



US 20090134007A1

(19) **United States**

(12) **Patent Application Publication**
Solis Herrera

(10) **Pub. No.: US 2009/0134007 A1**

(43) **Pub. Date: May 28, 2009**

(54) **PHOTO ELECTROCHEMICAL PROCEDURE
TO BREAK THE WATER MOLECULE IN
HYDROGEN AND OXYGEN USING AS THE
MAIN SUBSTRATE THE MELANINES, THEIR
PRECURSORS, ANALOGUES OR DERIVATES**

(76) Inventor: **Arturo Solis Herrera,**
Aguascalientes (MX)

Correspondence Address:
Arturo Solis Herrera
Lopez Velarde 108 Centro
Aguascalientes 20000 (MX)

(21) Appl. No.: **11/660,443**

(22) PCT Filed: **Oct. 13, 2005**

(86) PCT No.: **PCT/MX2005/000092**

§ 371 (c)(1),
(2), (4) Date: **Feb. 16, 2007**

(30) **Foreign Application Priority Data**

Jun. 9, 2005 (MX) GT/A/2005000006

Publication Classification

(51) **Int. Cl.**
B01D 57/00 (2006.01)
C07D 251/54 (2006.01)

(52) **U.S. Cl.** **204/157.5; 544/200**

(57) **ABSTRACT**

This invention consists essentially in the employment of the melanines, precursors of the melanines, derivates of the melanines, variants, analogues of the melanines, or their precursors natural or synthetic, pure or mixed with organic or inorganic compounds, metals ions drugs; as water electrolyzing materials, employing as its only or main energy source light, natural or synthetic, coherent or not, in the hydrogen producing systems from water known as photoelectrochemical. These systems integrate a semiconductor material and a water electrolyzing element within a monolytic design to produce hydrogen directly from water, employing light (from 200 to 900 nm wavelengths) as its only or main energy source. Although simple in concept, the challenge was to find a material that could bear or sustain the whole process. At least two basic criteria should be met: the system or compound that absorbs the Light should generate enough energy to Start, continue, support and finish the water photolysis or photoelectrolyzing reaction, within low price, being stable and durable in a watery environment, requisites that the melanines, their analogues, precursors or derivates, fulfill reasonably and efficiently, which is an important and critical advance in solving out the main problem of the photo electrochemical designs. The procedure may be used to generate hydrogen and oxygen atoms and high energy electrons or in reverse sense, synthesizing water molecules binding hydrogen and oxygen atoms, thus producing electricity, these can be employed together or with other new and important industrial processes to obtain energy and to store it, since the melanines may store the electricity and gasses; property that would have a multiplying effect, it may be used also to the reduction of carbon dioxide, nitrates, sulphates, and other molecules.

**PHOTO ELECTROCHEMICAL PROCEDURE
TO BREAK THE WATER MOLECULE IN
HYDROGEN AND OXYGEN USING AS THE
MAIN SUBSTRATE THE MELANINES, THEIR
PRECURSORS, ANALOGUES OR DERIVATES**

PURPOSE OF THE INVENTION

[0001] The technological field in which this invention may be applied is in the alternative procedures to obtain energy; different from petroleum, charcoal, hydroelectric, chemical and nuclear. It is particularly focused on the photoelectrochemical procedures, that break down the water molecule, generating Hydrogen and Oxygen atoms and high energy electrons, being energized by light. This has also applications as a new method for the redox of the carbon dioxide, nitrate and sulphate. Since the reactions with the substrate that we propose occur in both senses, our invention is also applicable for electricity generation, because this substance permits to bind hydrogen and oxygen atoms forming water molecules and generating electrical current too.

BACKGROUND

[0002] Referring to the actual techniques, the procedures known by now to break the water molecule into hydrogen and oxygen are among others:

[0003] a.) The use of high intensity electrical current (Electrolysis).

[0004] b.) Water heating up to two thousand ° C.

[0005] c.) Breaking the water molecule through the solar/electrochemical (photoelectrochemical) method, which is integrated by a semiconductor and a water electrolyzing material in a monolytic design, to obtain hydrogen directly from water employing light as its only energy source. Conceptually simple, the challenge was to find an adequate substrate or material that could support or sustain the whole process, and until now the ideal or adequate material was not found yet, since some are very expensive, pollutant, inefficient, scarce, mostly are quickly degraded or inactivated, water unstable or require very difficult and extreme working conditions, frequently only possible in the laboratory. Because of these, no one is cost-benefit, until now, economically, ecologically, politically to be used in high scale, reducing its utility to some specific and tiny processes.

[0006] d.—) Another method was to break down the water through solar energy (with mirrors for instance) to raise the water temperature to two thousand grades centigrades, temperature required in the laboratory to break down the water molecule.

[0007] e.—) Another method is the employment of photosynthetic organisms (autographs) such as green algae and cyanobacteriae, that produce hydrogen from water as part of their metabolic activities, using luminous energy as its mainly source. This photobiological technology promising, but since oxygen is produced together with hydrogen, this technology must resolve the limitations because most of these enzymatic systems are oxygen-labile. Besides, the amounts of hydrogen obtained are very low to be economically viable.

[0008] f.—) Another procedure is water electrolysis using electricity to break the water molecule in its components (hydrogen and oxygen). Two kinds of electrolyzes are used for the commercial hydrogen production: alkaline and proton interchange membranes, but these cannot compete economically with the natural gas hydrogen-produced. (Source: US

Department of Energy. Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cells and Infrastructure Technologies Program, Hydrogen, Production & Delivery).

[0009] Another natural material that breaks the water molecule and that has been studied is the chlorophyll, but since its light affinity is among is 400 nm and 700 nm wavelength, the rest of the luminous energy is lost, it is estimated that 80% of the employed energy is wasted, besides, its production is complex and very expensive, for example, it requires at least -8° C. to preserve, and it is only active in vivo, in vitro, it is rapidly degraded (approx. 20 sec).

[0010] These were the reasons why we decided to employ the melanines as water electrolyzing elements, because its light affinity is among 200 to 900 nm, besides, some of the physiologic characteristics of the tissues that normally contain them; it called up our attention specially the oxygen concentrations, so we decided to contrast the hypothesis that when the melanin or the melanines are enlightened, photolysis of the water molecule occurs generating hydrogen and oxygen atoms, as well as other products such as OH, hydrogen peroxide, super oxide anion and high energy electrons, also sustaining and catalyzing the inverse reaction; binding hydrogen and oxygen atoms forming water molecules and generating electricity.

DETAILED DESCRIPTION OF THE INVENTION

[0011] This invention consists mainly in relating that at room temperature, with natural or artificial light as the only energy source, is possible to achieve photolysis or to break down the water molecule in hydrogen and oxygen atoms, as well as high energy electrons, but also it is possible to bind the hydrogen and oxygen atoms, process through which we obtain water and electricity. All this reactions are supported as the main or principal electrolyzing material the melanines, their analogues, precursors or derivates (polihidroxiindol, eumelanine, pheomelanine, allomelanine, neuromelanite, humic acid, humic acid, fullerenes, graphite, polyindolquinones, acetylene-black, pyrrole-black, indole-black, benzene black, thiophene-black, aniline-black, hydrated polyquinones; sepiomelanines, dopa-black, dopamine-black, adrenaline-black, catechol-black, 4 amine catechol-black, in single linear chain, aliphatic or aromatic, or their precursor like phenols, amine phenols, bi phenols, indol poly phenols, semi quinones or hydroquinone, L-tyrosine, L-dopamine, morfoline or to benzo quinona, di morfolino orto benzoquinone, morfolicatecol, orto benzoquinona, porphyrin-black, pterin-black, ommochrome-black, and others), precursors nitrogen free, All of the compounds above mentioned, electro active, in suspension, solution or gel that absorb ultrasound in 1 Mhz interval, natural or synthetic, from mineral, animal or vegetal origin, pure or mixed with organic or inorganic compounds, ions, metals (gadolinium, iron, niquel, cupper, erbium, europium, praseodymium, dysprosium, holmium, chromium, or manganese; the Gadolinium is a very effective material. The metal is incorporated inside the melanines as ions or particles, as well as drugs or pharmaceutical energizing the photo electro chemic design with light (natural or synthetic, coherent or not, monochromatic or polychromatic) with wave lengths among 200 and 900 nm, even though other wave lengths and some other kinds of energy such as kinetic, are also variably effective, depending on the rest of the conditions (pH, temperature, pressure, etc Magnetic fields may be applied on these kind of designs, of low or significant intensities. The events on this design may happen either under

physical or chemical stimuli, internal or external. We propose the employment of the melanines (listed above) as water molecule electrolyzing materials, using as its principal or only source of energy light, particularly wavelengths among 200 and 900 nm, in the hydrogen production systems known as photo electro chemical methods. These methods integrate a semiconductor and a water electrolytic material in a monolithic design to produce hydrogen and oxygen atoms directly from water, employing light as its only source of energy, with the challenge of finding a substrate that could bear the whole process. At least two basic criteria should be met: that the light absorbing system or compound should generate enough energy to start, sustain and support the whole or at least a significant part of the process and the photolysis reaction (definition below). All this shouldn't be too expensive but stable and long lasting especially in an aqueous environment. Criteria that melanines, their analogues, precursors and or derivatives meet reasonably and efficiently, fact that represents an advance when solving out the main problem of the photo electro chemical designs. The shape of the container may be very varied; cubic, cylindric, spheric, polyedric, rectangular, etc. One of the main requisites for the material is to be translucent in order to allow the light to enter and depending on the wavelength of the light to be used, the walls could be made for example of quartz, so that the recipient's wall do not absorb the UV radiations, or when employing certain wavelengths, the material made for the recipient could be specially tailored in a color that allows the maximum transparency or absorption of the desired wavelengths from the electromagnetic spectrum. It can be glass, or any polymer whose characteristics of transmission of the electromagnetic radiations fits to the final needs of the photoelectrochemical design. The wavelengths that can be used to energize the design are among 200 nm to 900 nm.

[0012] Inside the cell, the main material, the indispensable solute to have our photo electrochemical design working is the melanines, their analogues, precursors and or derivatives. Properly dissolved in water and irradiated, the photolytic activity of the melanines is immediate, starting in 3 picoseconds (3×10^{-12} seconds) and this remarkable ability of the melanin to captivate photons among wavelengths from 200 and 900 nm (and some other wavelengths) probably accomplished by the peripheral portions of the molecule, followed by the generation of high energy electrons from low energy electrons.

[0013] This high energy electrons go to the free radical core of the compound, where they might probable be captivated by elements such as iron, copper, gadolinium, europium etc., and transferred to a primary electron acceptor, of unknown nature until now, binding that is complex and implies ionic interactions pH dependent. This electron transference releases energy which is used to establish a proton gradient within the system.

[0014] The combination of the water and melamine molecules is what can be named a photo system, which is capable of absorbing luminous energy to use it for at least 2 interrelated activities: removing electrons from water (water oxidation) and creating a proton gradient. Melanin's compounds are closely related fact that enhances the quickly energy transference. As soon as 3 picoseconds after lightning, the melanin's reaction cores respond transferring a photo excited proton, to the primary electron acceptor, leading to a positively charged donor and a negatively charged acceptor. The relevance of these opposite charged species, is evident when we

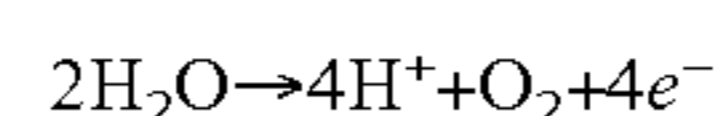
consider their oxy-reduction ability, since one is missing an electron, and can accept electrons, fact that makes it an oxidant agent. On the other side, the other compound has an extra electron that can easily lose becoming a reduction agent. This event: the creation of an oxidant and a reductor agent from light takes less than a billions part of a second and is the first essential step of the photolysis. Due to their opposite charges, these compounds exhibit an evident attraction among them, and their separation is estabilized (probably) through its own movement to opposite sides of the molecule, being the negatively charged compound the one that first lets go its electron to a quinone (Q1) and then the electron is transferred to a second kind of quinone (q2), and this produces a semi reduced kind of quinone molecule that can be strongly related or located to the melanin's reaction core. With every transference, the electron is closer to the reaction core of the molecule of melanin.

[0015] The positively charged portion of the melanin is reduced, and this prepares its reaction core for the absorption of another photon. The second photon sends a second electron into the same route (a negatively charged molecule towards the first and second molecule of quinone (Q1 and Q2), absorbs two electrons and mixes with two protons. The protons used in this reaction may derive from this same melanine molecule or from the water that surrounds it, leading to a diminishing hydrogen ions concentration in this photosystem, and this contributes to the formation of a proton gradient. Theoretically, the quinone reduced molecule is dissociated in the reaction core of the melanin, being replaced by a new quinone molecule. This reactions take place at room temperature, but when modifying it, this reactions may be somehow enhanced, depending on the rest of the variables, such as pH, magnetic fields, solutes and solvents concentrations, partial gasses pressure, electrodes composition and shape, distribution, shape and cells interconnections, and also, we must take into account the product we need from the process, hydrogen and oxygen or water and electricity. In the presence of metals or Bore, the hydrogen works with -1 .

[0016] The breaking down of the water molecule in hydrogen and oxygen atoms its a highly endergonic reaction, since it is a very stable binding. ($\Delta H = +286$ kJ)

[0017] In the laboratory, breaking the water molecule (in hydrogen and oxygen atoms) requires a high intensity electrical current or a high temperature up to almost 2000° C. All this (water electrolysis or photolysis) is made by the melanin in an environmental temperature employing only the energy take out of the light, mainly among 200 and 900 nm wavelengths (other wavelengths should not be excluded), either from a natural or an artificial source of light, coherent or not, collimated or disperse, mono or polychromatic.

[0018] It is estimated that the redox potential of the oxidized form of the quinone is approximately $+1.1$ V, which is strong enough to attract the strongly bind low energy electrons from the water molecule (redox potential of $+0.82$), and break it into hydrogen and oxygen atoms. The breaking of the water molecule by photo pigments is called photolysis. It is estimated that the oxygen molecule formation during photolysis requires the simultaneous toss of four electrons from two water molecules according to the reaction:



[0019] A reaction core can only generate a positive charge or its oxidant equivalent at a time. This problem can hypothetically be solved by the presence of 4 nitrogen atoms in the

reaction core of the melanin, and each one transfers an electron. This nitrogen concentration, may gather four positive charges when transferring the electrons, one at a time to the closest molecule of a quinone. This electron transference of the quinone's atoms present in the reaction core of the melanin is done through a positively charged tyrosine residue. After each electron is transferred to the quinone it is regenerated, the pigment is re oxidized (again to quinone) after the absorption of another photon to the photosystem. So the storage of the four positive charges (oxidative equivalent) by the nitrogen atoms in the reaction core, is modified by the successive absorption of four photons by the melanin photosystem.

[0020] Once this charges are gathered, the oxygen releaser quinone complex, is capable of catalyzing the $4e^-$ of $2H_2O$ removal, forming one O_2 molecule, and totally regenerating the reduced nitrogen stored in the reaction core. The photosystem must be irradiated several times before releasing O_2 and Hydrogen enough to be measured, which indicates that the effect of the individual photoreactions must accumulate before O_2 and Hydrogen are released. The protons produced by photolysis are released in the medium, where they favor the proton's gradient.

[0021] The quinones are considered as mobile electron transporters. Don not forget that all electron transference are exergonic and take place as the electrons are successively taken by transporters, with an increasing electron affinity (more positive redox potential). The need for electrons mobile transporters is obvious. The electrons generated by the photolysis may pass on several inorganic acceptors that reduce them. These electron pathways may get to (according to the composition of the compound) to the eventual nitrate (NO_3^-) molecule reduction into (NH_3) ammonia molecules or the sulphates in to sulphhydryl (SH^-); reactions that turn the inorganic waste into compounds needed for life. So the solar light energy may be used not only to reduce the most oxidized form of carbon atoms (CO_2), but also to reduce the most oxidized forms of Nitrogen and Sulphur.

[0022] The O_2 molecule production requires the removal of two water molecules and the absorption of four photons, one by each electron.

[0023] The cell design is an important parameter to optimize the obtention of the reaction product we particularly want, placing electrodes, their nature, the employment of magnetic fields, adding varied compounds (organic or inorganic, ions, metals, drugs or pharmacs) to the photosystem that initially it is only water and melanin, plus electrolytes, plus pharmacs, as weft as manipulating temperature, gasses's partial pressures, the management of the generated electric current, the magnetic field application, pH level, the material used to tailor the cells and the shape and distribution of the interior compartment, etcetera, as well as other variables that are susceptible of manipulation, in order to have the final design Retrieving electrons or protons or oxygen, and end compounds according to the media composition in which we solve the melanin. The melanines, their precursors, variants or analogues of the melanines (their analogues, synthetic or natural precursors, pure or mixed with organic or inorganic compounds, metals) allow a remarkable flexible design according to the objective we pursue.

[0024] The optimization of the photoelectrochemical design, is a matter of the objective we want to give it for example, to have a larger proton and oxygen generation, or electricity the biggest the area exposed of the liquid com-

pound to the light, through an extended continent, as well as other procedures such as the addition of electron carrier compounds, the melanines dopaje, or positive microlens to focus the light, etc. The continent design is practically illimited, it may be spheric, cubic, rhomboid, polyedric, concave-flat, convex-flat, biconvex, biconcave, with microlens aside (in the side exposed to light to focus it) and flat in the other side, cylindric, cylindric rounded, empty cylindric, rounded cone (straight), rectangular pyramidic, truncated spheric segment, spheric with cylindric perforation, sphere with conical perforations. Since the liquid fits in any shape, it only needs a translucent continent, to allow the light to enter the most, and depending on the kind of melanine used (doped or not) it will be de convenience of choosing a specific wavelength to enlighten the soluble melanine, but unto now, one of the greatest gifts of the synthetic soluble melanine is that it absorbs most wavelengths of the electromagnetic spectrum. Even though, it seems that the best absorption is of wavelengths among 200 and 900 nm.

[0025] The control of the gasses partial pressures on the inner cell is an important variable and depending on the shape of the cell and the use given, these pressures may go from 0.2 mm Hg up to 3 to 4 pressure atmospheres. Another variable that should be taken in to account is the concentration of the different substances solved in the liquid, being critical the melanines's which can go from 0.1% up to 100%, another variable susceptible of modification is the proportion between the different compounds of the formulae (according to what we want to use it for), because we can add potassium 0.1 up to 10%, sodium 0.1 up to 10%, chlorum 0.1 up to 10%, calcium 0.1 up to 10%, iron 0.1 up to 10%, cupper 0.1 up to 10%, arsenic 0.1 up to 10%, gold 0.1 up to 10%, PLATA 0.1 up to 10%, NIQHEL 0.1 up to 10%, gadolinium 0.1 up to 10%, europium, erbium, etc. The final volume may go from 1 microliter up to 10-20 titers depending on the size of the recipient and the available space for it, about the temperature, this can oscile from 2 to 45°C, the exchange time of the solution may be every 14 minutes, several months or up to 2 or 3 years. The compartments within the cell may be used in different shapes such as small spheres, (micro spheres, several tens), or bigger spheres whose size may fit only 3 or 4 times inside the entire design. About the shape of the inside cell it can have cubic interior, rhomboid, polyedric, concave flat, convexes flat, biconvexus, biconcave, with microlenses biconvexes, or flat-convexes, cylindrical, rounded cylindrical; empty cylindrical; rounded cone (straight), truncated cone, rectangled prism (straight) oblique prism; rectangled pyramidic (straight); truncated pyramid, truncated spherical segment, spherical segment, spherical section; spherical with cylindric perforation, spherical with conical perforations; torus (ring with circular section); cylindrical with sloped cut, cylindrical wedge, barrel, prism-like, and combinations between them. The microlens optic power may be from 0.1 up to 100 dioptries, the redox properties of the material employed in the manufacture of the compartment (iron, silver, niquel, gold, platinum, gallium arseniure, silicated, gadolinium, europium, erbium, praseodymium, dysprosium, holmium, chrome, manganese; plumb selenium; and alloys within them or others)) according to the best characteristics in order to get electrons or hydrogen, but we must not forget that in the presence of metals or bore, the hydrogen works with -1 ; another variable, is the solution initial pH, in may go from 2 or 3, up to 8 or 9 pH unities, being the most commonly used around 7, the forementioned are variables that may be modi-

fied in order to control the photo electro lysis process and adapt it to the needs of the protect in which we use the photoelectrochemic design. Even though the heart of any effective photo electro chemical design is the melanines

[0026] The melanines, the melanines's precursors, the melanines's derivates, variants and melanines's analogues, water solubles, where they catalyze the photolysis process without any significant change, except when some materials are present such as manganese, iron copper, plumb, and other, whose resultant products together with the oxygen partial reduction (superoxide anion, hydroxide radical, hydrogen peroxide, quinones and orthoquinones) may quickly or slowly damage the melanines efficiency, both when for example, pure melanine is employed in a 10% concentration, the lifetime of the compound is long enough to be economically convenient (years), and also, the melanin synthesis is really efficient, that's why economically and ecologically is a viable process, since the melanin is totally biodegraded The cell only requires a periodic distilled water supply, as well as a soluble melanin exchange, or in the given case a renewal of the substance that were added to the design to optimize or trigger the processes obtained after the tight exposure of the photoelectrochemic design. The ecologic advantage of having as end products only water molecules, oxygen atoms or molecules, hydrogen, high energy electrons and electrical current is easily noticeable. There is a scarce (if any) generation of CO₂ molecules, responsible of green house effect.

[0027] The electrons transference frees energy which is used to establish a proton gradient. The proton movement during the electron transportation in the reaction may be compensated by other ion displacement, so using a membrane and a solvent with the right solutes we can build a membrane potential with the proton captivated by the melanin.

[0028] The photo electrolyzing properties of the melanin explain coherent and congruously the peak seen in the electro retinogram generated by the Light irradiation. When the melanin is radiated, the intracellular pH drops, and this activates the chlorine channels pH-sensitive in the basolateral cellular membrane (the light peak is an increase in the potential that follows the FOT phase (Fast Oscillation through) and constitute the slowest and longest compound of the direct current electro retinogram. (Kris 1958, Kolder 1959, Kikadawa 1968, Steinberg 1982.)

[0029] The melanines, their analogues, precursors or derivates oxidize the water molecule into O, O₂ and H₂, spending the energy they get from the Light (photons) and also reduce oxygen atoms with hydrogen atoms producing H₂O molecules and releasing electricity. The cell design may be tailored, to what we want to obtain. It produces H₂ and O₂ atoms with the light but this production may be increased through the DOPAGE of the melanines (melanin, its precursors, variants, derivates or analogues natural or synthetic), with metals, or conditioning organic or inorganic molecules as well as modifying the electrolytes concentrations, adding pharmacs or controlling the light characteristics over the liquid containing water and melanines melanin, its precursors, variants, derivates or analogues natural or synthetic), for example with a design based on microlens to condens or select certain wavelength, employing coherent or disperse light, monochromatic, polychromatic, continuous, discontinuous, natural, artificial, etc The photoelectrochemical reactions occur in both senses, the water molecule is broken, but also built, so we can obtain electric current from the design and also it may be optimized through the melanin dopage, with different sub-

stances (pharmaceuticals, metals, electrolytes, inorganic or organic molecules and others) or focusing the light through lens among others. The box that contains the liquid may have different shapes adapted to the different needs in the roof of the houses, of the cars, buildings, industrial processes, plants, etc. cells interconnected, but the principal compound of the design still is the melanin (melanines, their precursors, derivates, variants, analogues, water soluble that lead to and effectuate the water photolysis in the presence of tight (invisible or not).

[0030] The melanines, their precursors, derivates, variants and analogues, remove electrons from the water and establish a proton gradient. The tight dependent reactions may also produce energy to reduce CO₂ a CH₂O, nitrates to ammoniac and sulphates to sulphhydriles. A compound described in the literature known to induce and carry out these processes is the chlorophyll, out it absorbs light mainly in the extreme regions of the visible electromagnetic spectrum, it is estimated that 80% of the irradiated energy is lost, opposite to our proposal of employing the melanin, because it absorbs electromagnetic radiations, soft and hard, all the visible spectrum and the infrared wavelengths close and far (Spicer & Goldberg 1996). It is not (unlikely that in may absorb some other kinds of energy such as kinetic or other wavelengths from the electromagnetic spectrum.

EXAMPLES

[0031] We have done several low scale experiments once we Inferred this interesting properties of the melanines, and according to the relation structure-activity of the molecule after placing synthetic soluble melanine in water, we got a 1% solution, that we stored in 5 polyethylene translucent high density bottles of 20 ml in room temperature, measuring pH before and after illuminating it for 30 minutes with visible natural light (sun) not concentrated at 8 am. We got an average drop of 2 tenths of pH unit (from 7.3 to 7.1) in an open design.

[0032] We consider it significant because the melanines have a buffer capability per se, and indubitable the variation should be bigger but it is masked by this intrinsic property of the melanines (buffer), reason why we only detected a part of these important pH changes, which magnitude depends on the biological system, if it was bigger it would probably destroy or harm importantly the cell, but a small variation such as the one we detected is enough to induce the biological responses in which this extraordinary compound is involved, in order to dimension the biological importance of a decrement of 0.2 pH units, we will quote that this decrement induces an increment of more than 10% of the calcium, in serum. Besides, the pH of the whole blood is between 7.38 to 7.44, in arterial blood is between 7.36 to 7.41 and the venous blood oscillates between 7.37 to 7.45, the variations are in a very narrow interval, therefore, the two tenths of pH unit variation in a biological system is really significant.

[0033] In a closed design, we estimated the hydrogen productions according to the electric current generation, and obtained average values of 50 uA (500 mV) and 150 uA (1100 mV) in between peaks, which means at least one or two pH unities, this is equivalent to a Hydrogen production of 1×10^{-7} mol/litter for each pH unit. The molecular weight of the hydrogen, indicates that a mot is equivalent to a gram of hydrogen. On the other side, the melanocyte, is the cell with the highest affinity for calcium in the body, thousand times more than the bone, because even though it has more quantity, only mineral calcium is deposited in the bone. It is worth

saying that such variation from 0.2 to 1.0 pH unit; and the reverse reaction that occurred once the containers were placed in a dark place, was anticipated by our theoretic background, when we performed the experiments, we known already what was going to happen, as the matter of fact, we didn't do many experiments, we only made two or three times, obtaining the results we expected. The melanin solutions employed in the experiments, had at least 3 years of prepared and were not doped, and as the theoretic background states, it is a long lasting compound, very water stable, doesn't requires preservers, does not need refrigeration despite of time, it doesn't get contaminated with microorganisms, because we only kept the solutions in fresh and dry environment; reason why we are quite sure that the reaction was going to happen, even though the magnitude couldn't be anticipated because the buffer capacity of the melanines is not known, or is impossible to measure precisely because the melanine chemical formula is not completely known. This experiment also proved that the melanin does not requires preservers, and their electrolyzing properties are kept despite of time (3 years of prepared). Now, we are working in protocols that lead us to answer some of the many questions generated from this experiments, but since the extraordinary possibilities of industrial medical energetic and laboratory applications of this electrolyzing property of the melanin, we decided to protect right away its employment in the energy production photoelectrochemical processes. Another example that sustains our patent is the fact that the blood that enters the eye (arterial blood) through the choroid vessels, all surrounded by melanocytes; presents an oxygen saturation of 97%, and when it exists the eye, in the vorticoses, the oxygen saturation is of 94%, while the CO₂ is of 40%. Notice only a 3% drop of the oxygen saturation is intriguing. This unusual characteristic is not explained by the quick ocular blood flow, that amazingly goes from 10 to 20 mL/min/g, 10 to 20 times more than the brain's (0.5 mL 7 min/g), besides, if true, then the oxygen saturation of the retinal vessels would be similar (97% in the artery and 94% in the central retinal vein, with a CO₂ of 40%), but it is not. In the retinal vessels it is like in the rest of the body, 97% oxygen at the entrance, and 60% oxygen saturation in the veins at the exit, and a CO₂ of 40%. This intriguing difference is not explained in the literature until now, but is solved if we take in to account the electrolyzing property of the melanin, which is never mentioned in the literature, and we are the first to infer and describe. Another biologic success that sustains our patent, is that when enlightening the pigmented epithelium cells of the retina, normally, a drop of the intracel pH is measured, fact that in all the searched literature until now, is not explained, they only say mat an unidentified substance might be responsible for it, but if we take in to account this electrolyzing property of the melanin whose employment we are patenting, that in presence of light, the melanin breaks the water molecule and generates hydrogen and oxygen atoms, then both previously described events are explained. The mysterious oxygen saturation of 94% of the venous choroid blood (normally the choroid is very pigmented), and the drop of the citoplasmatic pH of the pigmented epithelium cells of the retina when enlightened.

[0034] There must be a reason why the nature provided so much pigment in the eye, 40% more than in the skin. Another example that supports our patent is a peak generated by light observed in the electroretinogram; the recording of the electric activity of the retina, pigmented epithelium and choroids.

When enlightening, the melanin and with the generation of atoms of hydrogen, the intracellular pH drops, and it activates the chlorum pH dependant channels in the basolateral cell membrane. The tight peak is a increase in the potential that follows the FOT phase (fast oscillation through) and constitutes the slowest and longest compound of the direct current electroretinogram, fact whose molecular substrate was not dilapidated yet, but the electrolyzing properties of the melanin explain it quite.

After enough describing my invention, I consider it as a novelty and therefore I claim as my exclusive property the contents of the following clausules:

1. I start my claimings about the employment of the melanines as an electrolyzing material or MEDIO, of the water molecule, in presence of light, since it generates energy when tweaking the water molecule, obtaining hydrogen and oxygen atoms, as well as high energy electrons, or the opposite reaction, binding back hydrogen and oxygen atoms, obtaining water molecules and electric current. This are processes that are intensively pursued in the lab and in the industry because of the advantages that it provides to generate and control an event of this nature, having as its only energy source to start, drive and finish the whole process the visible luminous energy that is consider as a removable resource, and the end products are highly ecologic. Until now this process has never been done in the lab or in the industry because they lack of a subtract or a material that could bear these events completely, from the induction or beginning of the process, followed by the energizing of the process and the ending of it with the obtention of the desired products, commonly, hydrogen, oxygen atoms, high energy electrons, electric current, all depending on the direction of the reaction, going through the different chemical reactions that comprise these steps. This substrate should be tong tasting, efficient, trustable, easy to reproduce, not pollutant when made, when used or when recycled, and advantageous when compared with other known ways to produce hydrogen and/or electric energy, not applicable in high scale for different technic, ecologic, politic or economic reasons, and that are based in removable energy resources, unlike the actual processes that general and massively are applied to generate energy from not removable energy resources that are alarming getting to its depletion, not considering the energy generation from atoms, whose employment has generated catastrophes, and nature pollution worst than a nightmare Exposing in this patent the advantages of the employment of removable resources, based in ecologic processes whose economic, politic and technic feasibility is high, makes our claims characterized by the use of a substrate that fills the needed requisites to generate energy from removable resources such as the sunlight and water, whose production, employment and recycling are remarkably ecologic. The improvement we propose and claim comprises the employment of the melanines, their precursors, melanin's derivates, variants, analogues, natural or synthetic, pure or mixed (with organic or inorganic compounds, metals, ions or drugs) as the main element to any photo electro chemical process that allow us to break water molecules in hydrogen and oxygen atoms and/or its derivates in an incomplete reduction that use as its main source of energy light from any emission (natural, synthetic, coherent or not) with wavelengths among 200 and 900 nm, even though some other wavelengths and forms of energy may be useful (sound, mechanic agitation, magnetic fields, etc) depending on the physic-chemical configuration of the system, which will also led as a result high energy

electrons generations or the opposite reaction, the binding back of the hydrogen and oxygen atoms making water molecules, and generating electricity or electric current. There may be generation of incomplete oxygen atom reduction such as superoxide atoms, anion superoxide molecules, hydrogen peroxide and oxyhydrides. All these taking place in a room temperature and is susceptible of modification according to the variables and parameters surrounding this kind of design, for example the nature of the employed melanin, the addition of some metals, as well as inorganic or organic compounds, pharmins, pressure, temperature, pH, gasses, the shape of the container, rheologic characteristics of the contents. The energizing of the process is made through natural or artificial light, visible, invisible, focused, coherent, etc. The possibilities to modify the characteristics of the process are huge and so is the resultant efficiency on the generation of the desired end products such as the quantity of the generated hydrogen or oxygen atoms or high energy electrons, or in the reverse reaction water molecules, electricity or electric current, oxyhydrides, peroxide hydrogen. There is the possibility to optimize any photo electro chemical design with melanines, their analogues, precursors, or derivates, pure or mixed, natural or synthetic, but always having them as the central compound and this possibility permits the widespread or massive employment of alternate sources of energy (hydrogen oxygen, high energy electrons, water and electricity) from removable resources such as the water and sunlight. The processes above mentioned may be used isolated or adjoined with other known methods or to be known processes to produce energy through hydrogen or electric current.

2. Due to the improvement that suppose or comprises my proposal, I claim, like in number 1; the employment of the melanines, their precursors, derivates of the melanines, variants, analogues of the melanines, natural or synthetic, pure or mixed (organic or inorganic compounds, metals, ions, drugs) for photo electro chemical process as claimed in number 1 where such substances may be polyhydroxylindol, eumelanine, pheomelanine, allomelanine, neuromelanine, humic acid, fullerenes, graphite, polyindoquinone, acetylene-black, pyrrole-black, indole-black, benzene black, thiophene-black, aniline-black, hydrated polyquinones, sepiamelanines, dopa-black, dopamine-black, adrenaline-black, catechol-black, 4 amine catechol-black, (single linear chain, aliphatic, aromatic) and/or their precursors, such as phenols, aminophenols, diphenols, indol-polyphenols, cyclodope, DHI and DHICA, quinones, semiquinones or hydroquinones, L-tyrosine, L-dopamine, morpholine-ortho-benzoquinone, dimorpholine-orto-benzoquinone, morpholinacathcol, orthobenzoquinone, porphyrin-black, pterin-black, ommochrome-black, free nitrogen precursors any of the above mentioned, in any size of the particle (from 1 angstrom to 2-3 cm). Any of the compounds mentioned above, electro active, in suspension, solution or gel, that absorb ultrasound in 1 MHz interval, natural or synthetic of vegetal, animal or mineral origin, pure or mixed with organic or inorganic compounds, ions, metal, drugs or others as the main or accessory materials. In the process the concentrations mainly of the melanin, that may fluctuate from 0.1% to 100% or more, depending on the melanin's Physic-chemical characteristics and rheologic of the design. Given the melanin's characteristics, we claim its employment to the reduction of the carbon dioxide reduction, sulphate and nitrates. And overall, we claim its employment in any industrial, medical, laboratory process, isolated or as a part of series of processes based completely or partially

on the melanin's characteristics, its analogues, precursors or derivates, to generate oxygen atoms, hydrogen and high energy electrons, or the opposite reaction: binding hydrogen and oxygen atoms to form water molecules and electricity or electric current. The forementioned in an environment that has water molecules in any form or variant analogues precursors or derivates, employing as the only or main source of energy natural or synthetic light, coherent or not, concentrated or disperse, as well as other different wavelengths comprised among 200 and 900 nm of the electromagnetic spectrum. It is also possible to energize the process through sound, mechanic agitation and magnetic field and others.

3. We also claim as in number 1, the employment of the melanines, precursors of the melanines, derivates of the melanines, variants, analogues of the melanines, natural or synthetic, pure or mixed (with organic or inorganic compounds, metals, ions, drugs) in designs with the objective to produce energy either producing electric current when binding hydrogen and oxygen atoms, to form water molecules, or generating hydrogen and oxygen atoms when breaking photo-electro-chemically the water molecule, or profiting the melanines's properties to generate hydrogen peroxide, superoxide anion, oxyhydrides, and monoatomic or molecular oxygen, or high energy electrons. All these starts breaking the water molecule, employing as the main energy source electromagnetic radiations, in wavelengths among 200 and 900 nm, although some other wavelengths and other kinds of energy (sound, mechanic agitation, magnetic fields) may be useful. We also claim the melanines's property to store energy, it may function as a battery or accumulator, this means that they do not only generate energy, but also they are able to store it for a period of time within certain limits.

4. We claim according to number t, that in the apparatus or design that allows the employment of the melanines, derivates of the melanines, their variants analogues of the melanines, natural or synthetic, pure or mixed (with organic or inorganic compounds, metals, ions drugs), for photo-electro-chemic processes, or energy producing as claimed in 1 to 3, through the employment of magnetic fields in a low to significant intensity.

5. We claim as in number 1 the employment of melanines, precursors, derivates, variants, analogues of melanines, natural or synthetic, pure or mixed (with organic or inorganic compounds, metal, ions or drugs) for the photo electrochemical process that permits the breaking down of the water molecule in hydrogen and oxygen atoms and/or their derivates from incomplete reductions, using Light from any source (natural or synthetic, coherent or not) mainly in wavelengths among 200-900 nm,

6. We claim. Like in 1 and 2; the employment of the melanines, precursors of the melanines, derivates of the melanines, variants, analogues of the melanines, natural or synthetic, pure or mixed (With organic or inorganic compounds metals, ions or drugs) for photoelectrochemic processes, as claimed in number 1, where such substances substances may be polyhydroxiindol, eumelanine, pheomelanine, allomelanine, neuromelanine, humic acid, fullerenes, graphite, polyindoquinone, acetylene-black, pyrrole-black, indole-black, benzene-black, thiophene-black, aniline-black, hydrated polyquinones, sepiamelamines, dopa-black, dopamine-black, adrenaline-black, catechol-black, 4 amine catechol-black, (single linear chain, aliphatic, aromatic) and/or their precursors, such as phenols, aminophenols, diphenols, indol-polyphenols, cyclodope, DHI and

DHICA, quinones, semiquinones or hydroquinones, L-tyrosine, L-dopamine, morpholine-ortho-benzoquinone, dimorpholene-orto-benzoquinone, morpholincatheol, orthobenzoquinone, porphyrin-black, pterin-black, ommochrome-black, free nitrogen precursors any of the above mentioned, in any size of the particle (from 1 angstrom to 2-3 cm). Any of the compounds mentioned above, electro active, in suspension, solution or gel, that absorb ultrasound in 1 MHz interval, natural or synthetic of vegetal, animal or mineral origin, pure or mixed (with organic or inorganic compounds, ions, metal, drugs or pharms) as the main, central principal or essential materials. In the process the concentration of the melanines should be taken in to account and may fluctuate from 0.1% to 100% or more.

7. We claimed, like in **1** and **2**, the employment of the melanines, precursors of the melanines, derivates of the melanines, variants, analogues, natural or synthetic, pure or mixed (with organic or inorganic compounds, metals, ions or drugs) in designs that have the objective to produce energy either producing electric current when binding hydrogen and oxygen atoms, or generating hydrogen directly from breaking photoelectrochemically the water, or profittin the melanines's property to generate hydrogen peroxide, superoxide anion, oxyhydrides and monoatomic or molecular oxygen as in number **1**.

8. We claim, like in number **1**; the system that allows the employment of the melanines, precursors of the melanines, derivates of the melanines, derivates of the melanines, variants, analogues of the melanines, natural or synthetic, pure or mixed (with inorganic or organic compounds, metals, ions or drugs) to the photoelectrochemic process or energy production as claimed in number **1** to **3**, that comprises the application of magnetic fields in a low or significant energy, and with events that may occur under physic or chemic stimuli, internal or external. To expose such substances they must be in a container. Such apparatus permits the control of the partial pressure of the gases and these may vary from 0.1 mmHg to 3 or 4 pressure atmospheres, may fluctuate from 0.1 mm of Hg until some atmospheres of pression.

9. We claim, like in **1**; the apparatus that allows the employment of the melanines, precursors of the melanines, derivates of the melanines, variants, analogues of the melanines, natural or synthetic, pure or mixed (with organic or inorganic compounds, metals, ions, drugs, or pharms) to the photoelectrochemic process or energy producing as claimed in number **4**, whose container allow the exposure of such substances in a wider area through a flat shape or any other like the described before in this patent.

* * * * *