SYSTEM AND METHOD FOR PRODUCTION OF HYDROGEN PEROXIDE

BACKGROUND OF THE INVENTION

Annual global H_2O_2 production is 5 million tons, leading to 15 million tons of CO_2 emissions. The industrial thermocatalytic anthraquinone autoxidation (AO) method is the dominant production technology, but it involves high risks of pressurized hydrogen and air input and requires expensive palladium-based catalysts that can reduce anthraquinone to non-reactive molecules. A considerable amount of energy also must be put into the distillation and transportation of H_2O_2.

Accordingly, there is a need for new H_2O_2 production methods.

SUMMARY OF THE INVENTION

The invention provides a system and method of producing hydrogen peroxide. The disclosure provides an electrochemical system and method to produce hydrogen peroxide. The method involves four parts: (1) aqueous electrochemical reduction of a first redox active species, (2) interfacial electron transfer between the first redox active species and a second redox active species having a nonaqueous phase, (3) reduction of a oxygen by the second redox active species to produce H_2O_2, and (4) the extraction of H_2O_2 into water. The system includes an electrochemical cell, a first contactor, a first separator, a second contactor, a second separator, an oxygen source, e.g., a bubbler, and a purifier. The system and method include a first solution o containing the first redox active species, a second solution containing the second redox active species, and a third solution containing the oxygen (e.g., oxygen-containing gas, e.g., O_2 or air). The second solution of is immiscible with the first and third solutions. This system and method can facilitate the electrification and decentralization of industrial H_2O_2 production, reducing the major capital cost associated with the decomposition of anthraquinone molecules and major energy cost associated with concentrating and transporting H_2O_2.

[[Will be incorporated by C+E once the claims are finalized.]]

DEFINITIONS

As used herein, any values provided in a range of values include both the upper and lower bounds, and any values contained within the upper and lower bounds.

By “about” is meant ±10% of a recited value.

By “alkyl” is meant straight chain or branched saturated groups from 1 to 6 carbons. Alkyl groups are exemplified by methyl, ethyl, n- and iso-propyl, n-, sec-, iso- and tert-butyl, neopentyl, and the like, and may be optionally substituted with one or more substituents.

By “alkoxy” is meant a group of formula –OR, wherein R is an alkyl group, as defined herein.

By “alkyl thio” is meant –S-R, where R is an alkyl group, as defined herein.

By “alkyl ester” is meant –COOR, where R is an alkyl group, as defined herein.

By “amino” is meant $–NH_2$. An exemplary ion of amino is $–NH_3^+$.

By “amide” is meant -R(C=O)NR_2, wherein each R is H or alkyl, provided R is alkyl, as defined herein.

By “aryl” is meant an aromatic cyclic group in which the ring atoms are all carbon. Exemplary aryl groups include phenyl, naphthyl, and anthracenyl. Aryl groups may be optionally substituted with one or more substituents.

By “carbocyclyl” is meant a non-aromatic cyclic group in which the ring atoms are all carbon. Exemplary carbocyclyl groups include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl. Carbocyclyl groups may be optionally substituted with one or more substituents.

By “carboxyl” is meant –COOH. An exemplary ion of carboxyl is $–COO^-$.

By “halo” is meant fluoro, chloro, bromo, or iodo.

By “heteroaryl” is meant an aromatic cyclic group in which the ring atoms include at least one carbon and at least one O, N, or S atom, provided that at least three ring atoms are present. Exemplary heteroaryl groups include oxazolyl, isoxazolyl, tetrazolyl, pyridyl, thienyl, furyl, pyrrolyl, imidazolyl, pyrimidinyl, thiazolyl, indolyl, quinolinyl, isoquinolinyl, benzofuryl, benzothienyl, pyrazolyl, pyrazinyl, pyridazinyl, isothiazolyl, benzimidazolyl, benzothiazolyl, benzoxazolyl, oxadiazolyl, thiadiazolyl, and triazolyl**.** Heteroaryl groups may be optionally substituted with one or more substituents.

By “heterocyclyl” is meant a non-aromatic cyclic group in which the ring atoms include at least one carbon and at least one O, N, or S atom, provided that at least three ring atoms are present. Exemplary heterocyclyl groups include epoxide, thiiranyl, aziridinyl, azetidinyl, thietanyl, dioxetanyl, morpholinyl, thiomorpholinyl, piperazinyl, piperidinyl, pyrrolidinyl, tetrahydropyranyl, tetrahydrofuranyl, dihydrofuranyl, tetrahydrothienyl, dihydrothienyl, dihydroindolyl, tetrahydroquinolyl, tetrahydroisoquinolyl, pyranyl, pyrazolinyl, pyrazolidinyl, dihydropyranyl, tetrahydroquinolyl, imidazolinyl, imidazolidinyl, pyrrolinyl, oxazolidinyl, isoxazolidinyl, thiazolidinyl, isothiazolidinyl, dithiazolyl, and 1,3-dioxanyl. Heterocyclyl groups may be optionally substituted with one or more substituents.

By “hydroxyl” is meant –OH. An exemplary ion of hydroxyl is $–O^-$.

By “nitro” is meant $–NO_2$.

By “nitrile” is meant -C≡N.

By “oxo” is meant =O.

By “phosphoryl” is meant $–PO_3H_2$. Exemplary ions of phosphoryl are $–PO_3H^-$ and $-PO_3^{2-}$.

By “phosphonyl” is meant $–PO_3R_2$, wherein each R is H or alkyl, provided at least one R is alkyl, as defined herein. An exemplary ion of phosphonyl is $–PO_3R^-$.

As used herein, a species is “soluble” if it dissolves in the solvent with a solubility of at least 0.001 mol/L. For examples, a species has low solubility if it dissolves in the solvent of interest with a solubility of less than 0.001 mol/L. **[[Please confirm the solubility requirement.]]**[大席1][MJA2]

By “sulfonyl” is meant $–SO_3H$. An exemplary ion of sulfonyl is $–SO_3^-$.

By “thiol” is meant –SH.

As noted, substituents may be optionally substituted with halo, optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$; $-N(R_a)_2$; $-C(=O)R_a$; $-C(=O)OR_a$; $-S(=O)_2R_a$; $-S(=O)_2OR_a$; $-P(=O)R_{a2}$; $-O-P(=O)(OR_a)_2$, or $-P(=O)(OR_a)_2$, or an ion thereof; wherein each R_a is independently H, C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group. Cyclic substituents may also be substituted with C_{1-6} alkyl. In specific embodiments of alloxazines, substituents may include optionally substituted with halo, optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; $-NO_2$; $-OR_a$; $-N(R_a)_2$; $-C(=O)R_a$; $-C(=O)OR_a$; $-S(=O)_2R_a$; $-S(=O)_2OR_a$; $-P(=O)R_{a2}$; $-O-P(=O)(OR_a)_2$, or $-P(=O)(OR_a)_2$, or an ion thereof; wherein each R_a is independently H, C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group, and cyclic substituents may also be substituted with C_{1-6} alkyl. In specific embodiments of quinones, alkyl groups may be optionally substituted with one, two, three, or, in the case of alkyl groups of two carbons or more, four substituents independently selected from the group consisting of halo, hydroxyl, C_{1-6} alkoxy, SO_3H, amino, nitro, carboxyl, phosphoryl, phosphonyl, thiol, C_{1-6} alkyl ester, optionally substituted C_{1-6} alkyl thio, and oxo, or an ion thereof.

Exemplary ions of substituent groups are as follows: an exemplary ion of hydroxyl is $–O^-$; an exemplary ion of –COOH is $–COO^-$; exemplary ions of $–PO_3H_2$ are $–PO_3H^-$ and $-PO_3^{2-}$; an exemplary ion of $–PO_3HR_a$ is $–PO_3R_a^-$, where R_a is not H; exemplary ions of $–PO_4H_2$ are $–PO_4H^-$ and $–PO_4^{2-}$; and an exemplary ion of $–SO_3H$ is $–SO_3^-$.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGs. 1A and 1B show mechanisms for production of hydrogen peroxide. FIG. 1A shows the mechanism for industrial thermocatalytic anthraquinone autoxidation for production of hydrogen peroxide. FIG. 1B shows an electrochemical method for production of hydrogen peroxide of the disclosure including the aqueous phase solution (A), nonaqueous phase solution (B), and aqueous phase extraction solution (C). M is the first redox active species, and N is the second redox active species. M_{red} and N_{red} represents the reduced forms of the first and second redox active species.

FIG. 2 shows an example of the electrochemical method for electrolyte-free production of hydrogen peroxide. The first redox active species is 2,6-bis(3-phosphonopropyl-1-oxy)anthraquinone (DPPEAQ) in an aqueous buffer solution (pH = 7). The second redox active species is ethylanthraquinone (EtAQ) in a 3:2 toluene:decanol nonaqueous (oil) solution. Electrochemically reduced DPPEAQ reduces EtAQ through the aqueous-nonaqueous solution interface. Reduced EtAQ reacts with oxygen (O_2), forming hydrogen peroxide (H_2O_2) that is extracted by an aqueous extraction solution.

FIG. 3 shows a system 3000 for the electrochemical method for electrolyte-free production of hydrogen peroxide of the disclosure. The system includes: electrochemical cell 3001 to reduce a first redox active species; first contactor 3002 to contact a first solution containing the first redox active species and a second solution of a second redox active species; first separator 3003 to separate the first solution from the second solution; second contactor 3004 to contact the second solution with a third solution; and second separator 3005 to separate the second solution from the third solution..

FIG. 4 shows the quasi-steady state production of hydrogen peroxide using the electrochemical method and system. The aqueous extraction solution was cycled to accumulate the concentration of H_2O_2. The Coulombic efficiency was approximately 80% after the system reached steady state.

DETAILED DESCRIPTION

The present disclosure features a method and system for electrochemically producing hydrogen peroxide.

Conventional hydrogen peroxide production uses Pd catalysts and hydrogen gas to reduce quinones (e.g., anthraquinone or naphthoquinone) into dihydroquinones (e.g., dihydroanthraquinone or dihydronaphthoquinone) in nonaqueous solutions. The reduced quinones react with oxygen, producing oxidized quinones and hydrogen peroxide. The produced hydrogen peroxide can be extracted by water from the nonaqueous solution, producing H_2O_2 solution (see, e.g., FIG. 1A). The solution is further purified by heavy aromatic mixtures to remove nonaqueous residue and concentrated for shipping. This process has four drawbacks: (1) the usage of Pd; (2) the usage of hydrogen gas; (3) over-reduction reaction of quinones on Pd catalysts, forming inactive quinones; (4) energy cost for concentrating and shipping. The disclosure provides an electrochemical method to reduce nonaqueous quinones to avoid these four, existing disadvantages.

The invention employs the electrochemical reduction and oxidation of redox active species to produce hydrogen peroxide. A first redox active species that has a low solubility in a nonaqueous solution and a second redox active species that a low solubility in an aqueous solution are used to produce hydrogen peroxide without the need for electrolyte (see, e.g., FIGs. 1A and 1B). An exemplary embodiment of the mechanism is shown in FIG. 2. Briefly, the method includes a first redox active species in aqueous phase that is reduced. The reduced form of the first redox active species in aqueous phase contacts and reacts with the second redox active species that is dissolved in a nonaqueous solution, oxidizing the first redox active species and reducing the second redox active species. The reduced form

of the second redox active species then reacts with oxygen, oxidizing the second redox active species and producing hydrogen peroxide that can be extracted by an aqueous solution (e.g., water). This method involves three phases: one aqueous solution for the first redox active species, one nonaqueous solution for the second redox active species, and one aqueous solution for hydrogen peroxide extraction. The method allows for electron transfer from the first redox active species to the second redox active species by contacting immiscible solutions and without transfer of the redox active species between the aqueous and nonaqueous phases. Thus, the oxidized and reduced forms of the first redox active species have a low solubility (< 0.001 mol/L) in the nonaqueous solution, and the oxidized and reduced forms of the second redox active species have a low solubility (< 0.001 mol/L) in the two aqueous solutions. The nonaqueous solution has a low solubility (< 0.001 mol/L) in the two aqueous solutions. Because hydrogen peroxide is extracted from a non-aqueous phase, the hydrogen peroxide may be extracted without contaminating electrolytes from the electrochemical processes employed in the methods and systems.

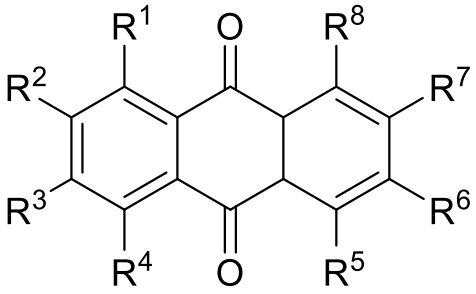
The invention also provides a system to produce hydrogen peroxide. Briefly, the system includes an electrochemical cell, a first contactor, a first separator, a second contactor, a second separator, an oxygen source, e.g., a bubbler, and a purifier. The system further includes a first, aqueous solution a first redox active species, a second, non-aqueous solution containing a second redox active species, and a third, aqueous solution oxygen for extraction of hydrogen peroxide. oxygen
The invention described herein, which utilizes two redox active species in different solution phases, produces hydrogen peroxide with a 100-fold higher efficiency than previous methods.

Redox Active Species

The present invention includes two, different redox active species. A first redox active species is included in a first, aqueous solution. A second redox active species is included in a second, non-aqueous solution. The potential of the first redox active species is sufficient to reduce the second redox active species.

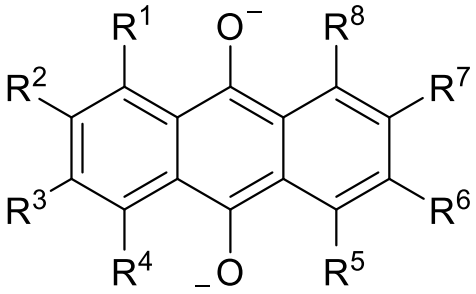
The first redox active species may be reduced in an electrochemical cell. Suitable redox active species include organic redox active species (e.g., anthraquinones, phenazines, phenoxazines, naphthoquinones, fluorenones, and redox states thereof), inorganic redox active species such as chromium or vanadium, e.g., V^{2+}, V^{3+}~~, VO^{2+}, and VO_2^+~~, and metalorganic redox active species such as ~~ferrocene/ferrocenium or ferricyanide/ferrocyanide~~CrPDTA. **[[Inventors: Please adjust the list as appropriate.]]** [大席3]Derivatives of suitable redox active species may include substitution groups to increase or decrease water solubility. Redox cores include, but are not limited to, para or ortho benzoquinone, naphthoquinone, anthraquinone, phenanthrenequinone, fluorenone, benzophenone, anthrone, xanthone, thioxanthone, acridone, phenazine, viologen, alloxazine, isoalloxazine, azobenzene, phthalimide, phenothiazine, naphthalimide, pyromellitic diimide, 1,4,5,8-naphthalenetetracarbodiimide, or benzo(c)cinnoline.

Suitable redox active species includes an anthraquinone or a redox state thereof. In some embodiments, the first state of the anthraquinone is of formula (Ia).



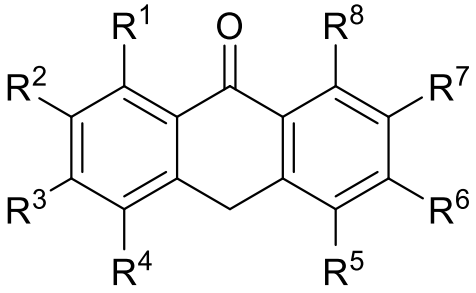
(Ia), or a salt, protonated form, or tautomer thereof.

In some embodiments, the second state of the anthraquinone is an anthrahydroquinone, e.g., an anthrahydroquinone of formula (Ib)



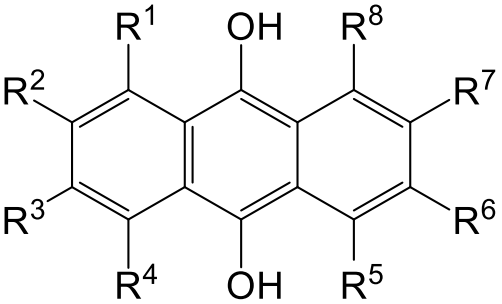
(Ib), or a salt, protonated form, or tautomer thereof.

In some embodiments, the third state of the anthraquinone is an anthrahydroquinone, e.g., an anthrahydroquinone of formula (Ic)



(Ic), or a salt, protonated form, or tautomer thereof.

In some embodiments, a suitable redox active species is the reduced form of an anthraquinone, a hydroquinone, e.g., a hydroquinone of formula (Id)



(Id), or a salt, protonated form, or tautomer thereof.

In any of formulas (Ia), (Ib), (Ic), or (Id) each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H; halo; optionally substituted C_{1-6} alkyl; oxo; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$ (e.g., hydroxyl or C_{1-6} alkoxy); $-SR_a$ (e.g., thiol or C_{1-6} alkyl thio); $-N(R_a)_2$ (e.g., amino); $-C(=O)R_a$; $-C(=O)OR_a$ (e.g., carboxyl); $-S(=O)_2R_a$; $-S(=O)_2OR_a$ (e.g., SO_3H); $-P(=O)R_{a2}$; and $-P(=O)(OR_a)_2$ (e.g., phosphonyl or phosphoryl); or any two adjacent groups selected from R^1, R^2, R^3, and R^4 are joined to form an optionally substituted 3-6 membered ring, or an ion thereof, where each R_a is independently H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group. In embodiments, the anthraquinone is water soluble. In embodiments, the anthraquinone is not water soluble.

In certain embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from halo, hydroxyl, carboxyl, sulfonate/sulfonic acid, alkylsulfonate/alkylsulfonic acid, phosphonyl, phosphoryl, alkylphosphonate/alkylphosphonic acid, amino, quaternary ammonium (e.g., tetraalkylamino), alkyl, heteroalkyl, alkoxy, glycoxy, polyalkyleneglycoxy, imino, polyimino, alkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, nitro, nitrile, thiyl, and/or carbonyl groups, any of which is optionally substituted, or, any two adjacent groups of R^1-R^8 can be joined together to form an optionally-substituted ring.

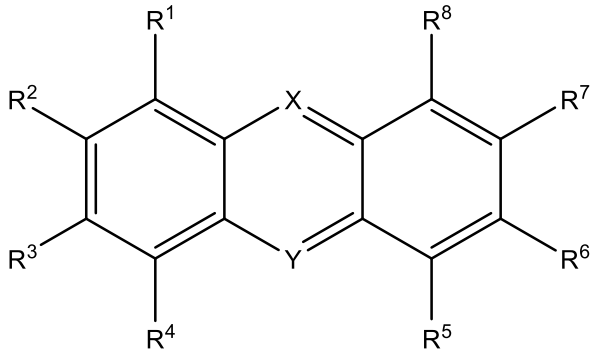
In certain embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H, optionally substituted C_{1-6} alkyl, halo, hydroxyl, optionally substituted C_{1-6} alkoxy, SO_3H, amino, nitro, carboxyl, phosphoryl, phosphonyl, and oxo, or an ion thereof. In particular embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl, carboxyl, and SO_3H, such as each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 being independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl (e.g., methyl), and oxo. In embodiments, at least one, e.g., at least two, of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is not H.

In other embodiments, the anthraquinone, such as a 9,10-anthraquinone, is substituted with at least one hydroxyl group and optionally further substituted with a C_{1-4} alkyl, such as methyl. Exemplary anthraquinones include is 2,6-bis(3-phosphonopropyl-1-oxy)anthraquinone (DPPEAQ), 2,6-dihydroxy-9,10-anthraquinone (2,6-DHAQ), 1,5-dimethyl-2,6-dihydroxy-9,10-anthraquinone, 2,3,6,7-tetrahydroxy-9,10-anthraquinone, 1,3,5,7-tetrahydroxy-2,4,6,8-tetramethyl-9,10-anthraquinone, and 2,7-dihydroxy-1,8-dimethyl-9,10-anthraquinone. Ions and reduced species thereof are also contemplated.

Other organic species amenable to use in hydrogen peroxide production of the invention include, but are not limited to, naphthoquinones (e.g., hydronaphthoquinones), reduced forms of phenazines (e.g., the reduced form of 7,8-dihydroxyphenazine-2-sulfonic acid), reduced monoquaternized or N,N′-

diquaternized phenazines, reduced phenoxazines, reduced phenothiazines, reduced fluorenones, or reduced forms of diquaternized bipyridines (e.g., alkyl viologen radical monocations).

Exemplary phenazines, N,N′-disubstituted phenazines, monoquaternized phenazines, or N,N′-diquaternized phenazines are, e.g., of formula (II):



(II), a salt thereof, or a reduced form (e.g., 5,10-dihydrophenazines) thereof, where X and Y are both N, or where X is NR_X and Y is N, or where X is NR^X and Y is NR^Y; where R^X and R^Y are independently selected from H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; or a nitrogen protecting group; where each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H; halo; optionally substituted C_{1-6} alkyl; oxo; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$ (e.g., hydroxyl or C_{1-6} alkoxy); $-SR_a$ (e.g., thiol or C_{1-6} alkyl thio); $-N(R_a)_2$ (e.g., amino); $-C(=O)R_a$; $-C(=O)OR_a$ (e.g., carboxyl); $-S(=O)_2R_a$; $-S(=O)_2OR_a$ (e.g., SO_3H); $-P(=O)R_{a2}$; and $-P(=O)(OR_a)_2$ (e.g., phosphonyl or phosphoryl); or any two adjacent groups selected from R^1, R^2, R^3, and R^4 are joined to form an optionally substituted 3-6 membered ring, or an ion thereof, where each R_a is independently H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group.

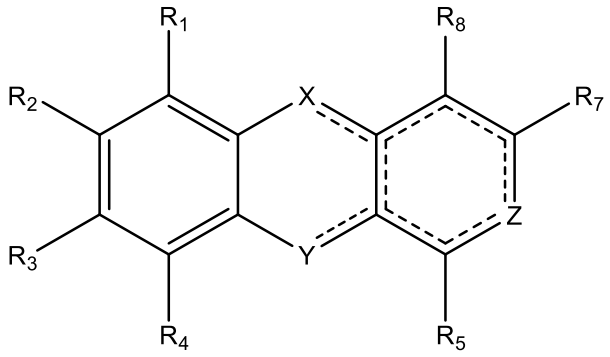
In certain embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H, optionally substituted C_{1-6} alkyl, halo, hydroxyl, optionally substituted C_{1-6} alkoxy, SO_3H, amino, nitro, carboxyl, phosphoryl, phosphonyl, and oxo, or an ion thereof. In particular embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl, carboxyl, and SO_3H, such as each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 being independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl (e.g., methyl), and oxo. In embodiments, at least one, e.g., at

least two, of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is not H. In some embodiments, at least one of R_1-R_8 is a substituted alky or substituted alkoxy.

In certain embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from halo, hydroxyl, carboxyl, sulfonate/sulfonic acid, alkylsulfonate/alkylsulfonic acid, phosphonyl, phosphoryl, alkylphosphonate/alkylphosphonic acid, amino, quaternary ammonium (e.g., tetraalkylamino), alkyl, heteroalkyl, alkoxy, glycoxy, polyalkyleneglycoxy, imino, polyimino, alkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, nitro, nitrile, thiyl, and/or carbonyl groups, any of which is optionally substituted, or, any two adjacent groups of R^1-R^8 can be joined together to form an optionally-substituted ring.

Exemplary phenazines include, e.g., 7,8-dihydroxyphenazine-2-sulfonic acid and phenazine-2,7-disulfonate. Ions and reduced species thereof are also contemplated. Exemplary phenazines as redox active species have been previously disclosed and are described in further detail in U.S. Patent No. 11,603,597.

Exemplary phenoxazines and phenothiazines are of, e.g., formula (III):



(III), a reduced form thereof, or a salt thereof,

where dashed bonds are single or double bonds; where X is N or NR^X, Y is O or S, and Z is CR^6, C=O, C=S, $C=NR^Z$, or $C=NH^+R^Z$;

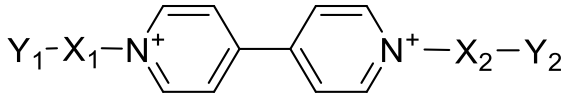
where R^X is selected from H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; or a nitrogen protecting group,

where R^Z is selected from H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; or a nitrogen protecting group,

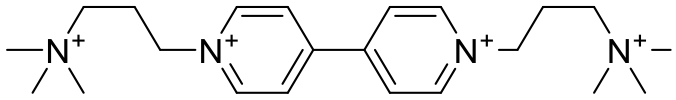
where each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H; halo; optionally substituted C_{1-6} alkyl; oxo; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$ (e.g., hydroxyl or C_{1-6} alkoxy); $-SR_a$ (e.g., thiol or C_{1-6} alkyl thio); $-N(R_a)_2$ (e.g., amino); $-C(=O)R_a$; $-C(=O)OR_a$ (e.g., carboxyl); $-S(=O)_2R_a$; $-S(=O)_2OR_a$ (e.g., SO_3H); $-P(=O)R_{a2}$;

and -P(=O)(OR_a)$_2$ (e.g., phosphonyl or phosphoryl); or any two adjacent groups selected from R^1, R^2, R^3, and R^4 are joined to form an optionally substituted 3-6 membered ring, or an ion thereof, where each R_a is independently H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group. In certain embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H, optionally substituted C_{1-6} alkyl, halo, hydroxyl, optionally substituted C_{1-6} alkoxy, SO_3H, amino, nitro, carboxyl, phosphoryl, phosphonyl, and oxo, or an ion thereof. In particular embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl, carboxyl, and SO_3H, such as each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 being independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl (e.g., methyl), and oxo. In embodiments, at least one, e.g., at least two, of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is not H. In some embodiments, at least one of R^1-R^8 is a substituted alky or substituted alkoxy.

Exemplary reduced diquaternized bipyridines are of, e.g., formula (IV):



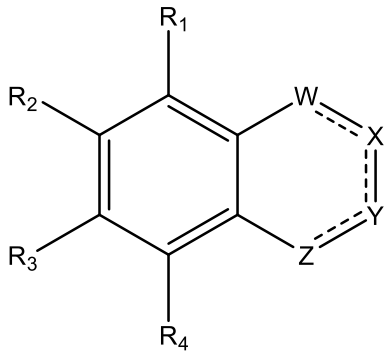
(IV), a reduced form thereof (e.g., singly reduced radical monocations or doubly reduced 4,4′-bipyridinylidenes), or a salt thereof,
where X_1 and X_2 are independently optionally substituted C_{1-20} hydrocarbyl (e.g., C_{1-10} alkylene) or heteroalkylene, and Y_1 and Y_2 are independently an optionally substituted water solubilizing group, e.g., a quaternary ammonium (e.g., trimethyl ammonium), ammonium, nitrogen-containing heterocyclyl, sulfonate, or sulfate. In certain embodiments, X_1 and X_2 are independently C_{1-10} alkylene, e.g., C_{3-6} alkylene. Exemplary groups for Y_1 and Y_2 are quaternary ammonium independently substituted with three C_{1-6} hydrocarbyl groups, e.g., trimethyl ammonium. An exemplary diquaternized bipyridine is



or a salt thereof.

In particular embodiments, the water-solubilizing group is charged at a pH between 6-8. Further embodiments of diquaternized bipyridines may have the above formula, except that the two pyridines are linked 2-2’ instead of 4-4’. Ions and reduced species thereof are also contemplated.

In some embodiments, the redox active species is a naphthoquinone. Exemplary naphthoquinones are of e.g., formula (V):

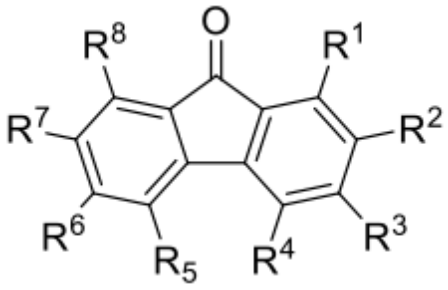


(V), a reduced form thereof (e.g., a naphthohydroquinone), or a salt thereof, wherein the dashed bonds are single or double bonds; where either W and X, W and Z, or Z and Y are C=O, and where the two of W, X, Y, or Z that are not C=O are independently selected from C-R, where R is H; halo; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$ (e.g., hydroxyl or C_{1-6} alkoxy); $-SR_a$ (e.g., thiol or C_{1-6} alkyl thio); $-N(R_a)_2$ (e.g., amino); $-C(=O)R_a$; $-C(=O)OR_a$ (e.g., carboxyl); $-S(=O)_2R_a$; $-S(=O)_2OR_a$ (e.g., SO_3H); $-P(=O)R_{a2}$; and $-P(=O)(OR_a)_2$ (e.g., phosphonyl or phosphoryl); or any two adjacent R groups are joined to form an optionally substituted non-aromatic 3-6 membered ring, or an ion thereof, where each R_a is independently H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group; where each of R^1, R^2, R^3, and R^4 is independently selected from H; halo; optionally substituted C_{1-6} alkyl; oxo; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$ (e.g., hydroxyl or C_{1-6} alkoxy); $-SR_a$ (e.g., thiol or C_{1-6} alkyl thio); $-N(R_a)_2$ (e.g., amino); $-C(=O)R_a$; $-C(=O)OR_a$ (e.g., carboxyl); $-S(=O)_2R_a$; $-S(=O)_2OR_a$ (e.g., SO_3H); $-P(=O)R_{a2}$; and $-P(=O)(OR_a)_2$ (e.g., phosphonyl or phosphoryl); or any two adjacent groups selected from R^1, R^2, R^3, and R^4 are joined to form an optionally substituted 3-6 membered ring, where each R_a is independently H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group. In certain embodiments, W and Z are C=O.

In certain embodiments, each of R^1, R^2, R^3, and R^4 is independently selected from H, optionally substituted C_{1-6} alkyl, halo, hydroxyl, optionally substituted C_{1-6} alkoxy, SO_3H, amino, nitro, carboxyl, phosphoryl, phosphonyl, and oxo, or an ion thereof. In particular embodiments, each of R^1, R^2, R^3, and R^4

is independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl, carboxyl, and SO_3H, such as each of R^1, R^2, R^3, and R^4 being independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl (e.g., methyl), and oxo. In embodiments, at least one, e.g., at least two, of R^1, R^2, R^3, and R^4 is not H. In some embodiments, at least one of R^1-R^4 is a substituted alky or substituted alkoxy. Ions and reduced species thereof are also contemplated.

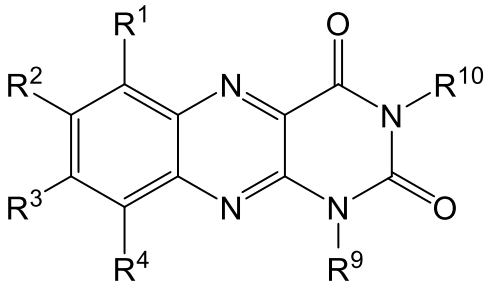
Exemplary fluorenones are of formula (VI):



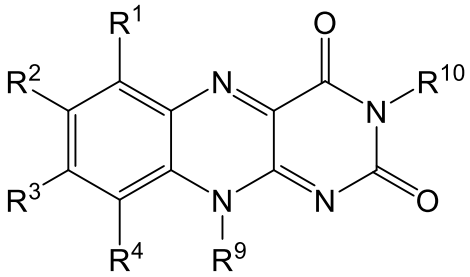
, reduced forms thereof, and salts thereof, wherein each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H; halo; optionally substituted C_{1-6} alkyl; oxo; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -CN; $-NO_2$; $-OR_a$ (e.g., hydroxyl or C_{1-6} alkoxy); $-SR_a$ (e.g., thiol or C_{1-6} alkyl thio); $-N(R_a)_2$ (e.g., amino); $-C(=O)R_a$; $-C(=O)OR_a$ (e.g., carboxyl); $-S(=O)_2R_a$; $-S(=O)_2OR_a$ (e.g., SO_3H); $-P(=O)R_{a2}$; and $-P(=O)(OR_a)_2$ (e.g., phosphonyl or phosphoryl); or any two adjacent groups selected from R^1, R^2, R^3, and R^4 are joined to form an optionally substituted 3-6 membered ring, or an ion thereof, where each R_a is independently H; optionally substituted C_{1-6} alkyl; optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group. In embodiments, the fluorenone is water soluble.

In certain embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 is independently selected from H, optionally substituted C_{1-6} alkyl, halo, hydroxyl, optionally substituted C_{1-6} alkoxy, SO_3H, amino, nitro, carboxyl, phosphoryl, phosphonyl, and oxo, or an ion thereof. In particular embodiments, each of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl, carboxyl, and SO_3H, such as each of R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 being independently selected from H, hydroxyl, optionally substituted C_{1-4} alkyl (e.g., methyl), and oxo. In embodiments, at least one, e.g., at least two, of R^1, R^2, R^3, R^4, R^5, R^6, R^7, and R^8 is not H.

In some embodiments, the compound is an alloxazine of formula (V) or isoalloxane of formula (VI):



(V)



(VI)

wherein each of R^9 and R^{10} is independently H; optionally substituted C_{1-10} alkyl (e.g., C_{1-6} alkyl, unsubstituted C_{1-10} alkyl, or unsubstituted C_{1-6} alkyl); optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -C(=O)R_a; and -C(=O)OR_a; and each of R^1, R^2, R^3, and R^4 is independently H; C_{1-10} alkyl (e.g., C_{1-6} alkyl); optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; -NO_2; -OR_a; -SR_a; -N$(R_a)_2$; -C(=O)R_a; -C(=O)OR_a; -S(=O)$_2R_a$; -S(=O)$_2$OR_a; -P(=O)R_{a2}; and -P(=O)$(OR_a)_2$; or any two adjacent groups selected from R^1, R^2, R^3, and R^4 are joined to form an optionally substituted 3-6 membered ring, or an ion thereof; wherein each R_a is independently H; C_{1-10} alkyl (e.g., C_{1-6} alkyl); optionally substituted C_{3-10} carbocyclyl; optionally substituted C_{1-9} heterocyclyl having one to four heteroatoms independently selected from O, N, and S; optionally substituted C_{6-20} aryl; optionally substituted C_{1-9} heteroaryl having one to four heteroatoms independently selected from O, N, and S; an oxygen protecting group; or a nitrogen protecting group.

In some embodiments, each of R^9 and R^{10} is independently H, optionally substituted C_{1-10} alkyl (e.g., C_{1-6} alkyl), or -C(=O)OR_a; and each of R^1, R^2, R^3, and R^4 is independently H, halo, optionally substituted C_{1-10} alkyl (e.g., C_{1-6} alkyl), -NO_2, -OR_a, -SR_a; -N$(R_a)_2$, -C(=O)OR_a, -S(=O)$_2$OR_a, -P(=O)R_{a2} or –P(=O)$(OR_a)_2$; wherein each R_a is independently H or optionally substituted C_{1-10} alkyl (e.g., C_{1-6} alkyl). In some embodiments, none of, any two of, any three of, any four of, any five of, or any six of R^1, R^2, R^3, R^4, R^9, and R^{10} are H.

Suitable second redox active species include those having low solubility in aqueous solutions. Examples include alkyl anthraquinones such as 2-ethyl anthraquinone, tetrahydro 2-ethyl anthraquinone (EtAQ), 2-isopropylanthraquinone, 2-sec-butylanthraquinone, 2-t-butylanthraquinone, 2-sec-amylanthraquinone, 1,3-di-methylanthraquinone, 2,3-dimethyl-anthraquinone, 1,4 dimethylanthraquinone, 2,7-dimethylanthraquinone, amylanthraquinone, and tetrahydroamylanthraquinone. Other exemplary second redox active species include phenazines, such as alkyl phenazines.

Any of the redox active species described herein may be designed to include one or more water-soluble or non-water-soluble substitution groups to increase solubility in one solution of interest and/or

decrease solubility in a second solution of interest. For example, a redox active species may be designed to include two water-soluble substitution groups (e.g., two phosphate groups) to increase solubility in a solution of the first fluid stream that is aqueous and to decrease solubility in a second solution that is nonaqueous. In some embodiments, the first redox active species is water soluble. In some embodiments, the first redox active species has a solubility less than 0.001 mol/L in the solution of the second fluid stream. In some embodiments, the first redox active species is an anthraquinone, a viologen, a naphthoquinone, a phenazine, a phenoxazine, a phenothiazine, a fluorenone, an alloxazine, a vanadium, a chromium, or water-soluble derivatives thereof. In some embodiments, the first redox active species includes one or more alkoxy, amide, amino, carboxyl, heteroalkyl, heteroaryl, hydroxyl, nitrile, nitro, phosphonyl, phosphoryl, sulfonyl and/or other water-soluble substitution groups. In some embodiments, the first redox active species is a substituted anthraquinone including of one or more alkoxy, amide, amino, carboxyl, heteroalkyl, heteroaryl, hydroxyl, nitrile, nitro, phosphonyl, phosphoryl, sulfonyl and/or other water-soluble substitution groups. In some embodiments, the second redox active species is soluble in nonaqueous solutions. In some embodiments, the second redox active species has a solubility less than 0.001 mol/L in aqueous phase solutions. In some embodiments, the second redox active species is an anthraquinone, a naphthoquinone, a phenazine, a fluorenone, an alloxazine, and non-water-soluble derivatives thereof. In some embodiments, the second redox active species includes one or more halo, aryl, alkyl or other non-water-soluble substitution groups. In some embodiments, the second redox active species is a substituted anthraquinone including of one or more halo, aryl, alkyl or other non-water-soluble substitution groups.

Methods

The invention provides methods for production of hydrogen peroxide. The method employs two redox active species, such as anthraquinones as described herein. In the methods of, a first solution and a second solution from a include a first redox active species and second redox active species, respectively. The first solution is aqueous, and the second solution is nonaqueous. Suitable nonaqueous solvents include aromatic solvents, long chain alcohols, alkyl phosphites, and/or carbonates, and combinations thereof. A third, aqueous solution is employed for extraction. In some embodiments, the first solution of has a pH below 9.

The first redox active species is water soluble and has a solubility less than 0.001 mol/L in the second solution. In some embodiments, the first redox active species is an anthraquinone, a viologen, a naphthoquinone, a phenazine, a phenoxazine, a phenothiazine, a fluorenone, an alloxazine, a vanadium, a chromium, or water-soluble derivatives thereof. In some embodiments, the first redox active species includes one or more alkoxy, amide, amino, carboxyl, heteroalkyl, heteroaryl, hydroxyl, nitrile, nitro, phosphonyl, phosphoryl, sulfonyl and/or other water-soluble substitution groups. In some embodiments, the first redox active species is a substituted anthraquinone including of one or more alkoxy, amide,

amino, carboxyl, heteroalkyl, heteroaryl, hydroxyl, nitrile, nitro, phosphonyl, phosphoryl, sulfonyl and/or other water-soluble substitution groups.

The second redox active species is soluble in nonaqueous solutions and has a solubility less than 0.001 mol/L in aqueous phase solutions. In some embodiments, the second redox active species is an anthraquinone, a naphthoquinone, a phenazine, a fluorenone, an alloxazine, or non-water-soluble derivatives thereof. In some embodiments, the second redox active species includes one or more halo, aryl, alkyl or other non-polar groups. In some embodiments, the second redox active species is a substituted anthraquinone including of one or more halo, aryl, alkyl or other non-polar groups.

The method includes reducing the first redox active species in an electrochemical cell (see, e.g., electrochemical cell 3001 of FIG. 3) . In some embodiments, the method includes performing an oxygen evolution reaction or a hydrogen oxidation reaction at the cathode of the electrochemical cell. In some embodiments, the reduced form of the first redox active species in the aqueous solution is transported into a first contactor (see, e.g., first contactor 3002 in FIG. 3)with the nonaqueous second solution including the second redox active species.

After reduction of the first redox active species, the method includes contacting, in the first contactor, the first solution with the second solution. During the step of contacting the first solution with the second solution, at least a portion of the first redox species transfers electrons to the second redox active species, to reduce the second redox species. In some embodiments, contacting, in the first contactor, the solution from the first fluid stream with the second solution includes agitating the solution from the first fluid stream with the solution from the second fluid stream. Agitation of the solution of the first fluid stream with the second solution promotes charge-transfer between the first redox active species and the second redox active species.. Agitation may be by any suitable means such as stirring, shaking, vortexing, or sonicating.

After reduction of the second redox active species, the method includes separating, in a first separator (see, e.g., first separator 3003 in FIG. 3), the first solution from the second solution. In some embodiments, separating the first solution from the second solution includes separating by gravity driven phase separation, centrifugal force, or filtration. In some embodiments, the first solution and second solution settles after agitation before being separated. In some embodiments, the method includes pumping the first solution back into the electrochemical cell after separating in the first separator. In some embodiments, the second solution is pumped into a second contactor (see, e.g., second contactor 3004 in FIG. 3) after separating in the first separator. In some embodiments, the third solution is pumped into the second contactor.

After separation of the first solution from the second solution, the method includes introducing oxygen to the second solution. In some embodiments, the oxygen is introduced with a bubbler (see, e.g., bubbler 3006 in FIG. 3).

After and/or while introducing the oxygen, the method includes contacting, in the second contactor, the second solution with a third solution from oxygen, wherein at least a portion of the reduced

form of the second redox active species reduces oxygen to hydrogen peroxide. In some embodiments, contacting, in the second contactor, the second solution with the third solution includes agitating the second solution with the third solution. Agitation (e.g., stirring) of the second solution with the third solution promotes charge-transfer between the second redox active species and oxygen. The produced hydrogen peroxide resides in the aqueous third solution. In some embodiments, the third solution is water, wherein the water further includes stabilizer to stabilize hydrogen peroxide, wherein the stabilizer is phosphate acid or ethylenediaminetetraacetic acid.

After production of hydrogen peroxide in the second contactor, the method includes separating, in a second separator (see, e.g., second separator 3005 in FIG. 3), the second solution from the third solution. In some embodiments, separating the second solution from the third solution includes separating by gravity driven phase separation, centrifugal force, or filtration. In some embodiments, the third solution and second solution settle after agitation before being separated. In some embodiments, the method includes transporting the second solution back into the first contactor after separating in the second separator.

In some embodiments, the method includes transporting the third solution back into the second contactor after separating in the second separator. The steps of the method may be repeated to produce hydrogen peroxide in each repetition, increasing the concentration of hydrogen peroxide in the solution of the third fluid stream.

In some embodiments, the method includes purifying the third solution with a purifier. In some embodiments, purifying the third solution with a purifier occurs after one or more repetitions of contacting the second solution in the second contactor. In some embodiments, purifying removes unwanted organic residues from the third solution. In some embodiments, the method includes collecting the purified third solution as the product or for use in downstream applications. In some embodiments, the hydrogen is extracted from the third solution.

System

The invention provides systems for production of hydrogen peroxide. In one embodiment (see, e.g., system 3000 of FIG. 3), the system includes an electrochemical cell, a first contactor, a first separator, a second contactor, a second separator, and an oxygen source, e.g., a bubbler. The system may also include a purifier. The first contactor is in fluid communication with the electrochemical cell and the first separator. The second contactor is in fluid communication with the first contactor, the first separator, and the second separator. In some embodiments, the oxygen source, e.g., bubbler, is in fluid communication with to the second contactor. In some embodiments, the oxygen source, e.g., bubbler, is connected between the second contactor and the first separator. In some embodiments, the system includes a pump for each solution to transport each solution. In some embodiments, the system includes a valve for each solution to control flow. Fluidic components may be connected with standard tubing as is known in the art.

The electrochemical cell (see, e.g., electrochemical cell 3001 in FIG. 3) includes a first electrode and the first solution including a first redox active species. In some embodiments, the electrochemical cell includes a first electrode compartment and a second electrode compartment, the first electrode compartment including the first electrode, and the second electrode compartment including a second electrode. In some embodiments, the first electrode compartment and the second electrode compartment are separated by a membrane, wherein the membrane is a cation exchange membrane, an anion exchange membrane, a bipolar membrane, or a size selective membrane. In some embodiments, the second electrode compartment is configured to perform an oxygen evolution reaction or a hydrogen oxidation reaction. Oxygen (or other gas) evolved in the system may be collected for other use, e.g., to produce hydrogen peroxide in the system.

The first contactor is in fluid communication with the electrochemical cell and houses the first solution and a second solution including a second redox active species. The first contactor may be a reservoir or other container for holding liquids. In some embodiments, the first contactor includes a agitating element that agitates the first solution with the second solution. Agitating elements include shakers, sonicators, and stirrers.

The first separator (see, e.g., first separator 3003 in FIG. 3) is in fluid communication with the first contactor. The first separator separates the first solution from the second solution. In some embodiments, the first separator achieves separation by gravity driven phase separation, centrifugal force, or filtration. In some embodiments, the system further includes a first pump to transport the first solution to the electrochemical cell after passing through the first separator. In some embodiments, the first separator includes a lipophilic membrane and a hydrophilic membrane.

The second contactor (see, e.g., second container 3004 of FIG. 3) is in fluid communication with the first separator. The second contactor houses the second solution of the second fluid stream, an aqueous third solution, and oxygen. In some embodiments, the second contactor includes a agitating element that agitates the first solution with the second solution. Agitating elements include shakers, sonicators, and stirrers. In some embodiments, the third solution is water, wherein the water further includes stabilizer to stabilize hydrogen peroxide, wherein the stabilizer is phosphate acid or ethylenediaminetetraacetic acid.

The oxygen source, e.g., bubbler (see, e.g., bubbler 3006 of FIG. 3), introduces the oxygen, e.g.,. pure or in mixture, such as air, to the second contactor or to the second solution after the first separator.

The second separator (see, e.g., second separator 3005 of FIG. 3) is in fluid communication with the second contactor. The second separator separates the second solution from the third solution. In some embodiments, the second separator achieves separation by gravity driven phase separation, centrifugal force, or filtration. In some embodiments, the system further includes a second pump to transport the second solution back into the first contactor after passing through the second separator. In some embodiments, the system further includes a third pump to transport the third solution back into the

second contactor after passing through the second separator. In some embodiments, the second separator includes a lipophilic membrane and a hydrophilic membrane.

The purifier is in fluid communication with the second contactor, wherein the purifier may purify the solution of the third fluid stream. In some embodiments, the purifier removes unwanted organic residues from the solution of the third fluid stream. In some embodiments, wherein the purified third solution is collected as the product by a collector. Alternatively, the purified third solution may be used for downstream applications.

EXAMPLES

The following examples are intended to illustrate the invention and not to limit it in any way.

Example 1. Electrolyte-free, electrochemical production of hydrogen peroxide.

An embodiment of the system and method disclosed herein, as shown in FIG. 3, was used to produce hydrogen peroxide. Electrochemical cell 3001 included a first compartment containing an anode and H_2SO_4 (pH = 0). The second compartment contained a cathode and a **[[X]]** [大帝4]mM of the first redox active species, DPPEAQ, in an aqueous buffer (pH = 7) (i.e., the first solution). The first and second compartment were separated by a Nafion membrane. Upon application of an electrical potential of **[[X]]**[MJA5] V, the oxygen evolution reaction occurred in the first compartment and reduction of DPPEAQ to H_2DPPEAQ occurred in the second compartment. H_2SO_4 was replenished during operation. The first solution, H_2DPPEAQ/DPPEAQ in aqueous buffer (pH = 7), was pumped into first contactor 3002. The second solution included a **[[X]]**[MJA6] mM of the second redox active species, EtAQ, in a 3:2 toluene:decanol solution. The second solution was also placed in the first contactor 3002. The two, immiscible solutions were stirred in first contactor 3002 to promote the charge-transfer between H_2DPPEAQ and EtAQ, causing a reduction of a portion of EtAQ to H_2EtAQ and an oxidation of H_2DPPEAQ to DPPEAQ. After stirring, the contents of the first contactor 3002 were passed through first separator 3003. The first solution was filtered through a hydrophilic membrane before returning to electrochemical cell 3001. The second solution was filtered through a lipophilic membrane and then pumped into second contactor 3004. A thid solution, water containing a hydrogen peroxide stabilizer, was also pumped into second contactor 3004. Oxygen gas (O_2) was bubbled into the second contactor 3004. The two, immiscible solutions were stirred in second contactor 3004 to promote the charge transfer between H_2EtAQ and O_2, causing an oxidation of H_2EtAQ to EtAQ and reduction of O_2 to hydrogen peroxide. After stirring, the contents of second contactor 3004 were separated by second separator 3005. The second solution was filtered through a lipophilic membrane before returning to first contactor 3002. The third solution was filtered through a hydrophilic membrane before returning to second contactor 3005. The process was repeated with the solution from the third stream (H_2O_2/H_2O/**stabilizer**[大帝7]) being cycled to accumulate an increasing concentration of H_2O_2. The concentration of H_2O_2 and the Coulombic

efficiency were measured over time as the system operated. Results of this experiment are shown in FIG. 4. The efficiency was about 80% after the system reached steady state (t = 600 seconds). After each 200-second interval for up to 1000 seconds, the concentration of H_2O_2 increased, demonstrating the continuous production of H_2O_2.

[[Inventors: Please confirm[MJA8] **the system of FIG. 3 was used to produce the data in FIG. 4. Please provide experimental conditions, such as concentrations, stirring times, reference electrodes, rpm for stirring, pressure of O2/air, applied potentials, measurement means (hydrogen peroxide concentration in FIG. 4), etc.]]** **Concentrations were 0.1 M of etAQ in the nonaqueous solvent and 0.1 M of DPPEAQ in water. Stirred at 1000 RPM for 5 seconds. Bubbled air at ambient pressure. No reference electrode. Applied potential of 3 volts. H2O2 concentration was measured by $KMnO_4$ titration.**

CLAIMS

1. A system for production of hydrogen peroxide, comprising:

(a) a first solution comprising a first redox active species, wherein the first solution is aqueous;

(b) a second solution comprising a second redox active species, wherein the second solution is nonaqueous and immiscible with the first solution and wherein first and second redox active species are different;

(c) an electrochemical cell comprising a first and second electrode and a barrier therebetween, where the electrochemical cell is configured to reduce the first redox active species in the first solution;

(d) a first contactor in fluid communication with the electrochemical cell, wherein the first contactor is configured to house the first solution in contact with the second solution ;

(e) a first separator in fluid communication with the first contactor, wherein the first separator separates the first solution from the second solution;

(f) a second contactor in fluid communication with the first separator, wherein the second contactor is configured to house the second solution in contact with a third solution and oxygen, wherein the third solution is aqueous and immiscible with the second solution;

(g) an oxygen source configured to provide oxygen into~~to~~ [MJA9]the second contactor; and

(h) a second separator in fluid communication with the second contactor, wherein the second separator separates the second solution from the third solution.

2. The system of claim 1, wherein the electrochemical cell is configured to perform an oxygen evolution reaction or a hydrogen oxidation reaction at the second electrode.

3. The system of claim 1 or 2, wherein the first redox active species has a solubility that is less than 0.001 [大席10]mol/L in the second solution.

4. The system of any one of claims 1-3, wherein the first redox active species is an anthraquinone, a viologen, a naphthoquinone, a phenazine, a phenoxazine, a phenothiazine, a fluorenone, an alloxazine, a vanadium ion or compound, or a chromium ion or compound, or a ruthenium compound, or a zinc compound, or a manganese compound, or an iron compound. **[[Please confirm the list of first redox active species.]]**

5. The system of any one of claims 1-4, wherein the second redox active species is an anthraquinone, a naphthoquinone, a phenazine, a fluorenone, or an alloxazine. **[[Please confirm the list of second redox active species.]]**[大席11]

6. The system of any one of claims 1-5, wherein the second redox active species has a solubility that is less than 0.001 mol/L in the first and third solutions.

7. The system of any one of claims 1-6, wherein the first contactor further comprises an agitating element that agitates the first solution with the second solution.

8. The system of any one of claims 1-7, wherein the second contactor further comprises an agitating element that agitates the second solution with the third solution.

9. The system of any one of claims 1-8, wherein the first separator or the second separator achieve separation by gravity driven phase separation, centrifugal force, or filtration.

10. A method for production of hydrogen peroxide, comprising:

(a) reducing a first redox active species in first solution, wherein the first solution is aqeuous;

(b) contacting, in a first contactor, the first solution with a second solution comprising a second redox active species to reduce the second redox active species, wherein second solution is nonaqueous and the first solution is immiscible with the solution from the second fluid stream and the first and second redox active species are different;

(c) separating, in a first separator, the first solution from the second solution;

(d) contacting, in a second contactor, the second solution from the second fluid with a third solution and oxygen to reduce the oxygen to hydrogen peroxide, wherein the third solution is aqueous and the second solution is immiscible with the third solution; and

(f) separating, in a second separator, the second solution from the third solution.

11. The method of claim 10, wherein the method is carried out in the system of any one of claims 1-9.

12. The method of claims 10 or 11, wherein in step (a), an oxygen evolution reaction or a hydrogen oxidation reaction reduces the first redox active species .

13. The method of any one of claims 10-12, wherein the first redox active species has a solubility less than 0.001 mol/L in the second solution.

14. The method of any one of claims 10-13, wherein the first redox active species is an anthraquinone, a viologen, a naphthoquinone, a phenazine, a phenoxazine, a phenothiazine, a fluorenone, an alloxazine, a vanadium ion or compound, or a chromium ion or compound, or a ruthenium compound, or a zinc compound, or a manganese compound, or an iron compound.

15. The method of any one of claims 10-14, wherein the second solution comprises an aromatic solvent, a long chain alcohol, an alkyl phosphite, and/or a carbonate.

16. The method of any one of claims 10-15, wherein the second redox active species is an anthraquinone, a naphthoquinone, a phenazine, a fluorenone, or an alloxazine.

17. The method of any one of claims 10-16, wherein the second redox active species has a solubility less than 0.001 mol/L in the first and third solutions.

18. The method of any one of claims 10-17, wherein contacting, in the first contactor, the first solution with the second solution comprises agitating the first solution with second solution.

19. The method of any one of claims 10-18, wherein contacting, in the second contactor, the second solution with the third solution comprises agitating the second solution with the third solution.

20. The method of any one of claims 10-19, wherein separating the first solution from the second solution or separating the second solution from the third solution comprises separating by gravity driven phase separation, centrifugal force, or filtration.

SYSTEM AND METHOD FOR PRODUCTION OF HYDROGEN PEROXIDE

ABSTRACT

The present disclosure relates, generally, to an electrochemical system and method of producing hydrogen peroxide.