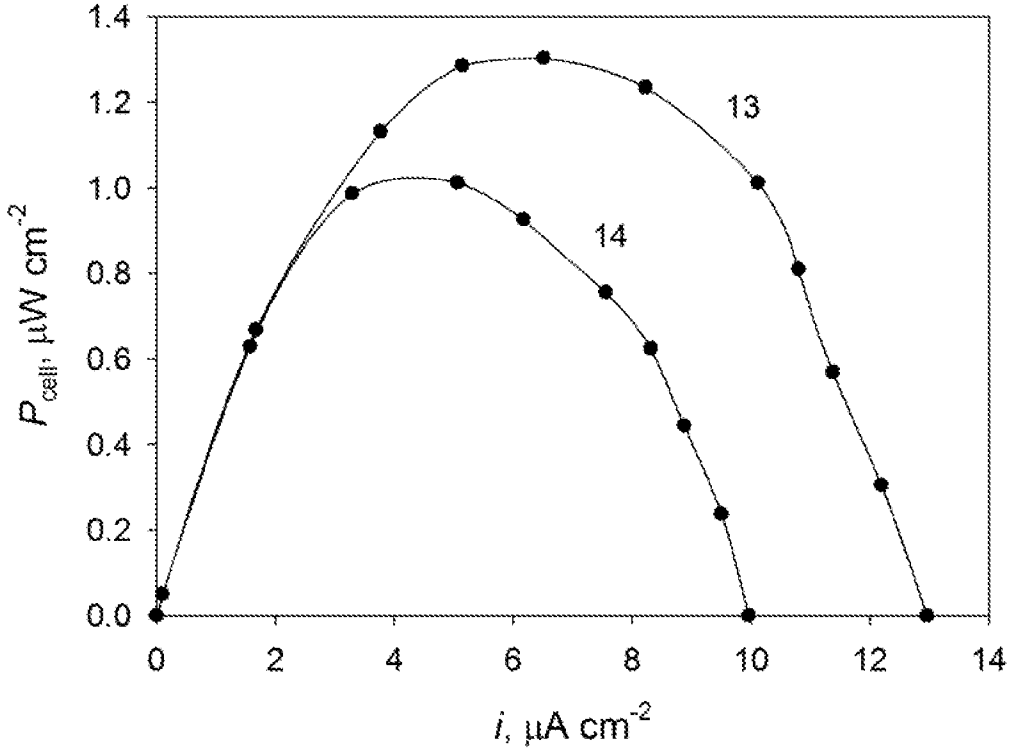

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
P_{cell}, µW cm^{-2}
13
14
0
2
4
6
8
10
12
14
i, µA cm^{-2}

FIG. 7A

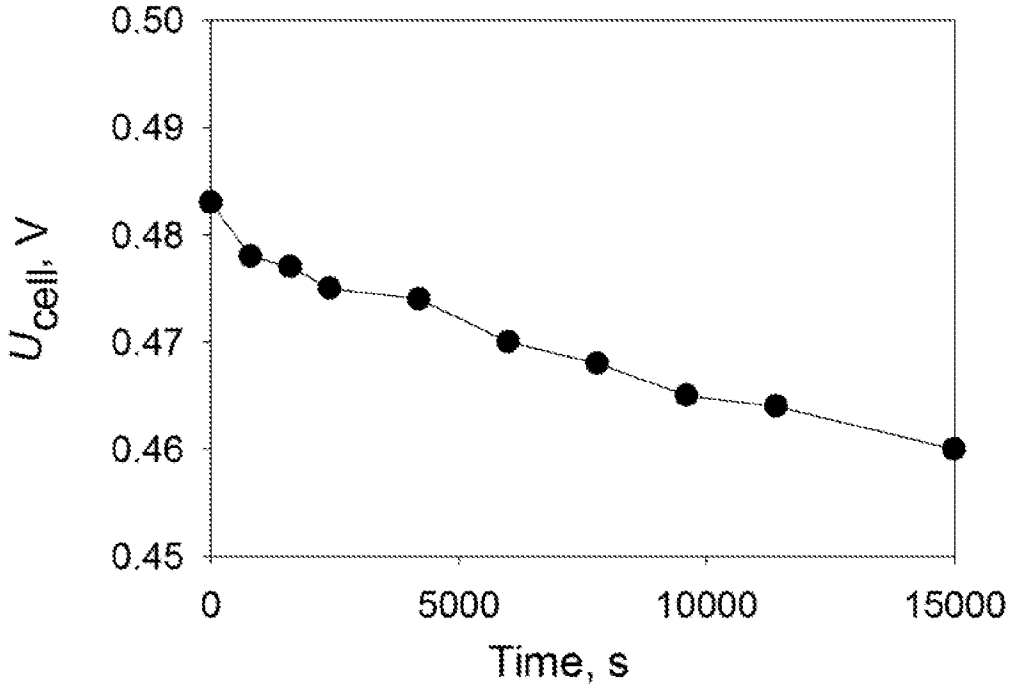

0.50
0.49
0.48
0.47
0.46
0.45
U_{cell}, V
0
5000
10000
15000
Time, s

FIG. 7B

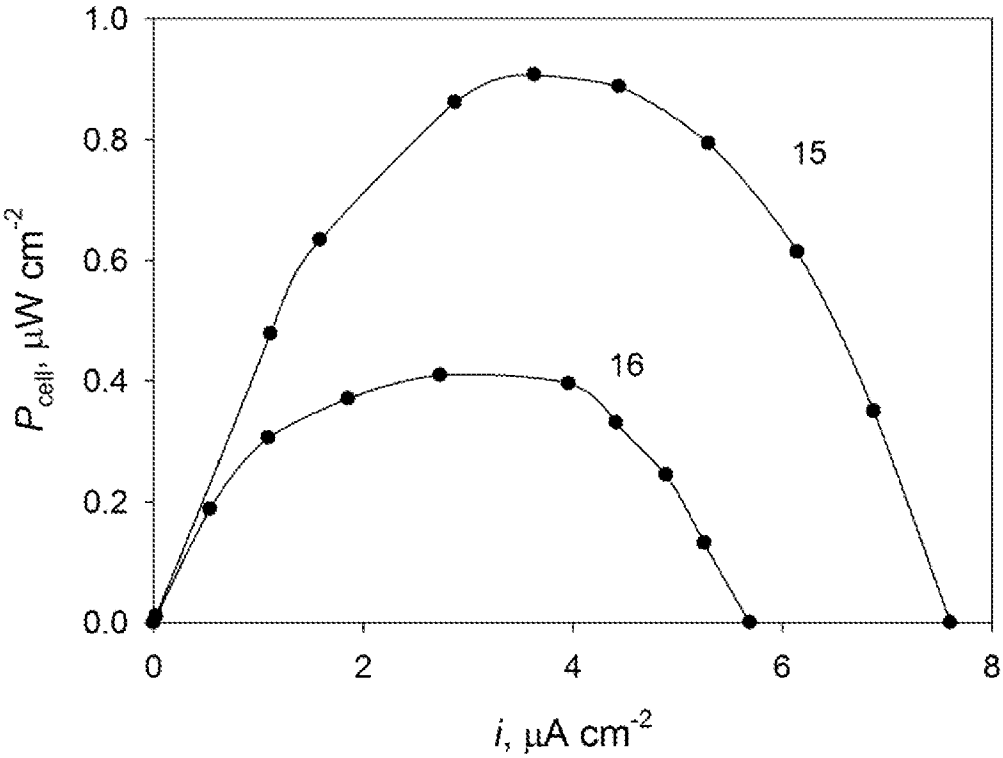


FIG. 8

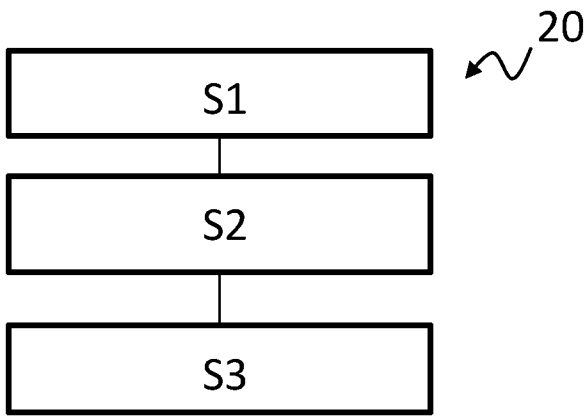


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2016/050263

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/32 C02F1/467 C02F3/34 C02F3/00 C02F1/46
ADD. C02F103/08

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)
C02F

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, COMPENDEX, 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	WO 2011/133492 A1 (BROWN UNIVERISTY [US]; PALMORE G TAYHAS R [US]; KIM SUNG YEOL [US]) 27 October 2011 (2011-10-27)	1-28,30
A	page 1, lines 9-26 page 2, line 30 - page 3, line 26 page 5, lines 1-19 page 9, line 7	29,31,32

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

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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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
3 October 2016	21/10/2016

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	Vaz, Miguel

1

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INTERNATIONAL SEARCH REPORT

International application No
PCT/DK2016/050263

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NAGHMEHALSADAT MIRBAGHERI ET AL: "Visible Light Driven Photoelectrochemical Water Oxidation by Zn- and Ti-Doped Hematite Nanostructures", ACS CATALYSIS, vol. 4, no. 6, 8 May 2014 (2014-05-08), pages 2006-2015, XP055219140, US ISSN: 2155-5435, DOI: 10.1021/cs500372v abstract page 2006, column 1, line 13 - column 2, line 1 page 2007, column 1, lines 37-44	1-32
A	UFFE B JENSEN ET AL: "Activation of laccase bioelectrocatalysis of Oreduction to HO by carbon nanoparticles", JOURNAL OF ELECTROANALYTICAL CHEMISTRY, ELSEVIER, AMSTERDAM, NL, vol. 667, 18 December 2011 (2011-12-18), pages 11-18, XP028454341, ISSN: 1572-6657, DOI: 10.1016/J.JELECHEM.2011.12.012 [retrieved on 2011-12-23] page 11, column 1, lines 1-5 page 11, column 2, lines 12-17	1-32
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A	US 2011/311887 A1 (HE ZHEN [US]) 22 December 2011 (2011-12-22) paragraphs [0004] - [0011] paragraphs [0031] - [0037]	1-32
X	US 2010/270158 A1 (LOGAN BRUCE [US]) 28 October 2010 (2010-10-28) paragraphs [0004], [0029], [0085]	29,31,32

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/DK2016/050263

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