Abstract: The present invention relates to a process for water oxidation using a polyoxometalate compound of formula (I) as water oxidation catalyst. It is also related to some polyoxometalate compounds. Formula (I): [M(09)(OH)3(H2O)4(HP04)2(L)]3[A] n wherein: M is selected from the group consisting of Co, Mn, and Fe; L is selected from the ligand of formula YM PO4 and Y2Mo5O36; Y is selected from the group consisting of P, Si, Ge, and As; M’ is selected from the group consisting of W, Mo, and V; A is a cation selected from the group consisting of Li+, Na+, K+, Rb+, Cs+, Ca2+, Ba2+, Mg2+, and mixture thereof; and n is an integer selected from 8 and 16, being the sum of positive charges of A equal to 16.
Process for water oxidation comprising the use of a polyoxometalate compound as water oxidation catalyst

The present invention relates to a process for water oxidation using a polyoxometalate compound as catalyst. It is also related to some polyoxometalate compounds, and their preparation process.

BACKGROUND ART

The production of renewable clean energy is one of the most challenging research objectives of the present century. Sunlight is the most abundant energy source. Plants are able to convert sunlight into chemical energy through photosynthesis. Therefore, one of the most promising possibilities for energy research is the development of viable artificial photosynthesis.

Photosynthesis is a biological process that allows bacteria, algae, and plants to use solar energy to sustain their growth through the production of biomass. Photosynthesis begins with light striking a light harvesting complex in Photosystem II, creating a charge-separated excited state where an electron is promoted to a higher energy level. Water oxidation catalyzed by an oxygen evolving complex (OEC) replenishes the hole derived from the charge-separated excited state. This process causes the release of four equivalents of H\(^+\) and one equivalent of molecular oxygen per two water molecules. Some of the generated protons are used in a proton gradient, which the plant employs to store energy by synthesizing ATP. The high-energy electrons move along an electron transport chain and are eventually used to reduce the remaining protons from the water oxidation process.

The study of new water oxidation catalysts (WOCs) to produce oxygen and therefore hydrogen has proven particularly challenging, because the oxidation of water to molecular oxygen is a highly demanding reaction since it is very complex from a mechanistic perspective and also because it has a very high kinetic activation energy.

It is known that water can be transformed into molecular oxygen, four hydrogen ions, and four electrons by reaction with an oxidant (OX) in the presence of a WOC. The net reaction of the oxidation of water is as follows:
There are two different types of WOC, heterogeneous and homogeneous. Heterogeneous WOCs are advantageous due to their low cost, ease to interface with electrode systems, and their oxidative stability. However, they are deactivated by surface poisoning or aggregation. In contrast, homogeneous WOCs are more amenable to spectroscopy, crystallographic, and computational investigation, being readily optimized. Unfortunately, most known homogeneous WOCs contain organic ligands being sensitive and prompt to oxidative deactivation.

There are also a few known homogeneous WOCs that do not contain organic ligands susceptible of oxidative degradation that belong to the class of polyoxometalate (POM) catalysts. POMs are basically composed by metal-O-metal bonds, where the metal is in a high oxidation state. POMs are typically negatively charged ions, and thus their solubility varies depending on the nature of the counterion with which they are paired. POMs are strongly resistant to oxidation due to their configuration, and they can also contain different structural elements bound to the core, such as for example other metals and inorganic ligands.

The international patent application number WO2010107919 disclosed the use of a self-assembling POM catalysts of formula [MpM’qOx(OH)n(H2O)m-Lr]u[A]v as a water oxidation catalysts. In particular, salts of the anion POM catalyst of formula [Co₄(H₂O)₂(γ-PW₉O₃₄)₂]₁⁰⁻, e.g. potassium salt, have been used for water oxidation using [Ru(bpy)₃]³⁺ as an oxidant. Turn over numbers (TON) of 75 with an oxygen yield of 64% were reported when a concentration of 0.032 mM of [Co₄(H₂O)₂(γ-PW₉O₃₄)₂]₁⁰⁻, and 0.06 mM of oxidant were used. The rate of water oxidation of [Co₄(H₂O)₂(γ-PW₉O₃₄)₂]₁⁰⁻ is sensitive to pH. The increase of pH from 7.5 to 8 provokes a decrease in the reaction time from 270 seconds to 90 seconds. Additionally, Stracke and co-workers have observed that the polyanion [Co₄(H₂O)₂(γ-PW₉O₃₄)₂]₁⁰⁻ is unstable above pH = 7, being converted into CoOX oxide species.

(J. J. Stracke, R. G. Finke, "Electrocatalytic Water Oxidation Beginning with the Cobalt Polyoxometalate [Co₄(H₂O)₂(PW₉O₃₄)₂]₁⁰⁻: Identification of

However, the only examples of salts of the

Those heteropolyanion salts were obtained as by-products in the preparation of the above mentioned POM catalyst of formula \[[\text{Co}\textsubscript{4}(\text{H}_2\text{O})\textsubscript{2}(\text{y-PW}\textsubscript{9}\text{O}\textsubscript{34})\textsubscript{2}]^{10-}\] (also named POM-Co4). The \[[\text{Co}\textsubscript{9}(\text{OH})\textsubscript{3}(\text{H}_2\text{O})\textsubscript{6}(\text{HPO}_4)\textsubscript{2}(\text{PW}\textsubscript{9}\text{O}\textsubscript{34})\textsubscript{3}]^{16-}\] heteropolyanion (also named POM-Co9) disclosed by Weakley was characterized by X-ray crystallographic analysis. The structure reveals that the POM-Co9 anion has crystallographic symmetry \(3/m-C3h\), and that the nine CoO6 octahedral are linked at the core by edge-sharing in three sets of three, with an OH\textsuperscript{-} corner-sharing bridging the sets. Each set shares six oxygen atoms with a PW\textsubscript{9}O\textsubscript{34}\textsuperscript{9-} moiety and also shares an oxygen atom with each of two additional HPO\textsubscript{4}\textsuperscript{2-} tetrahedral which lie on the triad axis above and below the equatorial plane. Rubidium salt of \[[\text{Co}\textsubscript{9}(\text{OH})\textsubscript{3}(\text{H}_2\text{O})\textsubscript{6}(\text{HPO}_4)\textsubscript{2}(\text{PW}\textsubscript{9}\text{O}\textsubscript{34})\textsubscript{3}]^{16-}\] was disclosed.

The POM-Co9 heteropolyanion can alternatively be described as consisting of three PCo3W\textsubscript{9}O\textsubscript{4}O\textsubscript{4} units with the a-PW\textsubscript{2}O\textsubscript{4}\textsuperscript{6-} structure, in which the Co atoms occupy adjacent edge-sharing octahedra. These units share oxygen atoms from a hydroxy OH\textsuperscript{-} group so that the terminal oxygen atom on Co(2) is coincident with the Co(1)-O-Co(1\textsuperscript{'} ) bridging atom in the next unit, while other Co-O-Co oxygen atoms on the periphery are shared with the axial phosphorus atoms. With the assignment of the terminal oxygen on Co(1\textsuperscript{'} ) as H\textsubscript{2}O, three terminal oxygen atoms of two HPO\textsubscript{4}\textsuperscript{2-} bridge also the three triads, with the fourth oxygen atom in the HPO\textsubscript{4}\textsuperscript{2-} unit remaining protonated as an OH group, the structure of the anion was elucidated. Potassium, rubidium, cesium, and guanidinium salts of \[[\text{Co}\textsubscript{9}(\text{OH})\textsubscript{3}(\text{H}_2\text{O})\textsubscript{6}(\text{HPO}_4)\textsubscript{2}(\text{PW}\textsubscript{9}\text{O}\textsubscript{34})\textsubscript{3}]^{16-}\] were also mentioned.
Thus, J.R. Weakley was able to synthesize the heteropolyanion of formula
\[ \text{[Co}_9\text{(OH)}_3\text{(H}_2\text{O})_6\text{(HPO}_4\text{)}_2\text{(PW}_9\text{O}_{34})_3\text{]}^{15-} \] in form of potassium, rubidium, cesium, and guanidinium salts and elucidate the heteropolyanion structure. However, the author is silent about the use of this heteropolyanion.

Therefore, from what is known in the art it is derived that there is still the need of providing hydrolytically, oxidatively, and thermally stable POMs catalysts for a rapid and efficient oxidation of water.

10 SUMMARY OF THE INVENTION

Inventors have found that a POM of formula (I) containing nine metal cations, six water molecules, three hydroxyl anions and two hydrogenophosphate anions, is useful as catalyst for water oxidation to obtain molecular oxygen and hydrogen ions. The use of the POM of formula (I) of the present invention proceeds without appearance of fatigue of the catalyst, and thus the catalysis is carried out without decomposition of the catalyst. Then, there is no change in the speed of catalysis, allowing a high turn over of oxygen and a high efficiency of the catalytic reaction.

Thus, a first aspect of the present invention relates to a process for water oxidation to obtain molecular oxygen and hydrogen ions which is carried out in the presence of a catalytically effective amount of a compound of formula (I),

\[ \text{[M}_9\text{(OH)}_3\text{(H}_2\text{O})_6\text{(HPO}_4\text{)}_2\text{(L)}_3\text{]}\text{[A]}_n \quad \text{(I)} \]

wherein: M is selected from the group consisting of Co, Mn, and Fe; L is selected from the ligand of formula YM'\text{O}_{34} and Y2M'15O_{56}; Y is selected from the group consisting of P, Si, Ge, and As; M' is selected from the group consisting of W, Mo, and V; A is a cation selected from the group consisting of Li+, Na+, K+, Rb+, Cs+, Ca^{2+}, Ba^{2+}, Mg^{2+}, and mixture thereof; and n is an integer selected from 8 and 16, being the sum of positive charges of A_n equal to 16.

The second aspect of the present invention relates to a cobalt oxide obtainable by the process as defined in alternative (b), or alternative (c), or alternative (d).
The third aspect of the present invention relates to a compound of formula (I) having the formula $[\text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_3\text{O}_{12})_3]\text{Na}_x\text{K}_y\text{Cs}_z$ wherein: $x$ is an integer selected from 1 to 15; and $y$ is an integer selected from 1 to 15; provided that $x+y$ is 16.

Finally, the fourth aspect of the present invention relates to a compound of formula (I) having the formula $[\text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_3\text{O}_{12})_3]\text{Na}_x\text{K}_y\text{Cs}_z$ wherein: $x$ is an integer selected from 1 to 14; $y$ is an integer selected from 1 to 14; and $z$ is an integer selected from 1 to 14; provided that $x+y+z$ is 16.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 shows the displacement ellipsoid plot of the central part, $\text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2$, of the molecular structure of the compound of formula (Ia) obtained by X-Ray crystallography analysis. The atoms are represented as follows: big white circles are Co; small white circles are P; black circles are water molecules (H$_2$O); duo-tone circles (half-white and half-black circles) are oxo groups (O$^2^-$); and beach-ball circles are hydroxo groups (OH$^-$).

Fig. 2 shows the turn over profile for oxygen evolution in a 2 mL phosphate buffer solution (pH = 8.0) with POM-Co9 of formula (Ia) or POM-Co4 in concentration 1 mM after addition of 100 equivalents of NaClO ([Cat]:[ClO$^-$]=1:100) in 2 mL of a phosphate buffer solution (pH = 8.0). Units are represented as follows: s are seconds.

Fig. 3 shows the turn over profile for oxygen evolution in a 2 mL phosphate buffer solution (pH = 8.0) with POM-Co9 of formula (Ia) in 0.1 mM concentration after addition of 1000 or 3260 equivalents of NaClO ([Cat]:[ClO$^-$]=1:1000; 1:3260) in 2 mL of a phosphate buffer solution (pH = 8.0). Units are represented as follows: s are seconds.

Fig. 4 shows the turn over profile for oxygen evolution in three 2 mL phosphate buffer solution (pH = 7.0, 8.0 and 9.0) with POM-Co9 of formula (Ia) in concentration 1.0 mM after addition of 100 equivalents of NaClO ([Cat]:[ClO$^-$]=1:100) in the corresponding 2 mL of a phosphate buffer solution (pH = 7.0, 8.0 and 9.0). Units are represented as follows: s are seconds.
Fig. 5 shows the turn over profile for oxygen evolution in a 2 ml phosphate buffer solution (pH = 8.0) with POM-Co9 in concentration 0.01 mM after addition of 32600 equivalents of NaClO ([Cat]:[ClO ]=1 :32600) in 2 ml of a phosphate buffer solution (pH = 8.0). Units are represented as follows: s are seconds.

Fig. 6 shows the turn over profile for oxygen evolution in a 2 ml phosphate buffer solution (pH = 8.0) with POM-Co9 of formula (la) in concentration 0.1 mM after three subsequent additions of 1000 equivalents of NaClO (final [Cat]:[ClO ]=1 :3000) in 2 ml of a phosphate buffer solution (pH = 8.0) at time 0h, 2h 30min, and 4h 30. Units are represented as follows: s are seconds.

Fig. 7 shows the turn over profile for oxygen evolution in a 2 mL phosphate buffer solution (pH = 8.0) with POM-Co9 of formula (la) in concentration 0.01 mM after three subsequent additions of 32600 equivalents of NaClO (final [Cat]:[ClO ]=1 :97800) in 2 mL of a phosphate buffer solution (pH = 8.0) at time 3 days, 4 days and 5 days (black arrows indicate time of addition). Units are represented as follows: h are hours.

Fig. 8 shows the electrical current passing through an electrochemical cell when a potential is applied. The water electrolysis was performed in a phosphate buffer solution (pH = 8) containing either 0.50 mM of POM-Co9 of formula (la), or 0.50 mM POM-Co4 or in the absence of POM type catalyst. Units are represented as follows; V are volts, and mA are miliAmpere.

Fig. 9 shows the cyclic voltammetry profile using an electrode containing the compound of formula (lb) supported on carbon paste. The cyclic voltammetry was carried out in a 20 mL of phosphate buffered solution at pH = 7.0 inside of a one-pot-cell. The electrical current measured in mA between -0.5 and 1.5 V corresponds to the electrons removed from water to generate molecular oxygen and, therefore, they are directly related to the amount of oxygen generated, taking into account that four electrons represent one oxygen molecule. Units are represented as follows; V are volts, and mA are miliAmpere.
Fig. 10 shows the electrical current passing through an electrochemical cell as described in Example 6 when a voltage of 1.4 V vs NHE applied. The current corresponds to the oxygen evolution. The constant current maintained for a long period of time demonstrates the stability of (lb) as a solid supported catalyst. Units are represented as follows: s are seconds, and mA are miliAmpere.

Fig. 11 shows the applied overpotential \( (E-E_0) \) needed to reach the corresponding electrical current density \( (i) \) when an electrode containing the compound of formula (lb) supported on carbon paste is used. Units are represented as follows: \( E \) is the applied potential and \( E_0 \) is the thermodynamic water oxidation potential, both in volts; \( i \) is the current density in A/cm\(^2\).

Fig. 12 shows the powder X-Ray diffraction analysis (XR-PD) of the compound of formula (lb) supported on amorphous carbon paste obtained following the process of Example 5. Units are represented as follows: \( \Theta \) is counts and \( 2\Theta \) is the change of angle of the electromagnetic wave.

Fig. 13 shows the electrical current generated by a constant potential of 1.4 V vs NHE in an electrochemical cell equipped with a fluorine doped tin oxide electrode (FTO) as working electrode; a Ag/AgCl NaCl 3M electrode as reference electrode; and a Pt mesh electrode as counter electrode. The water electrolysis was performed in a phosphate buffer solution \( (pH = 7) \) containing POM-Co9 of formula (la) \( (1 \text{ mM}) \), and 2,2'-bipyridyl \( (1.4 \text{ mM}) \). Units are represented as follows; mA are miliAmpere; t is time measured in minutes.

Fig. 14 shows the electrical current generated by a constant potential of 1.4 V vs NHE in an electrochemical cell equipped with a fluorine doped tin oxide electrode (FTO) as working electrode; a Ag/AgCl NaCl 3M electrode as reference electrode; and a Pt mesh electrode as counter electrode. The water electrolysis was performed in a phosphate buffer solution \( (pH = 7) \) in the presence of cobalt oxide film obtained following the process of Example 12. Units are represented as follows; mA are miliAmpere; t is time measured in minutes.

DETAILED DESCRIPTION OF THE INVENTION
All terms as used herein in this application, unless otherwise stated, shall be understood in their ordinary meaning as known in the art. Other more specific definitions for certain terms as used in the present application are as set forth below and are intended to apply uniformly throughout the specification and claims unless an otherwise expressly set out definition provides a broader definition.

In the context of the invention, the terms "water oxidation catalyst", "WOC", "oxygen evolving catalyst", or "OEC" have the same meaning and are used interchangeably. They refer to a catalyst used to oxidize water to form molecular oxygen (O₂), hydrogen ions (H⁺), and electrons (e⁻).

The term "hydrogen evolution catalyst" refers to a catalyst used to convert hydrogen ions (H⁺) into hydrogen (H₂).

The terms "electron scavenging agent" or "sacrificial electron acceptor" have the same meaning and are used interchangeably. They refer to the molecule that is reduced during the oxidation of water.

The term "chemical oxidant" refers to an oxidant which can be directly used in the reaction conditions, and is reduced during the oxidation of water.

The term "photochemically generated oxidant" refers to an oxidant which is generated by the light irradiation of a photosensitizing complex. The photochemically generated oxidant is reduced during the oxidation of water.

The term "self-assembly" refers to processes in which a disordered system of pre-existing components forms an organized structure as a consequence of specific, local interactions among the components themselves, without external direction or stimuli. Self-assembly allows for self-repairing of the catalyst which improves the turn over number and oxygen yield in the catalyzed reactions.

The terms "polyoxometalate" or "POM" have the same meaning and are used interchangeably. They refer to a polyatomic ion, usually an anion, which includes three or more transition metal oxyanions linked or shared by oxygen atoms.
The terms "turn over number" or "TON" have the same meaning and are used interchangeably. They refer to the number of moles of substrate that a mole of catalyst can convert during a certain unit of time. This term usually refers to the point where the oxidation reaction is finished, either because the oxidant has been consumed, or because the catalyst has been deactivated. TON is calculated as the number of moles of oxygen \( \text{no}_2 \) divided by the number of moles of catalyst \( n_{\text{ca}} t \).

The terms "turn over frequency" or "TOF" have the same meaning and are used interchangeably. They refer to the turn over per unit of time under turn over conditions. The TOF can be calculated by dividing the TON by the time period, in seconds, over which the TON was measured. The TOF is usually expressed in h\(^{-1}\).

The term "turn over conditions" refers to the conditions in which the catalytic water oxidation reaction takes place, such as for example pH, temperature, concentration of electron scavenging agent, and concentration of WOC.

The term "cell" refers to a device where an oxidation-reduction reaction (also called redox reaction) takes place in electrochemical cells. There are two types of electrochemical cells: galvanic or voltaic cells where the reaction occurs spontaneously; and electrolytic cells where the reaction occurs non-spontaneously. Both types of cells contain electrodes where the oxidation and reduction reactions occur. Oxidation occurs at the anode and reduction occurs at the cathode. The anode of an electrolytic cell is positive (cathode is negative), since the anode attracts anions from the solution. However, the anode of a galvanic cell is negatively charged, since the spontaneous oxidation at the anode is the source of the cell's electrons or negative charge.

The cathode of a galvanic cell is its positive terminal. In both galvanic and electrolytic cells, oxidation takes place at the anode and electrons flow from the anode to the cathode. A cell can also contain an electrolyte, which is a substance containing free ions that make the substance electrically conductive.

When electrodes are placed in an electrolyte and a voltage is applied, the electrolyte will conduct electricity. Lone electrons normally cannot pass
through the electrolyte; instead, a chemical reaction occurs at the cathode consuming electrons from the anode. Another reaction occurs at the anode, producing electrons that are eventually transferred to the cathode. As a result, a negative charge cloud develops in the electrolyte around the cathode, and a positive charge develops around the anode. The ions in the electrolyte neutralize these charges, enabling the electrons to keep flowing and the reactions to continue.

The terms "photo-electrochemical cell" or "PEC" refer to an electrochemical cell where the redox-reaction is conducted by light energy. PECs contain a cathode and an anode in contact with electrolyte containing reactants that are oxidized or reduced at the respective electrodes separated in a two-chamber cell, with the chambers connected for the interchange of electrons and ions. In photo-electrochemical cells at least one of the half reactions is driven by solar energy. The sunlight is converted into chemical energy.

The terms "photovoltaic cell" or "solar cell" have the same meaning and are used interchangeably. They refer to any cell having a light absorbing material to absorb photons, a semiconducting material able to generate a charge separation into electrons and holes, and an anode and cathode where these electrons are holes are directed, respectively. The light absorbing material may absorb light in any wavelength or combination of wavelengths, including, for example, wavelengths of solar light that reach the earth's surface, and/or wavelengths of solar light beyond the earth's atmosphere. Two or more light absorbing materials having specific wavelengths of light absorption may be used in combination to take advantage of different light absorption and charge separation mechanisms. The light absorbing material may be configured as, for example, bulk material, thin-film (e.g., inorganic layers, organic dyes, and organic polymers), and/or nanocrystals. The semiconducting material able to separate charges maybe configured as, for example, bulk material, thin film, organic polymer or dendrimer, and it is responsible to generate a forward bias when combined with the cathode and anode. So the electrons and holes are directed in only one direction when the cell is irradiated. The anode and cathode are the connections where a voltage difference is generated to yield the electrical current when the circuit is closed. The photovoltaic cells may be combined into arrays, strings, modules, or panels.
The term "electrolyte" refers to any substance containing free ions that make the substance electrically conductive. Examples of suitable electrolytes for the present invention can be, among others, ionic solution electrolytes; molten and solid electrolytes; and gas electrolytes.

The term "salt bridge" refers to a porous barrier which prevents the spontaneous mixing of the electrolytes of the anode of the first chamber and the cathode of the second chamber, but allows the migration of ions from the anode to the cathode, and vice versa, to maintain electrical neutrality.

The term "oxygen yield" refers to the percentage of molecular oxygen formed during the catalytic water oxidation reaction. It is expressed as the molar percent of oxygen of the total oxygen theoretically expected from total consumption of electrons taken by the scavenging agent, the anode, or the photo-anode.

The term "catalytically effective amount" refers to the fact that the amount of catalyst (i.e. the compound of formula (I)) is much smaller than the stoichiometric amounts of either starting materials and sufficient for the reaction to take place.

The term "room temperature" refers to indoor temperature which is of between 20 and 25°C.

The term "(Ci-C6)alkyl" refers to a saturated straight, or branched hydrocarbon chain which contains from 1 to 6 carbon atoms. Examples include the group methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, and n-hexyl.

The term "monocyclic ring" refers to a 5 to 6 membered ring, being the ring saturated, partially unsaturated or aromatic, where the members of the ring are independently selected from C, CH, CH₂, O, N, NH, and S, being one or more of the hydrogen atoms of the members of the ring optionally substituted by a radical selected from the group consisting of (Ci-C6)alkyl, (Ci-C6)haloalkyl, halogen, (Ci-C6)alkoxy, nitro, cyano, (Ci-C6)alkylcarbonyl, and (Ci-C6)alkyloxycarbonyl. Examples include, among others, phenyl, isoquinolyl, quinolyl, indenyl, triazolyl, tetrazolyl, indolyl, furyl, pyrrolyl, thienyl, benzofuryl,
pyridyl, naphthyridyl, imidazolyl, benzoxazolyl, benzisoxazolyl, benzotriazolyl, biphenyl, 1-naphthyl, and 2-naphthyl.

The term (Ci - C6)haloalkyl refers to a group resulting from the replacement of one or more hydrogen atoms from a (Ci - C6)alkyl group with one or more halogen atoms, which can be the same or different. Examples include, among others, trifluoromethyl, fluoromethyl, 1-chloroethyl, 2-chloroethyl, 1-fluoroethyl, 2-fluoroethyl, 2-bromoethyl, 2-iodoethyl, 2,2,2-trifluoroethyl, pentafluoroethyl, 3-fluoropropyl, 3-chloropropyl, 2,2,3,3-tetrafluoropropyl, 2,2,3,3,3-pentafluoropropyl, heptafluoropropyl, 4-fluorobutyl, and nonafluorobutyl.

The term "halogen" refers to F, Cl, Br, and I.

The term (Ci - Cs)alkoxy refers to an alkoxy group having from 1 to 3 carbon atoms, the alkyl moiety having the same meaning as previously defined. Examples include methoxy, ethoxy, propoxy, and isopropoxy.

The term (Ci - C3)alkylcarbonyl refers to a saturated straight or branched alkyl chain which contains from 1 to 3 carbon atoms, where the carbon atom is appended to the alkyl chain through a carbonyl group. Examples include acetyl, and 1-oxopropyl.

The term (Ci - C6)alkyloxycarbonyl refers to a saturated straight or branched alkyl chain which contains from 1 to 6 carbon atoms, where the carbon atom is appended to the alkyl chain through an oxycarbonyl group. Examples include methylcarboxy, ethylcarboxy, propylcarboxy, isopropylcarboxy, butylcarboxy, tert-butylcarboxy, pentylcarboxy, and hexylcarboxy.

The term "obtainable" and "obtained" have the same meaning and are used interchangeably. In any case, the expression "obtainable" encompasses the expression "obtained".

As mentioned above, the first aspect of the present invention refers to a process for water oxidation to obtain molecular oxygen and hydrogen ions which is carried out in the presence of a catalytically effective amount of a compound of formula (I). The first aspect of the present invention can also be formulated as the use of a compound of formula (I) as catalyst for water.
oxidation wherein M is selected from the group consisting of Co, Mn, and Fe; L is selected from the ligand of formula YM'O₃ₓ and Y₂M'O₅ₓ; Y is selected from the group consisting of P, Si, Ge, and As; M' is selected from the group consisting of W, Mo, and V; A is a cation selected from the group consisting of Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, Ba²⁺, Mg²⁺, and mixture thereof; and n is an integer selected from 8 and 16, being the sum of positive charges of Aₙ equal to 16.

In comparison with the catalysts of the prior art, the compound of formula (I) is more robust being not destroyed under the turn over conditions, thus allowing conducting a more efficient and rapid water oxidation reaction. Unlike the behavior of POM-CO₄, the compound of formula (Ia) of the present invention does not show any sign of decomposition after storage in phosphate buffer solution during a few days.

The efficiency of the reaction is shown by the high TON obtained, and the amount of oxygen evolved. The compound of formula (I) is a hydrolytically, oxidatively, photooxidatively and thermically stable homogeneous WOC suitable for the rapid, efficient and continuous oxidation of water.

In a preferred embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein M is Co.

In another embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein M is Fe or Mn.

In another preferred embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein L is YM'O₃ₓ.
In another preferred embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein Y is Si or As. Preferably, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein Y is Si or As; and M is Co.

In another preferred embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein M’ is W.

In another preferred embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein L is PW₉O₃₄.

In another preferred embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein A is selected from the group consisting of Na⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, Ba²⁺, and mixture thereof. In a more preferred embodiment of the first aspect of the invention, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein A is selected from the group consisting of Na⁺, K⁺, and mixture thereof.

Preferably, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein A is Na⁺.

Preferably, the compound used as catalyst for water oxidation of formula (I) of the present invention, is [Co₉(OH)₃(H₂O)₆(HPO₄)₂(PW₉O₃₄)₃]Nai₆.

In a preferred embodiment, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein A is a mixture of cations selected from the group consisting of Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, Ba²⁺, and Mg²⁺; more preferably, A is a mixture of Na⁺, K⁺, and/or Cs⁺.

In a preferred embodiment, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein A is a mixture of Na⁺, and K⁺.
In a particular embodiment, the compound used as catalyst for water oxidation of formula (I) of the present invention, is the compound of formula [Co(9)(OH)3(H2O)6(HPO4)2(PW9O34)3]NaxKy where: x is an integer selected from 1 to 15; and y is an integer selected from 1 to 15; provided that x+y is 16.

Preferably, the compound used as catalyst for water oxidation of formula (I) of the present invention, is the compound (la) obtainable by the process of Example 1. The process of Example 1 comprises: (a) reacting an aqueous solution of Co(OOC-CH3)2·4H2O with Na2WO4·2H2O, and Na2HPO4, in a 9:27:5 ratio wherein the pH is 7.6; (b) refluxing the solution obtained in step (a) for 9h, (c) filtering the solution obtained in step (b), and adding K(OOC-CH3); (d) cooling the solution obtained in step (c) at room temperature; and stirring for a time comprised of from 1 to 24 hours; and (e) isolating and drying the crystals obtained in step (d); wherein the molar ratio between Co(OOC-CH3)2·4H2O and K(OOC-CH3) is 1:2.

In another preferred embodiment, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that wherein A is a mixture of Na+, K+, and Cs+.

In a particular embodiment, the compound used as catalyst for water oxidation of formula (I) of the present invention, is the compound of formula [Co(9)(OH)3(H2O)6(HPO4)2(PW9O34)3]NaxKyCSz wherein: x is an integer selected from 1 to 14; y is an integer selected from 1 to 14; and z is an integer selected from 1 to 14; provided that x+y+z is 16. In a more preferred embodiment, the compound used as catalyst for water oxidation of formula (I) of the present invention, is that where z is an integer selected from 6 to 10; preferably, z is 8.

In another preferred embodiment, the compound used as catalyst for water oxidation of formula (I) of the present invention, is the compound (lb) obtainable by the step (a) of the process of Example 5. Step (a) of the process of Example 5 comprises: (a) reacting an aqueous solution of the compound of formula (I) obtainable by the process of Example 1 as defined above with an aqueous solution of CsCl at room temperature; until a precipitate is formed and; (b) filtering the precipitate obtained in step (a); and (c) drying in air the precipitate obtained in step (b).

In a preferred embodiment, the process of the first aspect of the invention can be carried out when the compound of formula (I) is in form of a solid-
supported catalyst, being the compound of formula (I) linked to the solid support by electrostatic forces, wherein the support is selected from the group consisting of metals, metal oxides, graphite, graphene, carbon nanotubes, amorphous carbon, mesoporous silica, mesoporous alumina, mesoporous aluminosilicates, mesoporous metal oxides, and hydrotalcites. The electrostatic forces include among others cation-anion interactions, and dipole-dipole interactions.

In another preferred embodiment, the compound of formula (I) as defined above used for the water oxidation reaction is in form of a solid-supported catalyst, being the solid support selected from the group consisting of metals, metal oxides, graphite, graphene, carbon nanotubes, and amorphous carbon such as for example carbon paste; and wherein the compound of formula (I) is adsorbed on the surface of the solid support; more preferably, the solid support is graphite, graphene, carbon nanotubes, and amorphous carbon; preferably, the solid support is amorphous carbon. Preferably the amorphous carbon is carbon paste.

When a compound of formula (I) is used in form of a solid-supported catalyst, and wherein the compound of formula (I) is adsorbed on the surface of the solid support; preferably, the solid support is a metal or a metal oxide.

In another preferred embodiment, the compound of formula (I) as defined above used for the water oxidation reaction is in form of a solid-supported catalyst, being the solid support selected from the group consisting of mesoporous silica, mesoporous alumina, mesoporous aluminosilicates, mesoporous metal oxides, and hydrotalcites; and wherein the compound of formula (I) is entrapped into the surface of the solid support. It means that the compound of formula (I) is accommodated or included in the channels, holes or interlayer spaces formed in the tridimensional structure of the solid support.

When a compound of formula (I) is used in form of a solid-supported catalyst, where the compound of formula (I) is entrapped into the solid support; preferably, the solid support is mesoporous silica or mesoporous metal oxides.

When the compound of formula (I) is in form of the above mentioned solid-
supported catalyst, the catalyst is advantageous because it is easier to handle and to remove from the reaction mixture by simple techniques such as for example filtration. They are also advantageous because the compound of formula (I) in form of solid-supported catalyst can be used in less restricted conditions, such as for example a broader pH range (from 1 to 9), where also a higher TON value is obtained. Additionally, the above mentioned compounds of formula (I) are more stable and therefore, they can be used in a prolonged period of time.

In an alternative preferred embodiment, the process for water oxidation of the present invention is carried out by reacting water with an electron scavenging agent selected from the group consisting of a chemical oxidant, and a photochemically generated oxidant.

In another alternative preferred embodiment, the process for water oxidation of the present invention is carried out applying an external bias.

In another preferred embodiment, the process for water oxidation of the present invention comprises: (a) reacting water with an electron scavenging agent selected from the group consisting of a chemical oxidant, and a photochemically generated oxidant; or alternatively, (b) applying an electrical power source to a two-chamber cell, wherein the cell comprises: a first chamber comprising an anode being in contact with an aqueous electrolyte; a second chamber comprising a cathode being in contact with an electrolyte; and a salt bridge connecting the electrolytes of the first and the second chamber; or, alternatively, (c) exposing to light irradiation a photo-anode or a photo-cathode in a photo-electrochemical two-chamber cell, wherein the cell comprises: a first chamber comprising an anode or a photo-anode, being in contact with an aqueous electrolyte; a second chamber comprising a cathode or photo-cathode being in contact with an electrolyte; an electrical connection between the first and the second electrode; and a salt bridge connecting the electrolytes of the first and the second chamber; with the proviso that at least one of the two chambers of the cell comprises a photo-anode or a photo-cathode.

In another alternative preferred embodiment, the process for water oxidation of the present invention comprises exposing to light irradiation a photovoltaic
solar cell, wherein the photovoltaic cell comprises: an absorbing light material selected from the group consisting of a semiconductor, a chromophore, and mixture thereof; a semiconducting material; a cathode; and an anode; being the cathode and the anode of the photovoltaic cell connected to a two-chamber cell, wherein the two-chamber cell comprises: a first chamber comprising an anode being in contact with an aqueous electrolyte; a second chamber comprising a cathode being in contact with an aqueous electrolyte; and a salt bridge connecting the electrolytes of the first and the second chamber (also mentioned as alternative d).

In alternatives (b), (c), and (d) as mentioned above, the compound of formula (I) is present in the anode of the two-chamber cell, either being dissolved in the aqueous electrolyte of the first chamber comprising the anode, or alternatively on the solid support.

In alternative (a) of the process of the invention, the water oxidation reaction is conducted by reacting water with an electron scavenging agent selected from the group consisting of a chemical oxidant and a photochemically generated oxidant, in the presence of the compound of formula (I).

In a preferred embodiment, the electron scavenging agent of alternative (a) is a chemical oxidant selected from the group consisting of Cl2, O3, NO, N2O, A'mX, H2O2, O3O2, Mn02O3, RuO4, OsO4, TZm, and Ru(L')3Z3, where: A' is a cation selected from the group consisting of Li+, Na+, K+, Rb+, Cs+ and (NH4)+; X is an anion selected from the group consisting of ClO−, ClO2−, NO2−, HSO3−, BrO−, IO−, IO4−, Mn04−, CrO4−, SO32−, SO42−, Cr2O72−, Cr3O72−, PdCl62−, IO65−, [Cu(HIO6)2]5−, [Ag(HIO6)2]5− and [Au(HIO6)2]5−; Q is a cation selected from the group consisting of Cr4+, Ni4+, Pd4+, Pt4+ and Pb4+; T is a cation selected from the group consisting of Tl3+, Cu3+, Ag3+, Au3+, Ce4+, Ru3+ and Ru4+; Z is an anion selected from the group consisting of F−, Cl−, Br−, I−, OH−, BF4−, PF6−, NO3− and ClO4−; L′ is 2,2'-bipyridyl; being the pyridyl ring unsubstituted or substituted at one or more position by a radical selected from the group consisting of COOR, and P(O)(OR)2; R is selected from the group consisting of (C1-C6)alkyl, and monocyclic ring; and m is an integer selected from 1 to 5, being the sum of positive charges of Am equal to the negative charges of X, and being the sum of the negative charges of Zm equal to the positive charges of T.
When a chemical oxidant is used as an electron scavenging agent in the oxidation of water of the present invention, the reaction can be conducted in dark conditions.

In a more preferred embodiment, the electron scavenging agent of alternative (a) is a chemical oxidant selected from the group consisting of Cl₂, A⁺, X, PbO₂, and Ru(L')₃Z₃, wherein: A' is a cation selected from the group consisting of Na⁺, K⁺, and (NH₄)⁺; X is an anion selected from the group consisting of ClO₄⁻, HSO₅⁻, SO₅²⁻, and IO₆⁵⁻; Z is an anion selected from the group consisting of Cl⁻, and Br⁻; L' is 2,2'-bipyridinyl; and m is an integer selected from 1 to 5, being the sum of positive charges of Aₘ equal to the negative charges of X.

Preferably, the electron scavenging agent used for water oxidation of the present invention is NaClO₄.

In another preferred embodiment, the electron scavenging agent of alternative (a) is a photochemically generated oxidant of formula Ru(L')₃Z₃, wherein: L' is 2,2'-bipyridinyl being the pyridinyl ring unsubstituted or substituted at one or more position by a radical selected from the group consisting of COOR, and P(O)(OR)₂; Z is selected from the group consisting of F⁻, Cl⁻, Br⁻, I⁻, OH⁻, BF₄⁻, PF₆⁻, NO₃⁻, and ClO₄⁻; and R is selected from the group consisting of (C₆H₅)₆alkyl, and monocyclic ring.

In a preferred embodiment, the electron scavenging agent used for water oxidation of alternative (a) of the process of present invention is the photochemically generated oxidant Ru(2,2'-bipyridinyl)₃Z₃, wherein Z is selected from the group consisting of Cl⁻, Br⁻, OH⁻, BF₄⁻, PF₆⁻, NO₃⁻, and ClO₄⁻.

The photochemically generated oxidant is generated by the light irradiation of a photosensitizing complex. The photosensitizing complex contains a group in its structure, such as for example a chromophore group, which is able to absorb light, the absorption of light transforms the photosensitizing complex into a charge separated excited state. In the excited state the photosensitizing complex is able to reduce a chemical oxidant, such as for example persulfate,
or [Co(NH$_3$)$_5$Cl]$_2^-$, to form the photochemically generated oxidant. The photochemically generated oxidant thus formed oxidizes water in the presence of the compound of formula (I) of the present invention. Then, the photochemically generated oxidant is converted into its original state to initiate another oxidation reaction of water molecules, which advantageously allows using the photochemically generated oxidant in catalytic amounts.

Scheme 1 illustrates a particular embodiment of the formation of the photochemically generated oxidant Ru(2,2'-bipyridinyl)$_3^{3+}$.

Scheme 1

In another particular embodiment, the photochemically generated oxidant used in the water oxidation reaction of the present invention is generated by sunlight irradiation.

The process of the invention which comprises the use of the compound of formula (I) as water oxidation catalyst is advantageous because regardless the electron scavenging agent used in the reaction, higher TON and faster TOF than the POMs of the state of the art were obtained.

In alternative (b) of the process of the invention, the water oxidation reaction is conducted by applying an electrical power source to a two-chamber cell, wherein the cell comprises: a first chamber comprising an anode being in contact with an aqueous electrolyte; a second chamber comprising a cathode being in contact with an electrolyte; and a salt bridge connecting the electrolytes of the first and the second chamber.

When an electrical current is applied to the electrochemical cell, water is
oxidized in the anode into molecular oxygen, and hydrogen ions in the presence of compound of formula (I), while the electrons are combined in the cathode with an electron acceptor substrate able to be reduced, such as for example hydrogen ions, CO2, aldehydes, ketones and organic polymers. The process of the present invention which comprises the use of the compound of formula (I) as water oxidation catalyst is advantageous because it allows the application of a lower voltage than that needed with the known POM catalysts of the state of the art to obtain equal or better efficiency. Thus, when a voltage difference is applied to the electrochemical cell in the presence of the compound of formula (I), higher TON and faster TOF than the ones obtained with the catalysts of the state of the art are obtained for water oxidation at the anode. The obtained TOF are the fastest reported for any WOC of the state of the art, reaching values over 500,000 h⁻¹.

In a more preferred embodiment, the electrical current applied to the cell is generated with a voltage difference between 0.1 and 2 V. In a more preferred embodiment, the electrical current applied to the cell is generated with a voltage difference between 0.8 and 1.3 V expressed vs a Ag/AgCl reference electrode.

In alternative (c) of the process of the invention, the water oxidation reaction is conducted by exposing to light irradiation a photo-anode or a photo-cathode in a photo-electrochemical two-chamber cell, wherein the cell comprises: a first chamber comprising an anode or a photo-anode, being in contact with an aqueous electrolyte; a second chamber comprising a cathode or photo-cathode being in contact with an electrolyte; an electrical connection between the first and the second electrode; and a salt bridge connecting the electrolytes of the first and the second chamber; with the proviso that at least one of the two chambers of the cell comprises a photo-anode or a photo-cathode.

When a photo-anode is irradiated, electronic charges on the surface of the anode are formed; those charges are also called electron-hole pairs. The oxidation of water is conducted by the above-mentioned holes at the anode yielding molecular oxygen, and hydrogen ions in the presence of compound of formula (I). The electrons flow to the cathode where they are combined with an electron acceptor substrate able to be reduced, such as for example
hydrogen ions, CO2, aldehydes, ketones and organic polymers.

When a photo-cathode is irradiated, electronic charges on the surface of the cathode are formed; those charges are also called electron-hole pairs. The reduction of an electron acceptor substrate able to be reduced, such as for example hydrogen ions, CO2, aldehydes, ketones and organic polymers is conducted by the above-mentioned electrons at the cathode. The holes flow to the anode where they are combined with water to produce molecular oxygen, and hydrogen ions in the presence of compound of formula (I).

The use of compound of formula (I) as water oxidation catalyst is advantageous because it allows performing the reaction of oxidation of water of the present invention with light irradiation of lower energy and intensity, achieving higher TON and faster TOF than the ones obtained with the catalysts of the state of the art. In a preferred embodiment, the light irradiation used to irradiate the photo-electrochemical cell of the first aspect of the present invention is sunlight.

The photo-electrodes of the present invention comprise a chromophore sensitizer supported on an electrode substrate electrically connected to the other electrode and in contact with the electrolyte. Alternatively, the photo-electrodes of the present invention comprise a chromophore sensitizer deposited on the electrode substrate as a film; or being dissolved in the electrolyte. In a preferred embodiment, the chromophore sensitizer is supported on an electrode substrate.

A suitable electrode substrate for the present invention can be any electrode substrate for photo-anodes or photo-cathodes known in the state of the art. In a preferred embodiment the electrode substrate is selected from the group consisting of metals such as for example platinum or gold; metal oxides such as for example Indium-Tin-Oxide (ITO); SnO2; TiO2 (also named titania); iron oxide (i.e. Fe2O3); tungsten oxide (i.e. WO3); silicium; carbon nanotubes, graphite, graphene or amorphous carbon; and mixtures thereof.

A suitable chromophore sensitizer for the present invention can be any sensitizer for photo-anodes and photo-cathodes known in the state of the art. In a preferred embodiment, the chromophore sensitizer is selected from the
group consisting of porphyrines, phtalocyanines, and metal complexes thereof; fullerene, and derivatives thereof; ruthenium (II) complexes with nitrogenated ligands such as for example polypyridyl ligand; and quantum dots such as for example CdSe, and CdS.

In a more preferred embodiment, the photo-anode comprises an electrode substrate, a chromophore photosensitizer, and a compound of formula (I) on the surface of the electrode substrate.

In alternative (d) of the process of the invention, the water oxidation reaction is conducted by exposing to light irradiation a photovoltaic cell connected to a two-chamber cell as defined above.

The absorbing light material of the photovoltaic cell is capable of absorbing the light, such as for example solar light, and the semiconducting material is capable of separating charges as promoted by the absorbing light material. The separated charges are driven to the corresponding cathode or anode creating a voltage difference. The cathode and the anode of the photovoltaic cell are connected to the two-chamber cell where the oxidation of water is carried out.

In another preferred embodiment, the chromophore is selected from the group consisting of porphyrines, phtalocyanines, and metal complexes thereof; fullerene, carbon nanotubes and derivatives thereof; chalcogenides such as CulnSe2 or CdTe; quantum dots such as for example CdSe, and CdS, and ruthenium (II) complexes with nitrogenated ligands such as for example polypyridyl ligand and 2,2'-bipyridinyl being the pyridinyl ring unsubstituted or substituted at one or more position by a radical selected from the group consisting of COOR, and P(O)(OR)2 being R selected from the group consisting of (C1-C6)alkyl, and monocyclic ring.

In a preferred embodiment, the semiconductor is selected from the group consisting of inorganic compounds such as for example silicon, tin-doped indium oxide (ITO) or fluorine doped tin oxide (FTO); metal oxides such as TiO2, and ZnO; and organic compounds such as for example Polyacetylene (PANI), and Poly(3,4-ethylenedioxythiophene) (PEDOT).
In another preferred embodiment, the process for water oxidation of the present invention is conducted at a pH of between 7 and 9. In a preferred embodiment, the process for water oxidation of the present invention is conducted at a pH of between 7 and 8; preferably, the pH is 7.

In another preferred embodiment, the process for water oxidation of the present invention is conducted in the sinus of a buffer solution. Preferably, the buffer solution is selected from the group consisting of phosphate and borate buffer solutions.

In another preferred embodiment, the process for water oxidation of the present invention is conducted at a pressure of between 0.1 and 2 bar. In a more preferred embodiment, the process for water oxidation of the present invention is conducted at atmospheric pressure about 1 bar.

In another preferred embodiment, the temperature of water oxidation of the present invention is of between 5 and 40 °C. In a more preferred embodiment, the temperature of water oxidation of the present invention is of between 20 and 30 °C. Preferably, the temperature of water oxidation of the present invention is of room temperature, i.e. about 25°C.

In a preferred embodiment of alternative (a) of the process for water oxidation of the present invention, the molar ratio between the catalytically effective amount of the compound of formula (I) and the electron scavenging agent is of between 1:100 and 1:60000, this ratio allows obtaining molecular oxygen in a high yield. In a more preferred embodiment, the molar ratio between the catalytically effective amount of the compound of formula (I) and the electron scavenging agent is of between 1:3000 and 1:33000.

In a preferred embodiment, the process for the oxidation of water alternative (c) or alternative (d) as defined above further comprises applying simultaneously an electrical power source to the two-chamber cell.

In another preferred embodiment, the process for the oxidation of water alternative (b), or alternative (c), or alternative (d), wherein when the compound of formula (I) is in form of a solid-supported catalyst, then the
anode of the first chamber of the two-chamber cell is in physical contact with the solid-supported catalyst. It is advantageous as it allows to reach higher TONs, and increase the stability of the compound of formula (I) used in the process of the invention.

In a preferred embodiment, the process as defined above of the first aspect of the invention further comprises adding a cobalt (II) sequestering agent. A cobalt (II) sequestering agent useful in the invention is any ligand known in the state of the art able to form strong coordination complexes with Co(II) cations in aqueous media. Preferably, the process as defined above of the first aspect of the invention further comprises adding a compound selected from the group consisting of 2,2'-bipyridinyl being the pyridinyl ring unsubstituted or substituted at one or more position by a radical selected from the group consisting of COOR, and P(O)(OR)₂ being R selected from the group consisting of (Ci-Ce)alkyl, and monocyclic ring; cyclam; and EDTA. It is advantageous because the process of the invention has values of TOF higher for a more prolonged period of time (cf. Example 11).

In a preferred embodiment, the process as defined above, comprising carrying out the alternative (b), the alternative (c) or the alternative (d) of the process for the oxidation of water of the first aspect of the invention, wherein the electrolyte of the second chamber of the two-chamber cell is an aqueous electrolyte, then the process further yields hydrogen.

Hydrogen production has gained increasing attention as fuel and as a renewable source of energy. In particular, efficient and economical water splitting would be a key technology component of a hydrogen economy. Water splitting is the general term for a chemical reaction in which water is separated into molecular oxygen (O₂) and hydrogen (H₂). The net reaction of water splitting is as follows:

\[
2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 2\text{H}_2
\]

When an electrical current is applied to the electrochemical cell as defined above wherein the electrolyte of the second chamber of the two-chamber cell is an aqueous electrolyte, water is oxidized in the anode into molecular
oxygen, and hydrogen ions in the presence of compound of formula (I), while hydrogen ions, and electrons are combined in the cathode to produce hydrogen.

When a photo-anode of the photo-electrochemical cell as defined above wherein the electrolyte of the second chamber of the two-chamber cell is an aqueous electrolyte is irradiated, the electron-hole pairs on the surface of the anode are formed. The oxidation of water is conducted by the above-mentioned holes at the anode yielding molecular oxygen, and hydrogen ions in the presence of compound of formula (I). The electrons flow to the cathode where they are combined with hydrogen ions to produce hydrogen.

When a photo-cathode of the photo-electrochemical cell as defined above wherein the electrolyte of the second chamber of the two-chamber cell is an aqueous electrolyte is irradiated, the electron-hole pairs on the surface of the cathode are formed. The reduction of hydrogen ions is conducted by the above-mentioned electrons at the cathode yielding hydrogen. The holes flow to the anode where they are combined with water to produce molecular oxygen in the presence of compound of formula (I).

In a preferred embodiment, the process for the oxidation of water of the invention as defined above, comprises carrying out the alternative (b), the alternative (c), or the alternative (d) of the process of the invention wherein the electrolyte of the second chamber of the two-chamber cell is an aqueous electrolyte; wherein the second chamber further comprises a hydrogen evolution catalyst. In a more preferred embodiment of the process for water oxidation of the first aspect of the invention as defined above, the hydrogen evolution catalyst is included in the cathode, or alternatively, the hydrogen evolution catalyst is coated on the surface of the cathode.

The molecular oxygen and the hydrogen ions are generated in the anode by the presence of the compound of formula (I), and hydrogen gas is evolved from the hydrogen ions at the cathode by the presence of the hydrogen evolution catalyst.

A suitable hydrogen evolution catalyst for the present invention can be any hydrogen evolution catalyst known in the state of the art. In a preferred
embodiment, the hydrogen evolution catalyst is selected from the group consisting of metals such as for example Au, Pt, Ni, Mo, and nanoparticles thereof; metal oxides such as for example NiO, RuO₂, and MoO₂; metal sulfides such as for example MoS₂, and WS₂; metal complexes such as for example cobaloxime, Co[1,4,8,1-tetraazacyclotetradecane]³⁺, [Ni(diphosphine)₂]²⁺, [Ni[1,5-diaza-3,7-diphosphacyclooctane]]²⁺; and hydrogenases. Preferably, the hydrogen evolution catalyst is Pt.

When the process as defined above comprises carrying out the alternative (b), or the alternative (c), or the alternative (d) of the process for the oxidation of water of the first aspect of the invention, the compound of formula (I) as defined above is partially transformed into a brown cobalt oxide comprising phosphate traces which is deposited on the surface of the anode. The third aspect of the invention is the amorphous cobalt oxide obtainable by the alternative (b), or alternative (c), or alternative (d) of the process as defined above. The above-mentioned amorphous cobalt oxide "obtainable by" the process of the invention is stable and efficient for the oxidation of water. Thus, it is also part of the invention the use of the compound obtainable by the above mentioned process as catalyst; preferably, the use as catalyst for the oxidation of water (cf. Examples 12, and 13).

The fourth aspect of the present invention refers to a compound of formula (I) as defined above having the formula [Co₉(OH)₃(H₂O)₆(HPO₄)₂(PW₅O₁₅)₃]NaₓKₙ wherein: x is an integer selected from 1 to 15; and y is an integer selected from 1 to 15; provided that x+y is 16. In a preferred embodiment, the compound of formula (I) is the compound (la) obtainable by the process of Example 1. The process of Example 1 comprises: (a) reacting an aqueous solution of Co(0 0 C-CH₃)₂-4H₂O with Na₂WO₄-2H₂O, and Na₂HPO₄, wherein the pH is 7.6; (b) refluxing the solution obtained in step (a) for 9h, (c) filtering the solution obtained in step (b), and adding K(OOC-CH₃); (d) cooling the solution obtained in step (c) and at room temperature; and stirring for a time comprised of from 1 to 24 hours; and (e) isolating and drying the crystals obtained in step (d); wherein the molar ratio between Co(OOC-CH₃)₂-4H₂O and K(OOC-CH₃) is 1:2.

The fifth aspect of the present invention refers to a compound of formula (I) as defined above having the formula...
[Co9(OH)3(H2O)6(HPO4)2(PW9O34)3]NaxKyCSz wherein: x is an integer selected from 1 to 14; y is an integer selected from 1 to 14; and z is an integer selected from 1 to 14; provided that x+y+z is 16. In a preferred embodiment, the compound of formula (I) of the present invention, is that where z is an integer selected from 6 to 10; preferably, z is 8. In another preferred embodiment, the compound of formula (I) is the compound (lb) obtainable by the step (a) of the process of Example 5. Step (a) of the process of Example 5 comprises: (a) reacting an aqueous solution of the compound of formula (I) obtainable by the process of Example 1 as defined above with an aqueous solution of CsCl at room temperature; until a precipitate was formed and; (b) filtering the precipitate obtained in step (a); and (c) drying the precipitate obtained in step (b).

The structure of compound of formula (lb) supported on amorphous carbon paste was confirmed by the powder X-ray diffraction analysis (XR-PD) (cf. Fig. 12).

As it is shown in comparative Example 3, in comparison with the POM-CO4 catalyst of the state of the art, the compound of formula (la) catalyzes more efficiently the oxidation of water with higher TON regardless the electron scavenging agent used (i.e. a chemical oxidant and a photochemical generated oxidant). When the oxidant is the chemical oxidant NaClO in a 1:100 ratio with respect to the compound of formula (la) and the reaction is carried out in a phosphate buffer at pH = 8, TON is 20.

As it is also shown in Examples 6-8, the compound of formula (lb) supported in a solid support as a heterogeneous water oxidation catalyst show a high catalytic activity for the oxidation of water, being stable under the reaction conditions, more efficient than the known catalysts of the state of the art, and the consumed energy for carrying out the process is lower than the energy needed for other catalysts, even when the oxidation of water is carried out in neutral conditions as it is shown in Examples 9-10.

As it is also shown in Examples 9-10, the compound of formula (lb) supported in a solid support as a heterogeneous water oxidation catalyst maintain the high performance during days without important signs of fatigue.
The majority of the water oxidation catalyst of the state of the art, such as for example POM-Co4 catalyst, is destroyed under the turnover conditions after several hours. Nevertheless, when the compound of formula (I) of the present invention is used as a catalyst for water oxidation, the reaction stops by the absence of the electron scavenging agent but not for the destruction of the compound of formula (I). Thus, the compound of formula (I) of the present invention is advantageous because it is stable, and more robust and soluble than POM-Co4 known in the state of the art at the turnover conditions, allowing a higher oxygen evolution.

It is also part of the invention a process for preparing the compound of formula (I) as defined above comprising:

- mixing $\text{A}_2\text{M}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$, and $\text{A}_x\text{H}_{(6-x)}\text{PO}_4$ and adjusting the pH between 6 and 9 with an acid;
- adding to the mixture obtained in step (a) a solution of $\text{M(OOC-CH}_3\text{)}\text{2-4H}_2\text{O}$ in water, and heating;
- filtering the mixture obtained in step (b), and adding solid $\text{A(OOC-CH}_3\text{)}$;
- cooling the mixture obtained in step (c) down to room temperature; and
- isolating the compound of formula (I);

wherein: $x$ is an integer of from 1 and 2; and A, M and M' are as defined above.

In a preferred embodiment, the acid used in step (a) of the process for preparing the compound of formula (I) is selected from the group consisting of acetic acid, formic acid, phosphoric acid, and hydrochloric acid. Preferably, the acid is acetic acid.

In another preferred embodiment, the filtration of the mixture obtained in step (b) is a hot filtration.

In another preferred embodiment of the process for preparing the compound of formula (I), A is Na, M is Co, M' is W and $x$ is 2.
In a preferred embodiment, the pH of the reaction mixture of step (a) is of between 6 and 9. In a preferred embodiment, the pH of the mixture of step (a) is about 7.5.

In a preferred embodiment, the mixture of step (b) is heated at a reflux temperature of the solvent.

In another preferred embodiment, the mixture of step (b) is heated for 1 to 24h. In a more preferred embodiment, the mixture in step (b) is heated for 6 to 9 h.

When the compound of formula (I) is in form of a solid-supported catalyst, then the process for the preparation of the compound of formula (I) as defined above further comprises mixing the compound of formula obtained with the solid support. The solid supported catalyst thus obtained can be introduced inside a commercially available electrode (cf. Example 5).

The compound of formula (I) can be used in a variety of devices. Therefore, it is also part of the invention a device comprising a compound of formula (I) of the present invention. In a more preferred embodiment, the device comprises a compound of formula (I) of the present invention, and an electron scavenging agent.

In a preferred embodiment, the device is a cell. The cell comprises an electrolyte, a cathode, and an anode. In a more preferred embodiment, the cell is an electrolytic cell. In another more preferred embodiment, the cell is a galvanic cell. Preferably, the cell is a photoelectrolytic cell.

As it was mentioned above, the hydrogen ions generated by the water oxidation reaction of the present invention can be transformed into hydrogen gas by methods known in the state of the art. Thus, the splitting of water is completed. The process for the hydrogen evolution can be carried out in the presence of a hydrogen evolution catalyst. Thus, in a preferred embodiment, the device as defined above further comprises a hydrogen evolution catalyst.

The compound of formula (I) can be provided as a kit. Therefore, it is also part of the invention a kit comprising a compound of formula (I). In a more
preferred embodiment, the kit as defined above further comprises an electron scavenging agent. The compound of formula (I) present in the kit of the present invention can be incorporated into one of the devices of the present invention for water oxidation as mentioned above.

Throughout the description and claims the word "comprises" and variations of the word, are not intended to exclude other technical features, additives, components or steps. Additional objects, advantages and features of the invention will become apparent to those skilled in the art upon examination of the description or may be learned by practice of the invention. The following examples and drawings are provided by way of illustration, and they are not intended to be limiting of the present invention. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments described herein.

EXAMPLES

Example 1: Preparation of $[\text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_4(\text{HPO}_4)_2(\text{PW}_{34}\text{O}_{112})_3]\text{Na}_5\text{K}_4\text{POM-Co}_9$; (Ia)

A solution of Co(OOC-CH$_3$)$_2$$\cdot$4H$_2$O (8 g, 32 mmol) in 30 mL of water was added to an aqueous solution of Na$_2$WO$_4$$\cdot$2H$_2$O (16.5 g, 50 mmol), and Na$_2$HPO$_4$ (0.78 g, 5.5 mmol) whose pH was previously adjusted to 7.6 with acetic acid. The resulting red solution was refluxed for 9 h. After that time the resulting mixture was hot filtered, and 5 g of solid K(OOC-CH$_3$)$_2$ was added. The resulting solution was allowed to cool at room temperature. After several hours small pink needle-shaped crystals of the compound of formula (I) were isolated by filtration, and dried under vacuum to yield 8 g of compound of formula (Ia) (40%). The obtained crystals were suitable for X-ray crystallographic analysis and found to be of compound of formula (Ia). (cf. Fig-1).

Reference Example 2: Preparation of $r\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_4\text{O}_{34})_2\cdot10\cdot\text{iPOM-Co}_4$.

POM-Co4 was prepared following the procedure disclosed in Weakley, T. J. R., "18-Tungstotetracobaltato(II)diphosphate and related anions. A novel structural class of heteropolyanions". *J. Chem. Soc. Chem. Commun.*, 1973,
Comparative Example 3: Water oxidation using NaClO as chemical oxidant

Results of the measurement of the oxygen evolution in the catalytic conditions defined below are shown in Table 1, and Table 2. The oxygen evolution profile is shown in Fig. 2-7.

The determination of TON and TOF values were measured by manometry and gas chromatography.

(A) Manometric Methodology

Manometric measurements:
Gas evolution profile was monitored by a Testo 521 manometer, with an internal differential pressure sensor from 0 to 100 hPa and accuracy within 0.2% of the measurement.

Equipment:
- One manometer’s port was connected to a thermostated vessel for the on-line monitoring of the headspace pressure above the catalysis reaction, and
- The other manometer’s port was connected to a thermostated vessel containing the same solvent and headspace volume as the sample vial.

Methodology:
- The water oxidation catalyst dissolved in phosphate buffer (1.8 ml.) at pH 8.0 was introduced in a vessel, and the pressure was stabilized at atmospheric pressure. Then, a solution of NaClO in phosphate buffer (0.2 ml.) was added to the initial solution. The resulting mixture was thermostated at 25°C. This experiment was performed for different concentrations of catalyst and NaClO.

Calibration of the method was carried out employing the same procedure as described above, filling the vessel water instead of the reaction mixture. A calibration slope was obtained by additions of different quantities of oxygen (0, 5, 10, 20 and 30 μl of O2) in the headspace of the reaction flask. After each addition, gas and aqueous phase were stirred until equilibria. The built-in internal pressure data were correlated with the amount of oxygen added. The
slope from the integrated data points was employed for the quantification of oxygen in the catalysis experiments carried out.

Table 1. Results from the water oxidation catalyzed by POM-Co9 and POM-Co4, employing NaClO as oxidant, in 1M sodium phosphate buffer solutions at the different pH and measured by manometry at 25°C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NaClO (mM)</th>
<th>pH</th>
<th>T(i) - T(i) (h)</th>
<th>TON (c)</th>
<th>TOF (h⁻¹) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM-Co9 (la)</td>
<td>1.0</td>
<td>100</td>
<td>7.0</td>
<td>0.0 – 1.7</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>100</td>
<td>8.0</td>
<td>0.0 – 1.7</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>100</td>
<td>9.0</td>
<td>0.0 – 1.1</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>100</td>
<td>9.0</td>
<td>0.0 – 1.0</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1000</td>
<td>8.0</td>
<td>0.0 – 3.5</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3260</td>
<td>8.0</td>
<td>0.0 – 1.4</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1000(x3)</td>
<td>8.0</td>
<td>0.0 – 2.5</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>32600</td>
<td>8.0</td>
<td>0.0 – 5.5</td>
<td>410</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>32600</td>
<td>8.0</td>
<td>0.0 – 1.6</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>32600</td>
<td>8.0</td>
<td>1.6 – 3.0</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>32600</td>
<td>8.0</td>
<td>3.0 – 4.5</td>
<td>217</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>32600</td>
<td>8.0</td>
<td>4.5 – 6.0</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>32600</td>
<td>8.0</td>
<td>6.0 – 7.0</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>32600</td>
<td>8.0</td>
<td>0.0 – 84.0</td>
<td>255</td>
</tr>
<tr>
<td></td>
<td>0.008</td>
<td>36200</td>
<td>84.0 – 108.0</td>
<td>215</td>
<td>468</td>
</tr>
<tr>
<td></td>
<td>0.006</td>
<td>36200</td>
<td>108.0 – 131.0</td>
<td>180</td>
<td>358</td>
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<tr>
<td></td>
<td>0.005</td>
<td>36200</td>
<td>131.0 – 137.0</td>
<td>173</td>
<td>689</td>
</tr>
<tr>
<td>POM-Co4</td>
<td>1.0</td>
<td>100</td>
<td>8.0</td>
<td>0.0 – 1.2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1000</td>
<td>8.0</td>
<td>0.0 – 1.8</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1000(x3)</td>
<td>8.0</td>
<td>0.0 – 1.8</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.8 – 5.8</td>
<td>4</td>
</tr>
</tbody>
</table>

(a) Experiment carried out in the presence of 1.0mM of 2,2’-bipyridyl (bpy) as a poisoning agent;
(b) t(i) - t(i): Range of time for obtaining the maximum oxygen turnover number;
(c) TON refers to the maximum oxygen turnover number (mol of O₂/mol of catalyst); and
(d) TOF refers to the maximum turnover frequency (TON/h) calculated as the first derivate of the TON vs time.

(B) Gas Chromatography (GC) methodology

Equipment:
Oxygen content was determined by using a 6890N GC Agilent with a thermal conductivity detector.
Methodology:
The catalyst was introduced in a 10 mL round-bottom flask and it was extensively degassed under cycles of vacuum and nitrogen for 30 minutes. Then, the catalyst was dissolved in 9 mL of degassed phosphate buffered solution at pH = 8.0, and 1 mL of a degassed NaClO solution was added in order to start the catalysis. This experiment was performed for different concentrations of catalyst and NaClO, as shown in Table 2.

200 µL samples from the generated gas phase in the reaction flask headspace were taken with a 250 µL Hamilton gas-tight syringe and immediately injected into the instrument for analysis.

Calibration of the method was carried out employing the same procedure as described above, using water instead of the reaction mixture. A calibration slope was obtained by additions of different quantities of oxygen (0, 5, 10, 20 and 30 µmol of O₂) in the headspace of the reaction flask. After each addition, gas and aqueous phase were stirred until equilibria. The integrated data peak was correlated with the amount of oxygen added. The slope from the integrated data points was employed for the quantification of oxygen in the catalysis experiments carried out.

Table 2. Results from the water oxidation catalyzed by POM-Co9 and POM-Co4, employing NaClO as oxidant, in 1M sodium phosphate buffer solutions at pH=8 and measured by gas chromatography.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (mM)</th>
<th>NaClO (mM)</th>
<th>pH</th>
<th>t₂ – t₁ (h)</th>
<th>TON (c)</th>
<th>TOF (h⁻¹) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM-Co9</td>
<td>1.0</td>
<td>100</td>
<td>8.0</td>
<td>0.0 – 6.1</td>
<td>23</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1000</td>
<td>8.0</td>
<td>0.0 – 1.9</td>
<td>72</td>
<td>49</td>
</tr>
<tr>
<td>POM-Co4</td>
<td>1.0</td>
<td>100</td>
<td>8.0</td>
<td>0.0 – 5.0</td>
<td>3</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>1000</td>
<td>8.0</td>
<td>0.0 – 4.0</td>
<td>9</td>
<td>3</td>
</tr>
</tbody>
</table>

(b) Range of time for obtaining the maximum oxygen turnover number; (c) the maximum oxygen turnover number (mol of O₂/mol of catalyst); and (d) the maximum turnover frequency (TON/h) calculated from the final TON divided by the final time.

The above results of Table 1, and Table 2 show that in comparison with POM-Co4 known in the state of the art which contains a Co₄O₄ core
stabilized by oxidatively and hydrolytically stable ligands, POM-Co9 of formula (la) of the present invention generates higher number of moles of oxygen per mol of catalyst (TON) and at a higher rate (TOF), wherein different molar ratios between the catalyst and the oxidant are tested even when the pH is of between 7 and 9.

The above results of Table 1 also show that:

1. The efficiency of POM-Co9 of formula (I) in the oxygen evolution is directly dependent of the molar ratio between POM-Co9 and the chemical oxidant used as electron scavenging agent. A maximum TON of 400 is obtained after 3 hours using a ratio between POM-Co9 of formula (la) and the chemical oxidant (CIO⁻) of 1:30000 ([([la]):[CIO⁻]=0.01:300)];

2. Once the catalysis of water oxidation has finished, a supplementary addition of an additional amount of the chemical oxidant allows for the re-starting of the water oxidation catalysis in the presence of POM-Co9 of formula (la). Additional oxidant can be added after a few hours, or even after days. The catalysis compound of formula (la) remains active, thus maintaining consistent TON and TOF, without lowering its activity;

3. The process for the oxidation of water of the present invention depends on the amount of the electron scavenging agent but not by the inactivation or destruction of the compound of formula (I) of the present invention. Thus, the electron scavenging agent can be considered as the limiting reagent. The robustness of the compound of formula (la) is also demonstrated by the fact that it can be recovered from solution after the catalytic procedure as single crystal; and

4. Even when a poisoning agent (i.e. bpy) is added to the reaction mixture as an inhibitor of the water oxidation, through the possible decomposition of the POM-Co9 by formation of simple cobalt salts (i.e. CoCl₂), and in the presence of the compound of formula (la) of the present invention, just a small decrease of the performance is observed. It demonstrates that the compound of formula (la) is indeed responsible for the catalytic activity.

Example 4: Water electrolysis by applying an external oxidation potential
The procedure for electrocatalytic water oxidation and the measurement of the oxygen evolution was carried out with a three-electrode cell: two platinum electrodes for the oxidation process, carried out on the anode, and the reduction process, carried out on the cathode; and one Ag/AgCl reference electrode to determine the voltage difference.

Water is oxidized at the anode by applying an electrical power source to a phosphate buffer solution (pH = 8) with a 50mM concentration of POM-Co9 (Ia) or POM-Co4 in contact with the three electrodes.

The electrical current measured in mA between 0.8 and 1.3 V corresponds to the electrons removed from water to generate molecular oxygen, and therefore, they are directly related to the amount of oxygen generated, taking into account that four electrons represent one oxygen molecule. The current profiles are shown in Fig. 8.

The results of Example 4 show that the electrical current is higher when the compound of formula (I) of the present invention is present, when compared to POM-Co4, indicating that a higher oxygen evolution is achieved, and at lower voltage differences. This confirms that the POM-CO9 of formula (I) is electrolytically faster, and more efficient than POM-CO4 of the state of the art. It also demonstrates that lower energy is consumed, when the compound of formula (I) is used in the process of the present invention than the energy consumed when the known POM-Co4 catalyst is used.

Example 5: Preparation of a working-electrode with
rCo(gOH)(g(H2O)g(HPO4)2(PWgO%4)3]NaxKvCs_z (Ib) supported on carbon paste [POM-CQ9 (Ib)]

A. Preparation of Na_xK_yCs_z [Co_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_34)_3] (Ia) obtained in Example 1, the solution thus obtained was stirred until a pink precipitate appeared. The precipitate obtained was vacuum filtered employing Nylon paper.
B. Preparation of the supported compound of formula (lb)

The compound of formula (lb) obtained in step (a) (5 mg) were manually mixed with carbon paste (40 mg) using an agate pestle and mortar. The obtained solid corresponds to the compound of formula (lb) supported on carbon paste, which was submitted to powder X-Ray diffraction (cf. Fig. 12).

C. Preparation of the working electrode

The supported compound of formula (lb) was introduced inside of a commercially available carbon paste electrode.

**Example 6. Catalytic activity of compound of formula (lb) supported in a solid support (Cyclic voltammetry)**

Cyclic voltammograms were collected with a Bio-Logic SAS SP-150 potentiostat, in a cell equipped with a Pt wire counter electrode, a Ag/AgCl (NaCl 3 M) reference electrode, and a working electrode prepared according to example 5 containing 40 mg of the supported compound of formula (lb). The cyclic voltammetry was carried out in 20 ml of a phosphate buffered solution at pH = 7.0 inside a one-pot-cell. The electrical current measured in mA between -0.5 and 1.5 V corresponds to the electrons removed from water to generate molecular oxygen and, therefore, they are directly related to the amount of oxygen generated, taking into account that four electrons represent one oxygen molecule. The current profiles are shown in Fig. 9.

The results of Example 6 show that a water oxidation wave appears above 0.9 V vs Ag/AgCl 3 M reference electrode, confirming the catalytic activity of the compound of formula (lb) supported in a solid support as a heterogeneous water oxidation catalyst.

**Example 7. Stability Test of the working-electrode of Example 5**

In a two-chamber H-cell with continuous stirring, 20 ml of a phosphate buffered solution at pH = 7.0 were added inside of each chamber, placing in
one of the chambers the counter-electrode (Pt mesh) and in the other chamber the reference-electrode (Ag/AgCl 3 M) and the working-electrode comprising 40 mg of the compound of formula (lb) supported in the solid support obtained in Example 5. The intensity of the generated current was measured when a potential of 1.10 V vs Ag/AgCl 3 M reference electrode was applied for 8 hours (cf. Fig. 10).

The results of Example 7 show that the intensity of the generated current is stable and constant during the tested period, and demonstrates the high stability of the compound of formula (lb) when used as a supported catalyst inserted into a working electrode.

**Example 8. Tafel plots**

In a two-chamber H-cell with continuous stirring, 20 ml of a phosphate buffered solution at pH = 7.0 were added inside of each chamber, placing in one of the chambers the counter-electrode (Pt mesh) and in the other chamber the reference-electrode (Ag/AgCl 3 M) and the working-electrode comprising 40 mg of the compound of formula (lb) supported in the solid support obtained in Example 5. The intensity of the generated current was measured when a potential of 1.10 V vs Ag/AgCl 3 M reference electrode was applied for 8 hours (cf. Fig. 10). Uncompensated resistance was corrected by the potentiostat software.

The stable current density (/) was measured after 10 minutes of applying a given potential in the 0.80-1.20 V range, increasing 0.02 V each step. The obtained data follows a linear trend that corresponds to a Tafel plot, where: Overpotential = A + B log(i)

According to the fitting of the experimental data, we can conclude that the overpotential needed for reaching an intensity (i) = 1 mA/cm² would be about 500 mV.

The results of Example 7 show that the potentials needed to reach high water oxidation rates are comparable to those when using known catalyst of the state of the art.
Comparative Example 9: Water electrolysis by applying an external oxidation potential

Results of the measurement of the oxygen evolution in the catalytic conditions defined below are shown in Table 3.

The determination of TOF values were measured by molecular oxygen fluorescence.

Equipment:

Bulk water electrolysis was carried out in a two-chamber cell, with a porous frit connecting both chambers. As working and counter electrodes a 20 x 20 mm Pt mesh electrodes (99.9% Pt Goodfellow plain weave mesh, 0.25 mm nominal aperture, 0.06 mm wire diameter, 82 x 82 wires/inch, 65% open area), and a Ag/AgCl (NaCl 3 M) reference electrode included in the anode compartment were used. Oxygen evolution in the gas phase was analyzed with an Ocean Optics NeoFOX oxygen sensing system equipped with a FOXY probe. Hydrogen evolution in the gas phase was determined with a UNISENSE Clark-type hydrogen microsensor with an internal reference electrode and a sensing anode. In all oxygen and hydrogen determination techniques, the set-up was calibrated by addition of known quantities of the corresponding pure gas. Constant pressure was maintained with mineral oil bubblers, connected to each cell compartment. All potentials were measured and reported versus a Ag/AgCl (NaCl 3 M) reference electrode.

Methodology:

An amount of solid POM-Co4, (or POM-Co9 (Ia)) was added in the anode compartment of the two-chamber cell as defined above, having 10 ml of a NaPi buffer solution (50 mM) with KNO3 (1 M) as electrolyte in each chamber. Final concentration of POM-Co4, or POM-Co9 (Ia) was as indicated in Table 3. Values of TOF were reported at 1.10 V vs a Ag/AgCl (NaCl 3 M) reference electrode with a scan rate of 5 mV.s\(^{-1}\).

The current rapidly reached over 1 mA, and then it decreased down to a stable value that remained constant for hours. When the current was stable a
potential was applied corresponding to an overpotential of 80 mV when compared with the thermodynamic value of water oxidation potential.

Table 3. Results from the water oxidation catalyzed by POM-Co9 (I) and POM-Co4.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Concentration (mM)</th>
<th>pH</th>
<th>TOF_i (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM-Co9</td>
<td>5x10^{-1}</td>
<td>8</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>5x10^{-2}</td>
<td>7</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>5x10^{-1}</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>POM-Co4</td>
<td>5x10^{-1}</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5x10^{-2}</td>
<td>7</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>5x10^{-1}</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>

The above results of Table 3 show that in comparison with the process of water oxidation involving POM-Co4 known in the state of the art, the process of water oxidation involving POM-Co9 of formula (Ia) of the present invention is slightly faster at pH=7 as it is observed by the values of TOF. In addition, values of TOF of POM-Co9 are higher than the values of POM-Co4 when a neutral pH (pH=7) is used. It is advantageous, because lower energy is consumed when the compound of formula (I) is used in the process of the present invention even when the oxidation of water is carried out in neutral conditions.

Example 10: Stability test

Results of the measurement of the oxygen evolution are shown in Table 4.

The determination of TON values were measured by molecular oxygen fluorescence following the method of Example 9, and the content of POM-Co9 (Ia) after cycle was measured through UV-vis spectroscopy.

Equipment:
The same equipment as in Comparative Example 9 is used.

Methodology:

The reaction of oxidation comprises successive 2-5 hour bulk electrolysis cycles changing the Pt mesh electrode in the anode for a new clean one. Each cycle was carried out in a different day. 0.01 mol of POM-CO9 (la) (1 mM) was added in 10 ml of a NaPi buffer (50 mM) with a pH=7 solution containing KNO3 (1 M) as electrolyte and a voltage of 1.10 V vs a Ag/AgCl (NaCl 3 M) was applied.

Table 4. Results from the water oxidation catalyzed of successive catalytic bulk electrolysis.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Catalyst (%) (a)</th>
<th>Cycle time (h)</th>
<th>µmol O2</th>
<th>Total time (h)</th>
<th>Total µmol O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>3</td>
<td>19</td>
<td>3</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>85</td>
<td>5</td>
<td>36</td>
<td>8</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>79</td>
<td>4</td>
<td>21</td>
<td>12</td>
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<tr>
<td>4</td>
<td>73</td>
<td>4</td>
<td>53</td>
<td>16</td>
<td>129</td>
</tr>
<tr>
<td>5</td>
<td>66</td>
<td>2</td>
<td>33</td>
<td>18</td>
<td>162</td>
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<td>4</td>
<td>36</td>
<td>22</td>
<td>198</td>
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<tr>
<td>7</td>
<td>57</td>
<td>4</td>
<td>38</td>
<td>26</td>
<td>236</td>
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<tr>
<td>8</td>
<td>48</td>
<td>4</td>
<td>59</td>
<td>30</td>
<td>295</td>
</tr>
</tbody>
</table>

(a) Percentage of POM-Co9 (la) remaining in solution respect to the initial one, calculated by the absorbance at λ = 538 nm.

The above results of Table 4 show that the POM-Co9(la) is highly active at neutral pH, and under more diluted conditions reaching over 200 turns per second (TOF> 700,000 h\(^{-1}\)). It is advantageous because the compounds of formula (I) of the present invention are active homogeneous catalyst for the oxidation of water at low overpotentials, maintaining the high performance during days without important signs of fatigue.

Example 11. Water electrolysis by applying an external oxidation potential in the presence of the compound of formula (la) and a 2,2'-bipyridyl compound.
The procedure for electrocatalytic water oxidation and the measurement of the oxygen evolution was carried out with a three-electrode cell: one fluorine doped tin oxide (FTP) as anode for the oxidation process; a platinum mesh electrode as cathode for the reduction process; and one Ag/AgCl reference electrode to determine the voltage difference.

Water is oxidized at the anode by applying an electrical power source to a phosphate buffer solution (pH = 7) with a 1 mM concentration of POM-Co9 (Ia) and with a 1.4 mM concentration of 2,2'-bipyridyl.

The electrical current measured in mA at a constant voltage of 1.2 V corresponds to the electrons removed from water to generate molecular oxygen, and therefore, they are directly related to the amount of oxygen generated, taking into account that four electrons represent one oxygen molecule. The current profiles are shown in Fig. 13.

The results of Example 11 show that the electrical current is higher when compared to the blank experiments in the absence of the catalyst indicating its catalytic activity for water oxidation. This confirms that the POM-CO9 of formula (I) is electrolytically fast, efficient and stable for long periods of time. In the absence of catalyst, the current profile of the as-used anode after catalytic water oxidation shows the same features than the initial blank; and the oxygen evolution in the absence of the catalyst before and after the catalytic water electrolysis is negligible and comparable. This demonstrates that the POM-CO9 of formula (I) has activity as water oxidation catalyst.

Example 12. Preparation of an amorphous cobalt oxide film on a working electrode from a solution of a compound of formula (la).

The procedure for electrodeposition of an amorphous cobalt oxide was carried out with a three-electrode cell: one fluorine doped tin oxide (FTP) as anode for the oxidation process and deposition of the cobalt oxide; a platinum mesh electrode as cathode for the reduction process; and one Ag/AgCl reference electrode to determine the voltage difference.
A cobalt oxide film is deposited at the anode by applying an electrical power source to a 20 ml phosphate buffer solution (pH = 7) with a 1 mM concentration of POM-Co9 (Ia). The film can be prepared by maintaining a constant voltage in 0.85-1.3 V vs Ag/AgCl for 20 minutes.

Example 13: Water electrolysis by applying an external oxidation potential using the cobalt oxide film of Example 12.

The procedure for electrocatalytic water oxidation and the measurement of the oxygen evolution was carried out with a three-electrode cell: one fluorine doped tin oxide (FTP) modified with a cobalt oxide film prepared following the process of Example 12 as anode for the oxidation process; a platinum mesh electrode as cathode for the reduction process, and one Ag/AgCl reference electrode to determine the voltage difference.

Water is oxidized at the anode by applying an electrical power source to a phosphate buffer solution (pH = 7). The electrical current measured in mA at a constant voltage of 1.2 V corresponds to the electrons removed from water to generate molecular oxygen, and therefore, they are directly related to the amount of oxygen generated, taking into account that four electrons represent one oxygen molecule. The current profiles are shown in Fig. 14.

The results of Example 13 show that the electrical current is higher when the cobalt oxide film prepared from compound of formula (I) of the present invention is present, when compared to the blank experiments in the absence of the catalyst indicating its catalytic activity for water oxidation. This confirms that the POM-CO9 of formula (I) is a convenient precursor for the formation of amorphous cobalt oxide films able to catalyze the oxidation of water. It is advantageous because the process as defined above for the preparation of the amorphous cobalt oxide of the invention in example 12 requires less time and therefore, it requires less energy consumption. Additionally, the amorphous cobalt oxide thus obtained is comparable to the ones described in the state of the art.
REFERENCES CITED IN THE APPLICATION

- International patent application number WO2010107919.
CLAIMS

1. A process for water oxidation to obtain molecular oxygen and hydrogen ions which is carried out in the presence of a catalytically effective amount of a compound of formula (I),

\[ [\text{M}_9\text{(OH)}_3\text{(H}_2\text{O)}_6\text{(HPO}_4\text{)}_2\text{(L)}_3][\text{A}]_n \]

wherein:

- M is selected from the group consisting of Co, Mn, and Fe;
- L is selected from the ligand of formula \( \text{YM}'_9\text{O}_3\text{O}_3 \) and \( \text{YM}'_2\text{O}_5\text{O}_6 \);
- Y is selected from the group consisting of P, Si, Ge, and As;
- \( \text{M}' \) is selected from the group consisting of W, Mo, and V;
- A is a cation selected from the group consisting of Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\), Ca\(^{2+}\), Ba\(^{2+}\), Mg\(^{2+}\), and mixture thereof; and
- n is an integer selected from 8 and 16, being the sum of positive charges of \( \text{A}_n \) equal to 16.

2. The process according to claim 1, wherein M is Co.

3. The process according to any of the claims 1-2, wherein Y is P.

4. The process according to any of the claims 1-3, wherein \( \text{M}' \) is W.

5. The process according to any of the claims 1-4, wherein the compound of formula (I) is \([\text{Co}_9\text{(OH)}_3\text{(H}_2\text{O)}_6\text{(HPO}_4\text{)}_2\text{(PW}_9\text{O}_3\text{)}_3]\text{Na}_x6\).

6. The process according to any of the claims 1-4, wherein the compound of formula (I) is \([\text{Co}_9\text{(OH)}_3\text{(H}_2\text{O)}_6\text{(HPO}_4\text{)}_2\text{(PW}_9\text{O}_3\text{)}_3]\text{Na}_x\text{K}_y \) wherein: x is an integer selected from 1 to 15; and y is an integer selected from 1 to 15; provided that x+y is 16.
7. The process according to any of the claims 1-4, wherein the compound of formula (I) is \([\text{Co}_{9}(\text{OH})_{3}(\text{H}_2\text{O})_{6}(\text{HPO}_4)_{2}(\text{PW}_{9}\text{O}_{34})_{3}]\text{Na}_x\text{K}_y\text{CS}_z\) wherein: x is an integer selected from 1 to 14; y is an integer selected from 1 to 14; and z is an integer selected from 1 to 14; provided that \(x+y+z\) is 16.

8. The process according to claim 7, wherein in the compound of formula (I) z is an integer selected from 6 to 10.

9. The process according to any of the claims 1-8, wherein the compound of formula (I) is in form of a solid-supported catalyst, being the compound of formula (I) linked to the solid support by electrostatic forces, wherein the support is selected from the group consisting of metals, metal oxides, graphite, graphene, carbon nanotubes, amorphous carbon, mesoporous silica, mesoporous alumina, mesoporous aluminosilicates, mesoporous metal oxides, and hydrotalcites.

10. The process according to claim 9, wherein the support is selected from the group consisting of graphite, graphene, carbon nanotubes, and amorphous carbon.

11. The process according to any of the claims 1-10, wherein the oxidation of water comprises:

   (a) reacting water with an electron scavenging agent selected from the group consisting of a chemical oxidant, and a photochemically generated oxidant; or alternatively,

   (b) applying an electrical power source to a two-chamber cell, wherein the cell comprises: a first chamber comprising an anode being in contact with an aqueous electrolyte; a second chamber comprising a cathode being in contact with an electrolyte; and a salt bridge connecting the electrolytes of the first and the second chamber; or, alternatively,

   (c) exposing to light irradiation a photo-anode or a photo-cathode in a photo-electrochemical two-chamber cell, wherein the cell comprises: a first chamber comprising an anode or a photo-anode, being in contact with an aqueous electrolyte; a second chamber comprising a cathode or photo-cathode being
in contact with an electrolyte; an electrical connection between the first and
the second electrode; and a salt bridge connecting the electrolytes of the first
and the second chamber; with the proviso that at least one of the two
chambers of the cell comprises a photo-anode or a photo-cathode.

12. The process according to any of the claims 1-10, wherein the oxidation
of water comprises exposing to light irradiation a photovoltaic solar cell, wherein
the photovoltaic cell comprises: an absorbing light material selected from the
group consisting of a semiconductor, a chromophore, and mixture thereof; a
semiconducting material; a cathode; and an anode; being the cathode and the
anode of the photovoltaic cell connected to a two-chamber cell, wherein the
two-chamber cell comprises: a first chamber comprising an anode being in
contact with an aqueous electrolyte; a second chamber comprising a cathode
being in contact with an aqueous electrolyte; and a salt bridge connecting the
electrolytes of the first and the second chamber.

13. The process according to claim 11, wherein the electron scavenging agent
of alternative (a) is a chemical oxidant agent selected from the group
consisting of Cl₂, O₃, NO, N₂O, A'X, H₂O₂, QO₂, Mn₂O₃, RuO₄, OsO₄, TZₙ,
and Ru(L')₃Zₙ wherein:

A' is a cation selected from the group consisting of Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ and
(NH₄)⁺;

X is an anion selected from the group consisting of ClO⁻, ClO₂⁻, NO₂⁻, HSO₅⁻,
BrO⁻, IO⁻, IO₄⁻, MnO₄⁻, CrO₄²⁻, SO₄²⁻, S₂O₅²⁻, Cr₂O₇²⁻, PdCl₆²⁻, IO₆⁵⁻,
[Cu(HIO₆)₂]⁵⁻, [Ag(HIO₆)₂]⁵⁻ and [Au(HIO₆)₂]⁵⁻;

Q is a cation selected from the group consisting of Cr³⁺, Ni⁴⁺, Pd⁴⁺, Pt⁴⁺ and
Pb⁴⁺;

T is a cation selected from the group consisting of Ti³⁺, Cu³⁺, Ag³⁺, Au³⁺, Ce⁴⁺,
Ru³⁺ and Ru⁴⁺;

Z is an anion selected from the group consisting of F⁻, Cl⁻, Br⁻, I⁻, OH⁻, BF₄⁻,
PF₆⁻, NO₃⁻ and ClO₄⁻;
L' is 2,2'-bipyridinyl being the pyridinyl ring unsubstituted or substituted at one or more position by a radical selected from the group consisting of COOR, and P(O)(OR)₂⁻:

R is selected from the group consisting of (CrC₆)alkyl, and monocyclic ring; and

m is an integer selected from 1 to 5, being the sum of positive charges of Aₘ equal to the negative charges of X, and being the sum of the negative charges of Zₘ equal to the positive charges of T.

14. The process according to claim 11, wherein the electron scavenging agent of alternative (a) is an oxidant selected from the group consisting of Ru(L')₃Z₃⁻, photochemically generated from Ru(L')₃Z₂, wherein:

L' is 2,2'-bipyridinyl being the pyridinyl ring unsubstituted or substituted at one or more position by a radical selected from the group consisting of COOR, and P(O)(OR)₂⁻:

Z is an anion selected from the group consisting of F⁻, Cl⁻, Br⁻, I⁻, OH⁻, BF₄⁻, PF₆⁻, NO₃⁻ and ClO₄⁻; and

R is selected from the group consisting of (Ci-C₆)alkyl, and monocyclic ring.

15. The process according to the claim 11 alternative (c) or claim 12, further comprising applying simultaneously an electrical power source to the two-chamber cell.

16. The process according to claim 11 alternative (b), or alternative (c), or claim 12, wherein when the compound of formula (I) is in form of a solid-supported catalyst, then the anode of the first chamber of the two-chamber cell is in physical contact with the solid-supported catalyst.

17. The process according to any of the claims 11 alternative (b), or alternative (c), or claim 12, or claim 15, or claim 16, comprising carrying out the process for the oxidation of water, wherein when the electrolyte of the second chamber of the two-chamber cell is an aqueous electrolyte, then the
process further yields hydrogen.

18. A cobalt oxide obtainable by the process according to any of the claims 11 alternative (b), or alternative (c), or claim 12, or claim 15, or claim 16, or claim 17.

19. A compound of formula (I) having the formula
\[ \text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]NaxKy \]
wherein: \( x \) is an integer selected from 1 to 15; and \( y \) is an integer selected from 1 to 15; provided that \( x+y \) is 16.

20. A compound of formula (I) having the formula
\[ \text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]NaxKyCSz \]
wherein: \( x \) is an integer selected from 1 to 14; \( y \) is an integer selected from 1 to 14; and \( z \) is an integer selected from 1 to 14; provided that \( x+y+z \) is 16.
Fig. 4
Fig. 10
Fig. 14
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J27/188 B01J27/19 B01J27/198 C25B1/04 C01B13/02

ADD.

According to International Patent Classification (IPC) onto both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C01B C01G C25B H01M

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

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

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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- Further documents are listed in the continuation of Box C.
- See patent family annex.

Date of the actual completion of the international search:

21 December 2012

Date of mailing of the international search report:

09/01/2013

Authorized officer:

Besselmann, Sonja

Form PCT/ISA/210 (second sheet) (April 2005)
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<td>T</td>
<td>SARA GOBERNA-FERRON ET AL: &quot;Identification of a Nonanuclear (Co III 9) Polyoxometalate Cluster as a Homogeneous Catalyst for Water Oxidation&quot;, INORGANIC CHEMISTRY, vol. 51, no. 21, 5 November 2012 (2012-11-05), pages 11707-11715, XP055048478, ISSN: 0020-1669, DOI: 10.1021/ic301618h</td>
<td>1-17, 19, 20</td>
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This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:  
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ✗ Claims Nos.: 1o  
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
   see FURTHER INFORMATION sheet PCT/ISA/210

3. □ Claims Nos.:  
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

This International Searching Authority found multiple inventions in this international application, as follows:

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest:  
- The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.
Continuation of Box II.2

Claims Nos.: 18

Present claim 18 relates to a cobalt oxide obtainable by the process according to any of the claims 11, 12, 15, 16, or 17. However, these claims define a process for water oxidation and do not contain any reference to the product of cobalt oxide. Claim 18 is therefore not clear in the sense of Art. 6 PCT. The non-compliance with the substantial provisions is to such an extent that no meaningful search of claim 18 could be carried out at all (Article 17(2) PCT).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examination Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.
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<tr>
<td>WO 2010107919 A</td>
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