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(71) Applicant *(for all designated States except US)*: **SIEMENS WATER TECHNOLOGIES CORP.** [US/US]; 181 Thorn Hill Rd., Warrendale, Pennsylvania 15086 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **ZOLOTARSKY, Vadim** [US/US]; 62 Henshaw Avenue, Springfield, New Jersey 07081 (US). **IVANTER, Irina** [US/US]; 14 Pero Court, Sayreville, New Jersey 08872 (US). **MARTIN, Barry L.** [US/US]; 8132 South Chariot Street, Concord, Ohio 44060 (US).

(74) Agents: **MUSACCHIO, Pasquale** et al.; Siemens Corporation- Intellectual Property Dept., 170 Wood Avenue South, Iselin, New Jersey 08830 (US).

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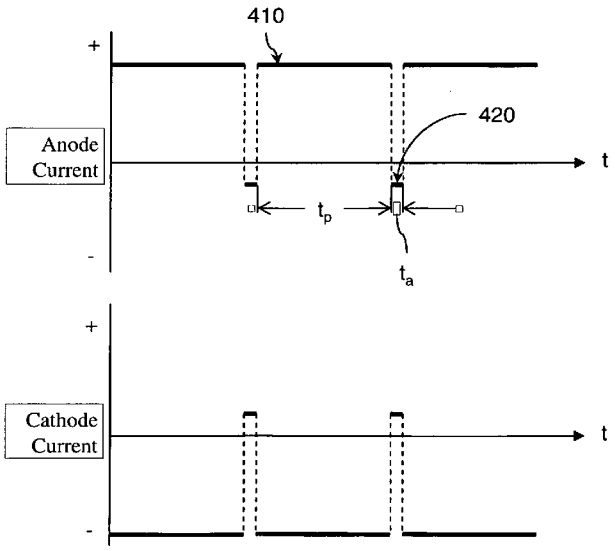

FIG. 4

(57) Abstract: Electrocatalytic generation of halogenated biocides are disclosed by electrolyzing low salinity water with an applied current. The direction of the applied current is reversed periodically, for a shorter duration, and at a lower current density. Mixed types of electrodes are utilized without a significant reduction in reliability and performance.

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METHOD AND SYSTEM OF ELECTROLYTIC TREATMENT

BACKGROUND OF INVENTION

1. Field of Invention

This invention relates to methods and system of electrolytic treatment and, more particularly, to methods and systems of electrolytic generation with asymmetric polarity reversal.

2. Discussion of Related Art

Bianchi et al., in U.S. Patent No. 3,948,751, disclose a valve metal electrode with a valve metal oxide semi-conductive face. The chlorine resistant metal electrodes are of valve metals, titanium and tantalum, having coatings of mixed metal oxides, valve metal oxides.

Beer, in U.S. Patent No. 3,933,616, discloses coatings of protected electrocatalytic material on an electrode.

Bennett, in U.S. Patent No. 4,087,337, discloses rejuvenation of sea water electrolysis cells by periodic removal of anodic deposits. The efficiency of the cell is rejuvenated by changing the polarity of the anode for from one to ten minutes at an amperage of from about 2 to 50 milliamps per square inch.

Elliott et al., in U.S. Patent No. 4,087,339, disclose electrowinning of sulfur-containing nickel. Sulfur-containing nickel is electrodeposited from a chloride electrolyte in a cell wherein each cathode is separated from any adjacent anode by a pair of diaphragms.

Stillman, in U.S. Patent No. 4,100,052, discloses electrolytic generation of halogen biocides. An electrolytic cell is used for the generation of a halogen biocidally active agent from an aqueous solution having a low halogen salt content.

Howlett, in U.S. Patent No. 4,997,540, discloses an in-pool saltwater chlorinator. The apparatus provides for the chlorination of water in a swimming pool where the water includes a soluble chlorine ion containing electrolyte.

Sadler et al., in U.S. Patent No. 5,807,473, disclose electrolytic water treatment. The electrodes used in the treatment are suitable for a continuous anodic or cathodic operation. A controller maintains the voltage and current provided to the electrodes. The duration of each voltage polarity applied to each electrode is substantially the same. The polarity of the voltage to the electrodes is periodically reversed during which there is a period of zero voltage between a first polarity and a second polarity.

SUMMARY OF THE INVENTION

Some aspects of the invention relate to a method of providing a biocide. The method can comprise introducing water having a chloride concentration of less than about 6,000 ppm into an electrolyzer, electrolyzing at least a portion the chloride with a first electric current applied through the electrolyzer in a first direction to produce the biocide, and passing a second electric current through the electrolyzer in an opposite direction relative to the first direction. A magnitude of the second electric current is less than a magnitude of the first electric current.

Some aspects of the invention relate to a method of modifying a treatment system having an electrolyzer. The method can comprise connecting a controller to the electrolyzer, the controller configured to regulate electric current to the electrolyzer in a first operating mode and in a second operating mode, the first operating mode having primary electric current regulated to a first current level, the second operating mode having an asymmetric electric current at an opposite polarity relative to the primary electric current and at a second current level that is less than the first current level; and replacing at least one electrode of the electrolyzer with at least one of a carbon-filled polymeric electrode, an electrode comprising an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide, and an electrode comprising electrocatalytic coating comprising ruthenium oxide and titanium oxide.

Some aspects of the invention relate to an electrolytic water treatment system. The system can comprise an electrolyzer fluidly connectable to a source of water having a salinity of less than about 2.5 %. The electrolyzer typically comprises at least one primary electrode and at least one secondary electrode. The system can further

comprise a power supply configured to deliver electrical current to the at least one primary electrode and the at least one secondary electrode, and a controller configured to regulate the power supply to deliver a first electrical current at a first current level and to deliver a second electrical current at a second current level, wherein the second current level differs from the first current level.

Some aspects of the invention relate to an electrolytic system. The electrolytic system can comprise an electrolyzer having a primary electrode and a secondary electrode. Typically, at least one of the primary and secondary electrodes has an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide. The electrolytic system can further comprise a power supply configured to energize the primary and secondary electrodes in a first mode at a first polarity with a first potential level and a first current level. The power supply can further be configured to energize the primary and secondary electrodes in an asymmetric mode at a reverse polarity relative to the first polarity. Typically, a magnitude of the second potential level differs from a magnitude of the first potential level.

Some aspects of the invention relate to a computer-readable medium including computer-readable signals stored thereon defining instructions that, as a result of being executed by at least one processor, instruct the processor to perform a method of controlling an electrolytic system comprising an electrolyzer fluidly connected to a source of non-thalassic water. The method can comprise generating a first control signal that regulates a power supply to provide a primary electrolytic current for a first duration to the electrolyzer, and generating a second control signal that regulates the power supply to provide an asymmetric current to the electrolyzer for a second duration that is less than the first duration.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are not drawn to scale. In the drawings, each identical or nearly identical component that is illustrated is represented by a like numeral. For purposes of clarity, not every component may be labeled in every drawing.

In the drawings:

FIG. 1 is a schematic illustration of an electrolytic system upon which some aspects of the invention may be practiced;

FIG. 2 is a schematic illustration showing the orientation of an electrode in an electrolyte flow path, in accordance with some aspects of the invention;

FIGS. 3A and 3B are graphs showing a typical profile of electrical current passed through an electrolytic device in a forward electrolytic operating mode, without a change in current polarity (FIG. 3A), and a typical profile of electrical current passed through an electrolytic device with a reversing operating mode, with a change in current polarity (FIG. 3B);

FIG. 4 is a graph illustrating a profile of electrical current passed through an electrolytic device with a primary and an asymmetric operating mode, in accordance with some aspects of the invention;

FIGS. 5A and 5B are schematic illustrations of electrolytic devices showing primary and secondary electrodes with various electrocatalytic coatings, in accordance with some aspects of the invention, in which FIG. 5A illustrates a monopolar electrode arrangement with mixed types of electrodes and FIG. 5B illustrates a bipolar electrode arrangement with mixed types of electrodes;

FIGS. 6A-6E are graphs illustrating the performance of different electrocatalytic coatings in electrolytic devices relative to coating loadings (amount of coating) and to various operating conditions, in accordance with some aspects of the invention;

FIG. 7 is a graph summarizing the performance of electrocatalytic coatings in an electrolytic devices under various operating conditions in accordance with some aspects of the invention; and

FIG. 8 is a schematic illustration of a control system that may be utilized to implement some aspects of the invention.

DETAILED DESCRIPTION

Some aspects of the invention involve systems that utilize at least one electrically-driven apparatus. Some particular aspects of the invention are directed to

electrolytic systems comprising at least one electrolytic device. Other aspects of the invention involve techniques or operating modes of systems comprising at least one electrically-driven apparatus. Other particular aspects of the invention are directed to techniques of operating systems that comprise electrolytic devices.

One or more aspects of the invention can relate to utilization of electrodes that comprise coatings intended for forward polarity or non-reversing techniques in electrolytic devices that are operated with reversing polarity. Other aspects of the invention can be considered can relate to the utilization of mixed types of electrodes in electrolytic devices operated with polarity reversing techniques.

Some particular aspects of the invention can involve treatment or disinfection of water in swimming pools and spas. In some cases, the water is non-thallasic water or water that is not seawater. Some aspects of the invention, however, contemplate the use of treated or modified seawater to have a salinity content that is less, preferably significantly less, than the salinity of seawater. Some advantageous aspects of the invention thus utilize water that has a salinity level less than the salinity level of seawater. Typical concentrations of the salt in swimming pool water typically not exceed 5,000 parts per million (ppm). In some cases, the electrolyte is water, such as fresh water, having a salinity of less than 5 %, typically, less than about 2.5 %, preferably less than 1 %, more preferably less than about 0.5 %. In accordance with some particular aspects of the invention, the concentration of chloride species in water to be electrolyzed is in a range of from 3,000 ppm to 5,500 ppm. For example, water with added sodium chloride can be utilized as an electrolyte to generate a biocide.

Treatment systems and techniques pertinent to some aspects of the invention may involve generating chlorine in-situ, for example, in swimming pool or spa water that is introduced into and electrolyzed in an electrochemical cell or system.

Forward current or forward polarity (FP) type cells or electrolyzers are typically energized in a manner or in an operating mode wherein the current always flows in a single direction, from one or more positively charged electrodes, anodes, to one or more negatively charged electrodes, cathodes. The current output profile of FP type electrolyzers is schematically illustrated in FIG. 3A. In FP type cells, anodes typically comprise titanium metal sheets coated with mixed metal oxide coating or platinum

metal serving as an electrocatalyst to facilitate chlorine generation. A typical choice of material for cathodes is titanium or nickel alloys such as those under the mark HASTELLOY. If a monopolar cell configuration is used, the anode conventionally has a coating on both sides. If a bipolar cell configuration is used the anode typically has a coating on one side only.

Typically, the maximum possible chlorine generation is preferred and a FP type coating is conventionally utilized to promote as much chlorine output. Conventionally utilized chlorine evolving coatings are typically based on ruthenium oxide as the main catalyst. However, low salinity and low water temperature can shift the anodic reaction to produce oxygen. Significantly, ruthenium oxide-based coatings do not exhibit desirable durability characteristics durable when used in oxygen-evolving operations. To improve reliability and performance, electrode coatings based on ruthenium oxide are complemented with other precious metals, or oxides thereof, such as iridium, rhodium and platinum that impart durability. Further, the amount of the applied electric current through the surface of the anode (the current density) is typically reduced to below 1,000 Amperes per square meter. Thus, FP type coatings are characterized by high selectivity toward chlorine production and excellent durability at relatively low coating loadings. These coatings are available commercially from Siemens Water Technology Corp. under the OPTIMA™ RUA-CL and OPTIMA™ RUA-SW series. Other non-limiting examples of FP type electrodes comprise valve metals such as titanium and tantalum and coatings of doped valve metal oxides doped comprising or consisting essentially of titanium oxide and tantalum oxide and at least one oxide of a dopant selected from the group consisting of silver, tin, chromium, lanthanum, aluminum, cobalt, antimony, molybdenum, nickel, iron, tungsten, vanadium, phosphorus, boron, beryllium, sodium, calcium, strontium, lead, copper and bismuth. Still other non-limiting FP type electrodes include those disclosed by Bianchi et al. in U.S. Patent No. 3,948,751, which is incorporated herein by reference in its entirety for all purposes, such as but not limited the coatings, loadings of electrocatalytic coatings, and fabrication techniques disclosed therein.

Chlorine and oxygen gas are typically produced at the anode, which provides acidic pH conditions as a result of protons generated at its surface. In contrast, the

cathode is typically exposed to alkaline or high pH conditions associated with the generation of negatively-charged hydroxyl ions. Such an alkaline pH environment promotes formation of insoluble inorganic compounds such as hydroxides and carbonates of calcium and magnesium, which typically undesirable deposit on cathode surfaces. This process of formation of water-insoluble calcareous deposits on a cathode surface is collectively called scaling. In pool and spa applications, forward polarity type cells are prone to scaling because hardness ions are typically present in tap water used in such systems. Indeed, the hardness level of pool water typically increases over time because evaporation of water and the consequent addition of make-up water would introduce more calcium and magnesium species. As calcareous deposit grows over time of service it may bridge the gap between the anodes and the cathodes which may result in short circuiting the electrodes and a permanent damage to the cell. Consequently, forward polarity type devices must be periodically cleaned, typically with an acid such as muriatic acid, to dissolve the scale.

Chlorine generators can utilize reversing polarity (RP) techniques to remove scale. RP type cells are also called self-cleaning cells. FIG. 3B shows the reversal of the polarity of the electrodes, which results in alternating the pH of the electrode surface or environment, from caustic to acidic, which facilitates removing the scale. Current reversal is typically performed every a few hours. When the direction of the applied current (polarity) is reversed, calcareous deposits do not dissolve but rather soften and become dislodged and washed away with the passing flow of water. This symmetrical reversing mode of operation utilizes identical time intervals and identical current densities or magnitudes during each of the alternating operating modes. Because the electrodes alternately serve both as anodes and cathodes in symmetric RP type devices, each of the electrodes requires mixed metal oxide or platinum metal electrocatalytic coating on all surfaces of all electrodes, in either the monopolar or bipolar configurations. Titanium then becomes the only choice of the substrate for all electrodes. These symmetrically reversed RP type apparatus require reverse polarity type coatings and typically operate at relatively low current densities. RP type coatings or electrodes are commercially available from Siemens Water Technology Corp. under the OPTIMA™ RUA and OPTIMA™ RUA-XL series. Examples of RP type

electrodes include those having a coating of a film-forming material comprising or consisting essentially of at least one of gold, silver, platinum, palladium, iridium, ruthenium, osmium, rhodium, iron, nickel, chromium, copper, lead, manganese, and nitrides, carbides, and sulfides thereof. In some cases, the coating can comprise or consist essentially of an oxide of any of gold, silver, iron, nickel, chromium, copper, lead, and manganese. In other cases, the coating comprises or consists essentially of an oxide of any of aluminum, tantalum, titanium, zirconium, bismuth, tungsten, and niobium. Preferred RP type electrodes comprise a coating of titanium oxide and ruthenium oxide. Still other preferred electrodes include those disclosed by Beer in U.S. Patent No. 3,933,616, which is incorporated herein by reference in its entirety for all purposes.

The systems and techniques of the present invention differ from such conventional symmetric RP type devices and methods by utilizing at least one operating mode with a shorter duration relative a primary operating mode. Further, some embodiments of the invention involve systems and techniques that involve asymmetric RP type cells that are operated at current densities greater than those utilized in symmetric RP type operations.

In accordance with some aspects of the invention, some embodiments can involve utilization of some advantageous features of FP type apparatus with some advantageous features of RP type apparatus for, for example, the in-line disinfection of the pool or spa water. In some cases, the present invention provides an electrochemical cell that operates in asymmetrical reversed polarity mode wherein an electrode is utilized as a primary anode and the counter-electrode is utilized as a primary cathode. FIG. 4 schematically illustrates a first operating mode and a second operating mode utilized in some aspects of the invention. In preferred embodiments, the primary anode typically comprises a titanium substrate with an electrocatalytic coating more typical utilized in forward polarity cells (Anode coating), and the primary cathode comprises a titanium substrate with an electrocatalytic coating typically utilized in reverse polarity cells (Cathode coating). In further preferred embodiments, the catalyst (precious metals) coating loadings are significantly less than typical loadings utilized in reverse polarity applications. In operation, the primary anode operates predominantly, with

respect to service time or operating duration, under a positive charge electrochemically producing the product, e.g., chlorine (production cycle) at current densities that are same or greater than those typically utilized in traditional, symmetrical reversed polarity applications. In a second operating mode, the direction of the applied current is reversed, typically periodically, for a duration or period of time to remove scale deposited on the Cathode in a de-scaling cycle. Some aspects of the invention relate provide reduced likelihood of damage to the primary anode (which is now operationally considered a cathode) under a negative polarization by utilizing a lower current density and a shorter duration. Because chlorine generators for pool or spa water disinfection typically operate on a 30 – 70 % duty cycle, the reduction of chlorine production capacity during the de-scaling cycle is not expected to reduce overall performance.

The coating on the primary cathode can be selected from a range of reverse polarity coatings that are tolerant to cathodic polarization. In advantageous embodiments, the coating loading of the primary cathode can be significantly reduced, providing additional cost benefits.

Some aspects of the present invention provide increased durability and operational and cost flexibility of self-cleaning cells by facilitating or providing flexibility as to coatings that may be utilized. Indeed, some aspects of the invention advantageously provide an anode coating that is durable under adverse process conditions, such as water with high hardness or low salinity or conditions typically found in neglected pools, or process conditions with low water temperature operates during cold seasons.

Some aspects of the present invention relate to electrochemical systems and techniques for producing chlorine from water with low concentrations of sodium chloride, such as, but not limited to, systems utilized in swimming pool or spa installations. At least one electrode of such systems can have a chlorine-evolving, oxygen-tolerant electrocatalytic coating typical of a forward polarity coating, such as those comprising or consisting essentially of a mixed ruthenium and iridium oxide coating. The systems and techniques of the invention can also involve at least one counter electrode with or without electrocatalytic coating tolerant to polarity reversal conditions, such as those comprising or consisting essentially of ruthenium oxide based

and titanium oxide. The electrochemical cell can be operated with two distinctive regimes or operating modes of chlorine production; a positive charge can be applied to the electrodes with a forward polarity type coating for several hours or less at a current density in a range of from 50 A/m^2 to 1000 A/m^2, preferably in a range of from about 200 A/m^2 to about 700 A/m^2, and more preferably in a range of from about 300 A/m^2 to about 600 A/m^2; and of a cathode de-scaling regime or operating mode when a positive charge is applied to the counter electrode or electrodes with a reversed polarity coating, for a duration of about 2 minutes to about 30 minutes, at a current density in a range of from about 1 A/m^2 to 100 A/m^2, preferably for a duration of about 5 minutes to about 20 minutes, at a current density of from about 10 to about 70 A/m^2, and more preferably for a duration of about 5 minutes to about 15 minutes, at a current density in a range of from about 15 A/m^2 to about 50 A/m^2.

Some aspects of the invention provide techniques of fabricating electrodes that have electrocatalytic coating on substantially all wetted surfaces. In some cases, the electrodes have an electrocatalytic coating on a surface with the least surface area. Conventional fabrication techniques typically involve applying an electrocatalytic coating on substrate surfaces and cutting the coated substrate to desired dimensions. The electrodes in accordance with some aspects of the invention can be prepared from a plurality of substrates having desired or predetermined dimensions. The coating techniques thus advantageously provide or facilitate electrodes with surfaces coated with the electrocatalytic coating, in contrast to conventional techniques that result in exposed, uncoated surfaces at cutting surfaces. The coating can be applied by utilizing brush, rollers or spray techniques to dispose a precursor mixture or coating solution on the, for example, titanium, substrates. The precursor coatings are dried and, if desired, additional mixtures are applied to achieve a desired coating loading. Where electrodes utilize a FP type coating on one side and a RP type coating another other side, the various types of coating can be applied with masks preventing undesirable application of the precursor mixture. The precursor coated substrates can then be heated to convert at least a portion of the precursor mixture into the desired mixed oxide electrocatalytic coating. Non-limiting examples of precursor mixtures can include salts of ruthenium, iridium, titanium dissolved in a solvent as disclosed in the above-noted references.

Some techniques and embodiments of the invention thus provide electrodes with wetted surfaces that are coated with, for example, RP type coatings that promote acid generation during a second or alternate operating mode.

As exemplarily illustrated in FIG. 1, a system 100 in accordance with some aspects of the invention can comprise at least one reactor, such as an electrolytic device or electrolyzer 110. Although the embodiments described herein involve electrolytic devices, the various aspects of the invention are not limited to such devices, and other systems utilizing electrically-driven apparatus or reactors may be implemented with the systems and techniques of the present disclosure. Electrolytic device 110 is typically connected to at least one source 160 of at least one reactant, electrolyte or, preferably, a fluid comprising at least one precursor species that can be converted to at least one desirable species or product. For example, source 160 can provide water having a nominal level of a precursor species that is catalyzed into a biocide or one or more biocidal precursory compounds. An outlet of electrolyzer 110 is typically fluidly connected to at least one point of use 170. Other embodiments of system 200, however, may involve in situ conversion of the precursor species into the desirable product. For example, electrolyzer 110, or at least a portion thereof, may be immersed in source 160 or in point of use 170, or both, to convert chloride species into hypochlorite or chlorine compounds.

Electrolyzer 110 can serve as a reactor that converts or at least facilitates conversion of one or more precursor species into at least one intermediate species that can be subsequently converted or modified into at least one desirable compound. In some embodiments, system 200 can be implemented as a treatment system such as a water treatment system. Thus, some advantageous embodiments of the invention can involve electrocatalytically converting a halogenated precursor species into a biologically active compound that renders at least one microorganism or at least one type of microorganism at least partially inactivated, or incapable of further biological activity. For example, source 160 can provide water having dissolved chloride species that can be electrocatalyzed in electrolyzer 110 into a hypochlorite biocide. In such aspects of the invention, electrolyzer 160 can be immersed in source 160, or in point of use 170. Preferably configured embodiments can involve at least one electrolyzer 110

immersed in a fluid that serves as a source and a point of use. For example, electrolyzer 110 can be submerged in a swimming pool or spa having one or more openings or ports serving as water inlets or outlets. In other cases, however, a side stream can be established between, for example, a body of water to be treated. In such embodiments, electrolyzer 110 can be disposed in a flow path defining the side stream from and to the body of water.

Electrolyzer 110 can comprise at least one set of electrodes. For example, electrolyzer 110 can comprise at least one first electrode 120 and at least one second electrode 130. System 200 can comprise at least one ancillary component that facilitates the operation, such as the conversion of the reactor. For example, as an electrolyzer, reactor 110 can be electrically driven with one or more power supplies 150, which provides electrical current to electrodes 120 and 130. In some particular embodiments of the invention, one or more controllers or control systems 140 can be utilized in system 200, which, as described below, can facilitate various advantageous features of the invention.

The power supply typically provides energy, such as an electric current, to the reactor to facilitate the operation of reactor. In particular, power supply 150 is preferably configured to provide electrical current to facilitate electrochemical conversion of at least one precursor species into at least one desirable product. In still particular embodiments, power supply 150 provides a direct current passed through electrodes 120 and 130 that facilitates electrochemically converting one or more precursor species into a desirable intermediate compounds or a biocide or microorganism inactivating agent.

Any of the electrodes can have a variety of configuration or arrangements. For example, any of electrodes 120 and 130 can be at least partially immersed such that surfaces thereof are wetted by the fluid having at least one precursor species flowing along a flow path 240, as illustrated in FIG. 2. In the exemplarily illustrated configuration, a leading edge or leading surface 230 which is typically a smaller planar dimension relative to a larger dimension 250. Electrode 120 is typically connected to the power supply at terminal 225.

As illustrated in FIG. 3A, forward polarity type electrolyzers are operated in a single operating mode wherein the applied electric current is relatively constant. In such cases, one of electrodes 120 and 130 typically serves as an anode and the other corresponding electrode 130 or 120 can serve as a cathode during all operating modes of the electrolyzer. As illustrated in FIG. 3B, reversing polarity type electrolyzers are operated in a first mode with an electric current, wherein a first electrode serves as an anode and a second electrode serves as a cathode, and in a second mode with an electric current wherein the first electrode serves as a cathode and the second electrode serves as an anode. The polarity of the applied electric current in the second operating mode is reversed or in an opposite direction relative to the polarity or direction of applied electric current in the first operating mode.

The characteristics of the applied electric through electrolyzer 110 can be regulated by control system 140. However, power supply 150 can have an integrated control module that provides, adjusts or maintains one or more characteristics of the supplied electric current. Control system 140 can provide one or more output signals to one or more power supplies 150 to regulate at least one characteristic of the supplied electric current. For example, control system 140 can be configured to regulate the magnitude of the potential or voltage of the supplied current to electrolyzer 110. In other cases, control system 140 can generate an output signal that regulates a magnitude of the current supplied to electrolyzer 110, or the current density of the applied electric current through electrodes 120 and 130. In still other cases, control system 140 can generate an output signal that regulates a polarity of electric current supplied or passing through electrolyzer 110. In yet other cases, control system 140 can generate an output signal that regulates a duration or period of electric current supplied to or passing through electrolyzer 110. Any such output control signals can be in addition to or in lieu of any of the other types of control signals.

In accordance with some aspects of the invention, control system 140 can also be configured to regulate the electric current from one or more power supplies 150 to provide composite operating conditions comprising a plurality of operating modes. In accordance with one aspect of the invention, the plurality of operating modes can refer to regulating a characteristic of electric current passing through electrolyzer 110 at a

plurality of levels. In accordance with another aspect of the invention, the plurality of operating modes can refer to regulating a plurality of characteristics of electric current passing through electrolyzer 110. In accordance with still another aspect of the invention, the plurality of operating modes can refer to a plurality of characteristics including, but not limited to polarity or direction of the current, the duration of the current in any of the directions, the magnitude of the potential of the electric current, and the magnitude of the electric current.

In accordance with some advantageous aspects of the invention, control system 140 can be configured to regulate the polarity or direction of the applied electric current to, for example, the electrolyzer to be in a first operating mode such that an electrode of the electrolyzer serves as an anode with an applied current having a first magnitude, as represented as 420 in FIG. 4. The associated electrode, in the first operating mode typically has a corresponding cathodic current. Control system 140 can be further configured to control power supply 150 to provide electric current in the first mode for a duration t_p. Control system 140 can be further configured modify the operating parameters of system 200 into a second control mode. The second control mode can involve an applied electric current through electrolyzer 110 having a polarity or direction that is opposite the current in the first operating mode. Thus, as illustrated in FIG. 4, the electric current 420 in the second mode through electrolyzer 110 renders the previously serving anode to be cathodic, and the previously serving cathode is rendered anodic. The second operating mode can be applied for a duration t_a, which is typically different from t_p. Notable embodiments of the invention can be implemented utilizing a plurality of levels or magnitude of characteristics of the applied electric current. For example, the amount or magnitude of the potential, e.g., volts, of the electric current in the second mode can differ from the potential of the applied electric current in the first mode. In other cases, the amount or magnitude of the current or current density through the electrodes of the electric current in the second mode can differ from the amount of current or current density of the electric current in the first mode. Depending on several considerations, such as but not limited to, any of an acceptable coating wear rate, applied current density and/or potential, coating loading, and salinity of the electrolyte or concentration of the precursor species, duration t_p can be at least

about 10 % greater than duration t_a, preferably, greater than about 25 %, more preferably greater than about 50 %, even more preferably greater than about 100 %. Also depending on similar considerations, the current density or applied current in the first mode can be at least 10 % greater than the current density or current in the second mode, preferably at least 25 % greater, more preferably at least 50 % greater, even more preferably at least 100 % greater.

In other aspects of the invention, the current densities in the various operating modes can be varied. For example, in some embodiments, electrolyzer 110 can have a plurality of primary electrodes and a plurality of secondary electrodes. At least one of the primary electrodes can have a first electric current in a first direction and at a first current level or potential whereas, in a second operating mode one or more of the primary electrodes can have a different current density applied therethrough, relative to the current density in the first operating mode.

Electrodes 120 and 130 can comprise a conductive substrate and, on at least a portion of a surface of the substrate, an electrocatalytic coating. The electrocatalytic coating can promote or inhibit one or more electrochemical reactions. In some cases, at least one electrode can have an electrocatalytic coating conventionally utilized in reversing polarity operating conditions. In other cases, at least one electrode can have an electrocatalytic coating comprising metal oxides conventionally utilized only in forward polarity conditions.

At least one embodiment pertinent to some aspects of the invention can involve utilization of mixed types of electrodes, including, but not limited to, at least one primary electrode 510 and at least one secondary electrode 520. At least one primary electrode 510, exemplarily illustrated as a cathode in FIG. 5A in a first operating mode, can comprise an electrocatalytic coating 515 on at least a portion of a surface of a substrate 518. In some embodiments pertinent to some aspects of the invention, electrocatalytic coating 515 can comprise or consist essentially of RP type coatings. At least one secondary electrode 520, illustrated as an anode, can comprise an electrocatalytic coating 525 on at least a portion of at least one surface of a substrate 528. Electrocatalytic coating 525 typically differs in composition from the composition

of the electrocatalytic coating on the primary electrode. Coating 525 can comprise or consist essentially of FP type coatings.

The non-limiting embodiment illustrated in FIG. 5A depicts a monopolar type cell arrangement. Other coatings, electrodes, or cell arrangements may be utilized. For example, electrolyzer 110, as illustrated in the bipolar cell in FIG. 5B, can comprise at least one primary electrode 540, illustrated in a first operating mode as an anode, comprising at least one type of electrocatalytic coating 545 disposed on at least a portion of a surface of a substrate 548 thereof. Electrocatalytic coating 545 can comprise or consist essentially of FP type coatings. The electrolyzer can further comprise at least one secondary electrode 550, illustrated as a cathode, comprising at least one type of another electrocatalytic coating 555 disposed on at least a portion of a surface of a substrate 558. Coating 555 typically differs from the coating on electrode 540. In some particular embodiments, coating 555 can comprise or consist essentially of RP type coatings.

Another electrode can be utilized. Electrolyzer 110 can utilize a bipolar cell arrangement and can comprise a third electrode 560 having, for example, a conductive substrate 568 with a plurality of types of electrocatalytic coatings. Electrode 560 can comprise at least one RP type coating 555 and at least one FP type coating on surfaces of substrate 568.

In some embodiments of the invention, the electrocatalytic coating on at least one electrode can be at a loading that is less than conventionally utilized when such electrodes are utilized in conventional reversing polarity applications. In some cases, the electrolyzers are operated, in at least one operating mode, with current densities that are the same or greater than current densities utilized in conventional electrolyzers, and, in a second operating mode, typically at an opposite polarity, at current densities that are less than current densities conventionally utilized. In particularly advantageous embodiments, the current densities utilized in the second or other operating mode, are at least 50 % less than current densities in applied in the first operating mode, preferably at least 75 % less.

In any of the above-noted operating modes, the applied electrical current facilitates conversion of at least one precursor species into a desirable product. For

example, at an anode of the electrolyzer, anodic half-cell reaction according to equation (1a) and (1b) may occur. At a cathode of the electrolyzer, cathodic reactions according to equation (2) may be promoted.

(1a) $2Cl^- - 2e^- \rightarrow Cl_2$

(1b) $2H_2O - 4e^- \rightarrow O_2 + 4H^+$

(2) $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

The overall reaction is represented according to equation (3).

(3) $Cl_2 + OH^- \rightarrow HOCl + Cl^-$

Some notable embodiments of the invention, however, may utilize non-metallic electrodes or at least one electrode having a polymeric material. For example, a carbon-filled polymeric electrode may be utilized as an electrode or at least a portion of any of the primary and secondary electrodes. Examples of polymeric materials that may be utilized in some embodiments of the invention include, but are not limited to, those commercially available as GRAFCELL® graphite from GrafTech Advanced Energy Technology Inc., Cleveland, Ohio.

Substrates 518, 528, 548, and 558 can comprise an electrically conductive material. Non-limiting examples of materials that can be utilized as substrates include titanium metal, and alloys of corrosion resistant metals such as those under the mark HASTELLOY.

Other techniques may be utilized to prevent or at least inhibit deposition of a hardness compounds. For example, a non-conductive coating can be applied to surface 230 to prevent the scaling thereon by inhibiting electrocatalytic activity.

Control system 140 can be configured to provide at least one control signal that regulates or controls one or more operating parameters of power supply 150, electrolytic device 110.

Some advantageous embodiments of the invention can be implemented with a power supply or power source 150 configured to provide the electrical current without an external control system. Thus, for example, some aspects of the invention can be implemented utilizing one or more power supplies 150, having an integrated controller, that provide the various operating modes described herein.

The controller or control system 140 may be implemented using one or more computer systems. The computer system may be a general-purpose computer such as those based on an Intel PENTIUM®-type processor, a Motorola PowerPC® processor, a Sun UltraSPARC® processor, a Hewlett-Packard PA-RISC® processor, or any other type of processor or combinations thereof. Alternatively, the computer system may include specially-programmed, special-purpose hardware, for example, an application-specific integrated circuit (ASIC) or controllers intended for analytical systems.

Control system 140, schematically illustrated in FIG. 8, can include one or more processors 805 typically connected to one or more memory devices 810, which can comprise, for example, any one or more of a disk drive memory, a flash memory device, a RAM memory device, or other device for storing data. Memory 810 is typically used for storing programs and data during operation of the system and/or control system 140. For example, memory 810 may be used for storing historical data relating to the parameters over a period of time, as well as operating data. Software, including programming code that implements embodiments of the invention, can be stored on a computer readable and/or writeable nonvolatile recording medium 810, and may then be copied into volatile memory 820 wherein it can then be executed by processor 805. Such programming code may be written in any of a plurality of programming languages, for example, Java, Visual Basic, C, C#, or C++, Fortran, Pascal, Eiffel, Basic, COBAL, or any of a variety of combinations thereof.

Components of control system 140 may be coupled by an interconnection mechanism 830, which may include one or more busses (e.g., between components that are integrated within a same device) and/or a network (e.g., between components that reside on separate discrete devices). The interconnection mechanism typically enables communications (e.g., data, instructions) to be exchanged between components of the treatment system or control system 140.

Control system 140 can also include one or more input components 840 such as, but not limited to, a keyboard, mouse, trackball, microphone, touch screen, configured to provide input signals , i_1, i_2, i_3, ..., i_n, and one or more output devices 850 such as, but not limited to, a printing device, display screen, or speaker, configured to generate one or more output signals, drive signals, or control signals, , s_1, s_2, s_3, ..., s_n, any one or

more may be utilized in one or more components or subsystems of the systems of the invention. In addition, control system 140 may contain one or more interfaces (not shown) that can connect control system 140 to a communication network (in addition or as an alternative to the network that may be formed by one or more of the components thereof).

According to one or more embodiments of the invention, the one or more input devices may include sensors for measuring parameters. Alternatively, the sensors, the metering valves and/or pumps, or all of these components may be connected to a communication network that is operatively coupled to control system 140. For example, one or more sensors may be configured as input devices that are directly connected to control system 140. Any one or more of the control system or subsystem components may be coupled to another computer system or component so as to communicate with another computer system over a communication network.

As exemplarily shown in FIG. 8, controller 140 can include one or more computer storage media such as readable and/or writeable nonvolatile recording medium in which signals can be stored that define a program to be executed by one or more processors 805. The medium may, for example, be a disk or flash memory. In typical operation, processor 805 can cause data, such as code that implements one or more embodiments of the invention, to be read from the storage medium into a memory 820 that allows for faster access to the information by the one or more processors than does the computer readable medium. Memory 820 is typically a volatile, random access memory such as a dynamic random access memory (DRAM) or static memory (SRAM) or other suitable devices that facilitates information transfer to and from processor 805.

Although control system 140 is shown by way of example as one type of computer system upon which various aspects of the invention may be practiced, it should be appreciated that the invention is not limited to being implemented in software, or on the computer system as exemplarily shown. Indeed, rather than implemented on, for example, a general purpose computer system, the controller, or components or subsections thereof, may alternatively be implemented as a dedicated system or as a dedicated programmable logic controller (PLC) or in a distributed

control system. Further, it should be appreciated that one or more features or aspects of the invention may be implemented in software, hardware or firmware, or any combination thereof. For example, one or more segments of an algorithm executable by the controller can be performed in separate computers, which in turn, can be communication through one or more networks.

Examples

The function and advantages of these and other embodiments of the invention can be further understood from the examples below, which illustrate the benefits and/or advantages of the one or more systems and techniques of the invention but do not exemplify the full scope of the invention.

In the examples, accelerated aging tests were performed under various conditions.

Failure of the electrode or electrocatalytic coating was defined to be when the applied potential of the electrical current increased by one volt over the initial applied potential.

Example 1. RP Type Electrodes in Conventional Reverse Polarity Operation.

Three samples with RP type coatings at electrocatalyst loadings of about 8 g/m^2, about 20 g/m^2, and about 28 g/m^2 were evaluated in accelerated aging test with an applied current density of about 1500 A/m^2 in symmetrical reversed polarity regimes. The periodic reversal durations cycled of two hours and four hours, for either current direction. All electrodes had the same coating and coating loading.

The results are presented in Table 1 and FIG. 6A. The data show that the lifetime of the electrodes was found to be proportional to their corresponding electrocatalyst loadings (based on total precious metal). Further, for the same electrocatalyst loading, failure was about 20 % lower for electrodes exposed to the two hour duration cycles. Wear rate of the coating was about 8.5 μg/A·hr and 5.0 μg/A·hr for each electrode in the pair for 2 and 4 hour reversal time, correspondingly. More frequent reversal led to 45 % increase in the coating wear rate.

Table 1

Coating Type on each electrode		Reversal Time, hours		Electrocatalyst Loading, Grams of precious metal per square meter		Time to failure in accelerated aging test, hours	Average Electrocatalyst Wear Rate on each electrode, μg/A·hr	
1	2	Forward	Reverse	1	2		1	2
RP	RP	2	2	7.7	7.7	19		
RP	RP	2	2	19.2	19.2	40.5	8.3	8.9
RP	RP	2	2	28.2	28.2	58		
RP	RP	4	4	7.7	7.7	23		
RP	RP	4	4	21.7	21.7	52	5.0	4.8
RP	RP	4	4	28.4	28.4	84		

Example 2. FP Type Electrodes in Conventional Reverse Polarity Operation.

Electrodes with FP type coatings at electrocatalyst loadings of about 3 g/m², about 6 g/m², and about 8.5 g/m² were evaluated tested under accelerated aging conditions. The applied electrical current was about 1,500 A/m² in symmetrical reversed polarity modes. The production cycles were also two hours and four hours, for either current direction. All electrodes had the same coating and coating loading.

The results are presented in Table 2 and FIG. 6B. The data show that forward polarity type coatings used in symmetrical reversed polarity operating modes do not have any significant advantages over reversed polarity coatings. Indeed, the performance of electrodes utilizing FP type coatings undesirably fail before coatings intended for reverse polarity operations. Thus, FP type coatings cannot tolerate current reversal conditions.

Table 2

Coating Type on each electrode		Reversal Time, hours		Electrocatalyst Loading, Grams of precious metal per square meter		Time to failure in accelerated aging test, days	Average Electrocatalyst Wear Rate on each electrode, μg/A·hr	
1	2	Forward	Reverse	1	2		1	2
FP	FP	2	2	2.8	2.8	8.0	4.8	4.6
FP	FP	2	2	6.1	6.2	17		
FP	FP	2	2	8.5	8.3	23		
FP	FP	4	4	2.8	2.8	9	3.4	3.5
FP	FP	4	4	5.8	5.8	26		

Example 3. RP Type Electrodes in Asymmetric Operation.

One out of the three electrode samples having the RP type coating as in Example 1, with an electrocatalyst loading of 7.7 g/m², were evaluated in accelerated aging tests using an asymmetrical reversed polarity operations in accordance with some aspects of the invention. The production cycles (first operating mode) were performed for two hours or four hours. The asymmetrical, reverse polarity, de-scaling cycle (second operating mode) was performed for ten minutes. The applied current density was at about 1,500 A/m² during the production cycle and about 50 A/m² during the de-scaling cycle.

The results are presented in Table 3 and FIG. 6C. The data show that the asymmetrical regime does not provide notable advantages relative to electrode service life when reversed polarity type coatings are used on all electrodes. The wear rate of the coating was found to be about 7.2 μg/A·hr and 5.5 μg/A·hr for a primary anode and 2.2 μg/A·hr and 1.0 μg/A·hr for a primary cathode in the electrode pair for the two hour and four hour production cycle tests, respectively. More frequent reversal led to about a 24 % increase in the coating wear rate as compared to a 45 % increase in Example 1. Increase in the wear rate at the four hour production cycle is attributable to exposure of the RP type coating to the anode polarization for an extended period of time, compared to a symmetrical reverse polarity operating mode. Coating wear rate on a primary cathode has been significantly reduced as compared to the symmetrical reverse polarity

operating mode, as the primary cathode is exposed to anodic polarization only for a short period of time and at reduced current density.

Table 3

Coating Type on each electrode		Reversal Time, hours		Electrocatalyst Loading, Grams of precious metal per square meter		Time to failure in accelerated aging test, days	Average Electrocatalyst Wear Rate on each electrode, μg/A·hr	
1	2	Forward	Reverse	1	2		1	2
RP	RP	2	1/6	7.6	7.6	19	7.2	2.2
RP	RP	4	1/6	7.7	7.7	19	5.5	1.0

Example 4. Mixed Type Electrodes in Asymmetric Operation.

Electrode samples with FP type coatings, as in Example 2, were used as primary anodes and electrodes with RP type coatings (at electrocatalyst loadings of between about 6 g/m^2 and 8 g/m^2) were used as primary cathodes in accelerated aging tests under asymmetrical reversed polarity operating modes. The production cycle was performed for about two hours and for about four hours; and a de-scaling cycle or asymmetric operating mode (with an opposite polarity relative to the polarity during the production cycle) was performed for about ten minutes. The current density during the production cycle was applied at about 1,500 A/m^2; and the current density during the asymmetric reverse operating mode was applied at about 50 A/m^2.

The results are presented in Table 4 and FIG. 6D. The data show that utilizing an asymmetrical operating mode improves service life when forward polarity type coatings are used on primary anodes and when reversed polarity type coatings are used on primary cathodes. The data also show that coating wear rate on the primary anode and the primary cathode can be significantly reduced when using asymmetric reversed polarity regimes, as compared to when symmetrical reversed polarity regimes are employed.

Table 4

Coating Type on each electrode		Reversal Time, hours		Electrocatalyst Loading, Grams of precious metal per square meter		Time to failure in accelerated aging test, days	Average Electrocatalyst Wear Rate on each electrode, μg/A·hr	
Primary Anode	Primary Cathode	Forward	Reverse	Primary Anode	Primary Cathode		Primary Anode	Primary Cathode
FP	RP	2	1/6	2.8	7.7	11	3.1	0.9
FP	RP	2	1/6	6.3	7.6	24		
FP	RP	4	1/6	2.8	7.7	14	3.0	0.7
FP	RP	4	1/6	5.8	5.9	52		

Example 5

An electrode with FP type coating (at electrocatalyst loading of about 6 g/m^2) was used in an electrolyzer as a primary anode. A graphite electrode comprising GRAFCELL carbon-based material, manufactured by GraphTech, Cleveland, Ohio, was utilized as a primary cathode in the electrolyzer. Accelerated aging test were performed utilizing asymmetrical reversed polarity operation. The chlorine production cycle was operated for about four hours; and the asymmetric operating mode, the de-scaling cycle was performed for about ten minutes. The electrical current density was at about 800 A/m^2 during the production cycle; and the current density was at about 50 A/m^2 during the de-scaling operating mode. At the same time, two electrodes with RP type coating with electrocatalyst loading of about 8 g/m^2 have been tested in accelerated aging test using symmetrical reversed polarity regime with reversal cycle of 4 hours at the same current density of about 800 A/m^2.

The results are presented in Table 5 and in FIG. 6E. The data show that asymmetrical reversed polarity regime allows utilization of a cathode material other than a titanium substrate coated with expensive precious metal coatings.

Table 5

Coating Type on each electrode		Reversal Time, hours		Electrocatalyst Loading, Grams of precious metal per square meter		Time to failure in accelerated aging test, days	Average Electrocatalyst Wear Rate on each electrode, μg/A·hr	
Primary Anode	Primary Cathode	Forward	Reverse	Primary Anode	Primary Cathode		Primary Anode	Primary Cathode
FP	Graphite	4	1/6	6.1	n/a	82	2.3	n/a
RP	RP	4	4	7.6	7.7	59	4.2	4.1

FIG. 7 summarizes the results from the Examples and shows that an asymmetric reversed polarity regime with a FP type coating on a primary anode and a RP type coating on a primary cathode can provide significantly improved durability performance over traditional reversed polarity types, at the same electrocatalyst loading.

Having now described some illustrative embodiments of the invention, it should be apparent to those skilled in the art that the foregoing is merely illustrative and not limiting, having been presented by way of example only. Numerous modifications and other embodiments are within the scope of one of ordinary skill in the art and are contemplated as falling within the scope of the invention. In particular, although many of the examples presented herein involve specific combinations of method acts or system elements, it should be understood that those acts and those elements may be combined in other ways to accomplish the same objectives.

Those skilled in the art should appreciate that the parameters and configurations described herein are exemplary and that actual parameters and/or configurations will depend on the specific application in which the systems and techniques of the invention are used. Those skilled in the art should also recognize or be able to ascertain, using no more than routine experimentation, equivalents to the specific embodiments of the invention. It is therefore to be understood that the embodiments described herein are presented by way of example only and that, within the scope of the appended claims

and equivalents thereto; the invention may be practiced otherwise than as specifically described.

Moreover, it should also be appreciated that the invention is directed to each feature, system, subsystem, or technique described herein and any combination of two or more features, systems, subsystems, or techniques described herein and any combination of two or more features, systems, subsystems, and/or methods, if such features, systems, subsystems, and techniques are not mutually inconsistent, is considered to be within the scope of the invention as embodied in the claims. Further, acts, elements, and features discussed only in connection with one embodiment are not intended to be excluded from a similar role in other embodiments.

As used herein, the term "plurality" refers to two or more items or components. The terms "comprising," "including," "carrying," "having," "containing," and "involving," whether in the written description or the claims and the like, are open-ended terms, i.e., to mean "including but not limited to." Thus, the use of such terms is meant to encompass the items listed thereafter, and equivalents thereof, as well as additional items. Only the transitional phrases "consisting of" and "consisting essentially of," are closed or semi-closed transitional phrases, respectively, with respect to the claims. Use of ordinal terms such as "first," "second," "third," and the like in the claims to modify a claim element does not by itself connote any priority, precedence, or order of one claim element over another or the temporal order in which acts of a method are performed, but are used merely as labels to distinguish one claim element having a certain name from another element having a same name (but for use of the ordinal term) to distinguish the claim elements.

U.S. Provisional Application Serial No. 60/910,353, entitled METHOD AND APPARATUS FOR IN-LINE CHLORINATION OF POOLS AND SPAS, filed on April 5, 2007, is incorporated herein by reference in its entirety.

CLAIMS

1. A method of providing a biocide, comprising:

introducing water having a chloride concentration of less than about 6,000 ppm into an electrolyzer;

electrolyzing at least a portion the chloride with a first electric current applied through the electrolyzer in a first direction to produce the biocide; and

passing a second electric current through the electrolyzer in an opposite direction relative to the first direction,

wherein a magnitude of the second electric current is less than a magnitude of the first electric current.

2. The method of claim 1, wherein electrolyzing is a performed for a first duration and passing the second electric current is performed for a second duration less than the first duration.

3. The method of claim 2, wherein the magnitude of the first electric current in the first operating mode is at least twice the magnitude of the second electric current in the second operating mode.

4. The method of claim 3, wherein the electrolyzer comprises at least one primary electrode having an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide disposed on a conductive substrate.

5. The method of claim 4, wherein the electrolyzer comprises at least one secondary electrode having an electrocatalytic coating comprising ruthenium oxide and titanium oxide disposed on a conductive substrate.

6. A method of modifying a treatment system having an electrolyzer, comprising:

connecting a controller to the electrolyzer, the controller configured to regulate electric current to the electrolyzer in a first operating mode and in a second operating mode, the first operating mode having primary electric current regulated to a first current level, the second operating mode having an asymmetric electric current at an opposite polarity relative to the primary electric current and at a second current level that is less than the first current level; and

replacing at least one electrode of the electrolyzer with at least one of a carbon-filled polymeric electrode, an electrode comprising an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide, and an electrode comprising electrocatalytic coating comprising ruthenium oxide and titanium oxide.

7. The method of claim 6, further comprising replacing an electrode of the electrolyzer with an electrode comprising an electrocatalytic coating consisting essentially of ruthenium oxide and titanium oxide.

8. The method of claim 6, further comprising replacing an electrode of the electrolyzer with an electrode comprising an electrocatalytic coating consisting essentially of ruthenium oxide, iridium oxide, and titanium oxide.

9. The method of claim 6, further comprising replacing at least one electrode of the electrolyzer with at least one carbon-filled polymeric electrode.

10. The method of claim 6, wherein the controller is configured to regulate the primary electric current to the electrolyzer for a first duration and the controller is configured to regulate the asymmetric electric current for a second duration that is less than the first duration.

11. An electrolytic water treatment system, comprising:

an electrolyzer fluidly connectable to a source of water having a salinity of less than about 2.5 %, the electrolyzer comprising at least one primary electrode and at least one secondary electrode;

a power supply configured to deliver electrical current to the at least one primary electrode and the at least one secondary electrode; and

a controller configured to regulate the power supply to deliver a first electrical current at a first current level and to deliver a second electrical current at a second current level, wherein the second current level differs from the first current level.

12. The treatment system of claim 11, wherein the controller is configured to regulate the power supply to deliver the first electrical current for a first predetermined duration and to regulate the power supply to deliver the second electrical current for a second predetermined duration that differs from the first predetermined duration.

13. The treatment system of claim 12, wherein the first predetermined duration is at least twice the second predetermined duration.

14. The treatment system of claim 13, wherein the at least one primary electrode comprises a first substrate having a first electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide.

15. The treatment system of claim 14, wherein the at least one secondary electrode comprises a second substrate having a second electrocatalytic coating comprising ruthenium oxide and titanium oxide.

16. The treatment system of claim 15, wherein the first electrocatalytic coating consists essentially of ruthenium oxide, iridium oxide, and titanium oxide.

17. The treatment system of claim 16, wherein the second electrocatalytic coating consists essentially of ruthenium oxide and titanium oxide

18. The treatment system of claim 11, wherein the magnitude of the first current level is at least 25 % greater than the magnitude of the second current level.

19. The treatment system of claim 11, wherein a polarity of the second electrical current is opposite a polarity of the first electrical current.

20. The treatment system of claim 19, wherein all wetted surfaces of the at least one primary electrode are coated with an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide.

21. The treatment system of claim 19, wherein all wetted surfaces of the at least one secondary electrode are coated with an electrocatalytic coating comprising ruthenium oxide and titanium oxide.

22. The treatment system of claim 19, wherein the at least one primary electrode has a leading edge coated with an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide.

23. The treatment system of claim 19, wherein the at least one secondary electrode has a leading edge coated with an electrocatalytic coating comprising ruthenium oxide and titanium oxide.

24. The treatment system of claim 19, wherein one of the at least one primary electrode and the at least one secondary electrode comprises a carbon-filled polymeric electrode.

25. The treatment system of claim 11, wherein the electrolyzer is fluidly connected to a source of water having a salinity of less than about 0.5 %.

26. An electrolytic system comprising:

an electrolyzer having a primary electrode and a secondary electrode, at least one of the primary and secondary electrodes having an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide; and

a power supply configured to energize the primary and secondary electrodes in a first mode at a first polarity with a first potential level and a first current level, and to energize the primary and secondary electrodes in an asymmetric mode at a reverse polarity relative to the first polarity, wherein a magnitude of the second potential level differs from a magnitude of the first potential level.

27. The electrolytic system of claim 26, wherein the power supply is configured to energize electrodes in the first mode for a first duration and to energize the electrodes in the asymmetric mode for a second duration that is less than the duration of the first duration.

28. The electrolytic system of claim 26, wherein the primary electrode has an electrocatalytic coating comprising ruthenium oxide, iridium oxide, and titanium oxide.

29. The electrolytic system of claim 26, wherein the secondary electrode has an electrocatalytic coating comprising ruthenium oxide and titanium oxide.

30. The electrolytic system of claim 26, wherein at least one of the one primary electrode and the secondary electrode comprises a carbon-filled polymeric electrode.

31. A computer-readable including computer-readable signals stored thereon defining instructions that, as a result of being executed by at least one processor, instruct the processor to perform a method of controlling an electrolytic system comprising an electrolyzer fluidly connected to a source of non-thalassic water, the method comprising:

generating a first control signal that regulates a power supply to provide a primary electrolytic current for a first duration to the electrolyzer; and

generating a second control signal that regulates the power supply to provide an asymmetric current to the electrolyzer for a second duration that is less than the first duration.

32. The computer-readable medium of claim 31, wherein a polarity of the asymmetric current is opposite a polarity of the primary electrolytic current.

33. The computer-readable medium of claim 32, wherein a magnitude of the primary electrolytic current is greater than a magnitude of the asymmetric current.

34. The computer-readable medium of claim 33, wherein the method further comprises controlling a rate of flow of non-thalassic water from the source.

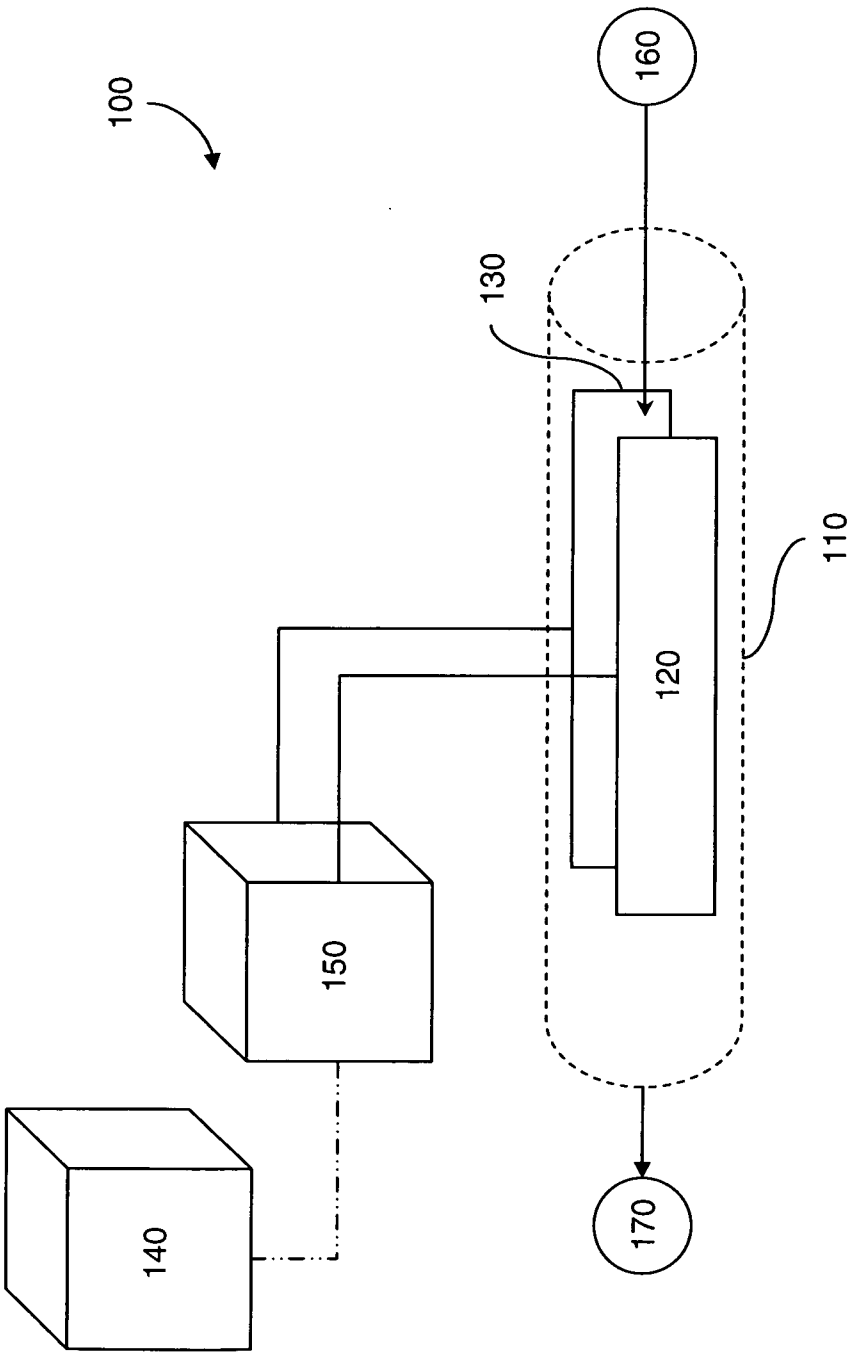

FIG. 1

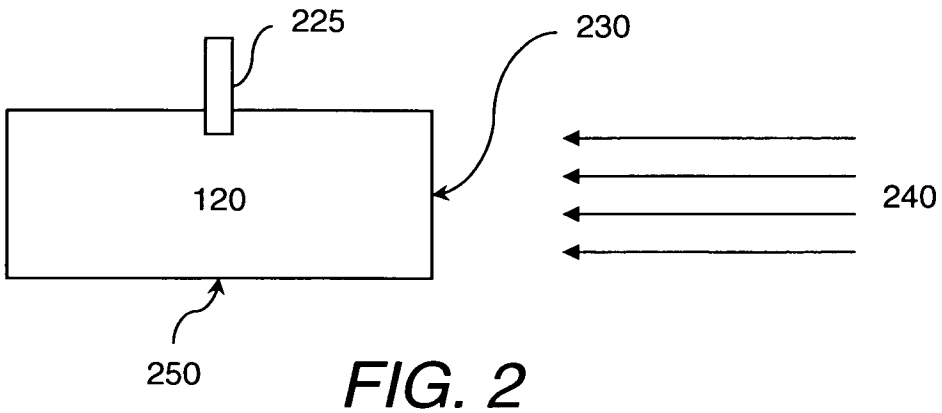
225
230
120
240
250

FIG. 2

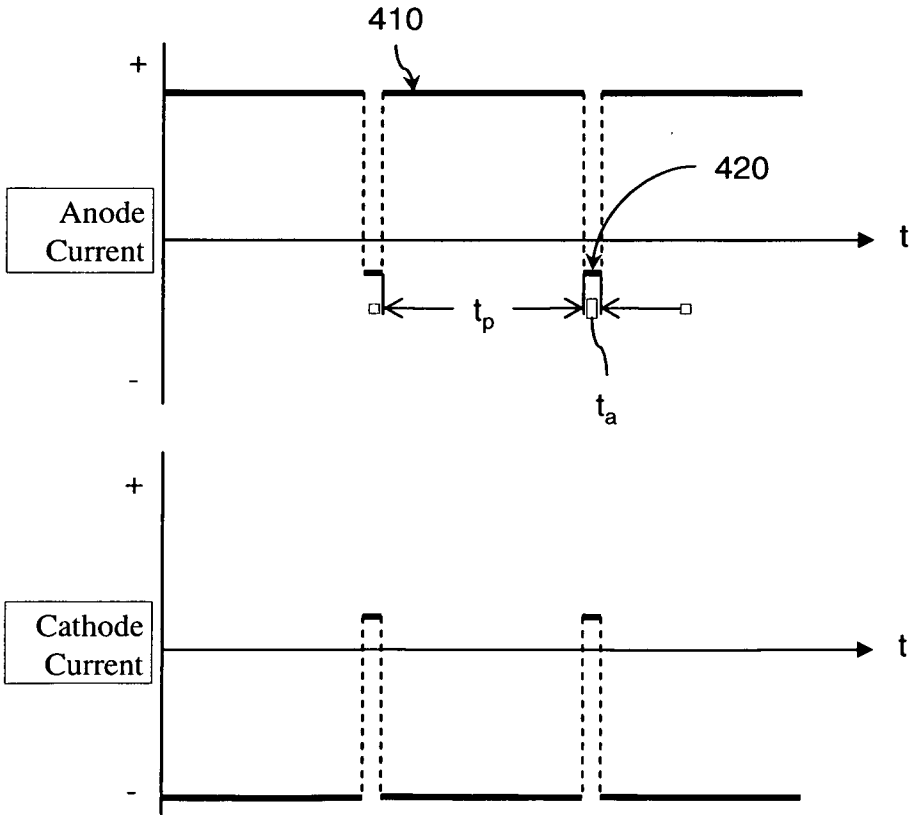
410
+
420
Anode Current
t
t_p
-
t_a
+
Cathode Current
t
-

FIG. 4

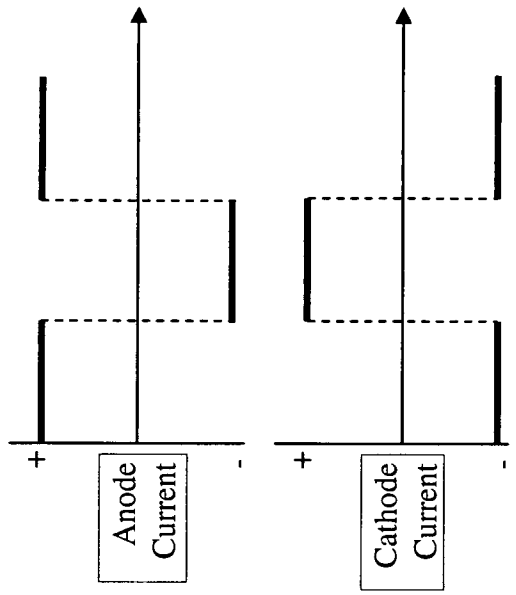
+
Anode Current
-
+
Cathode Current
-

FIG. 3B

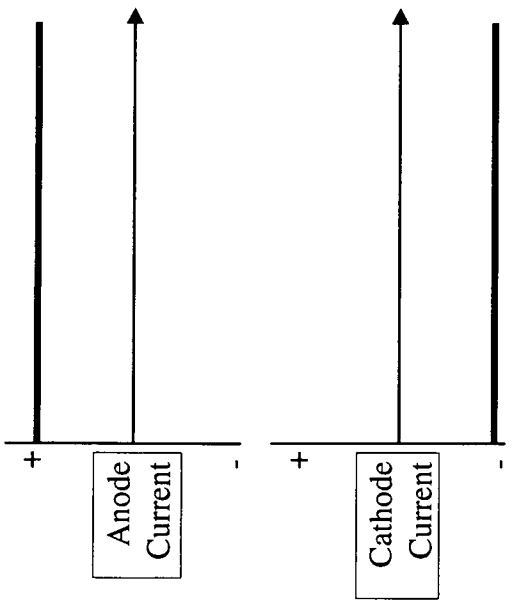
+
Anode Current
-
+
Cathode Current
-

FIG. 3A

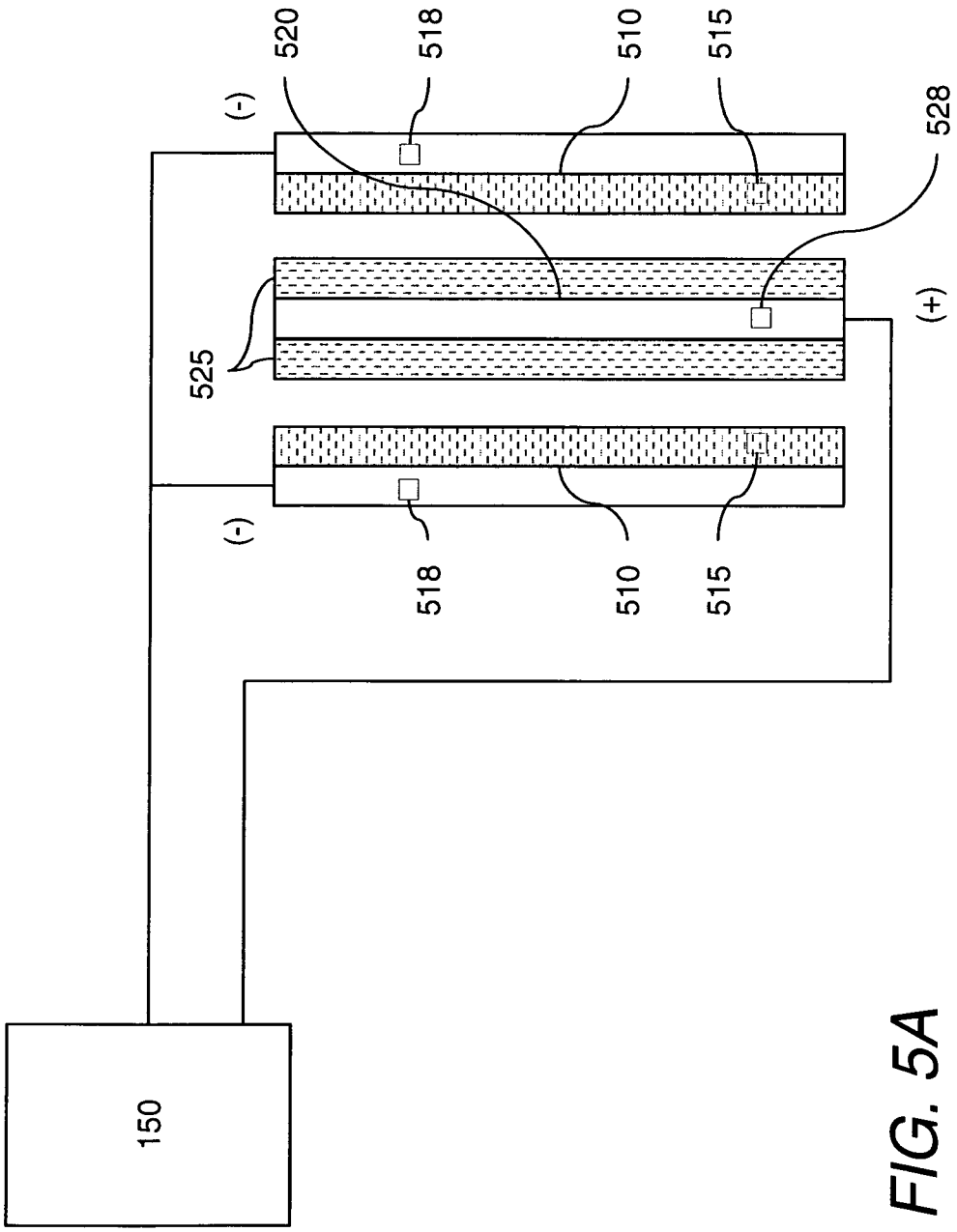

FIG. 5A

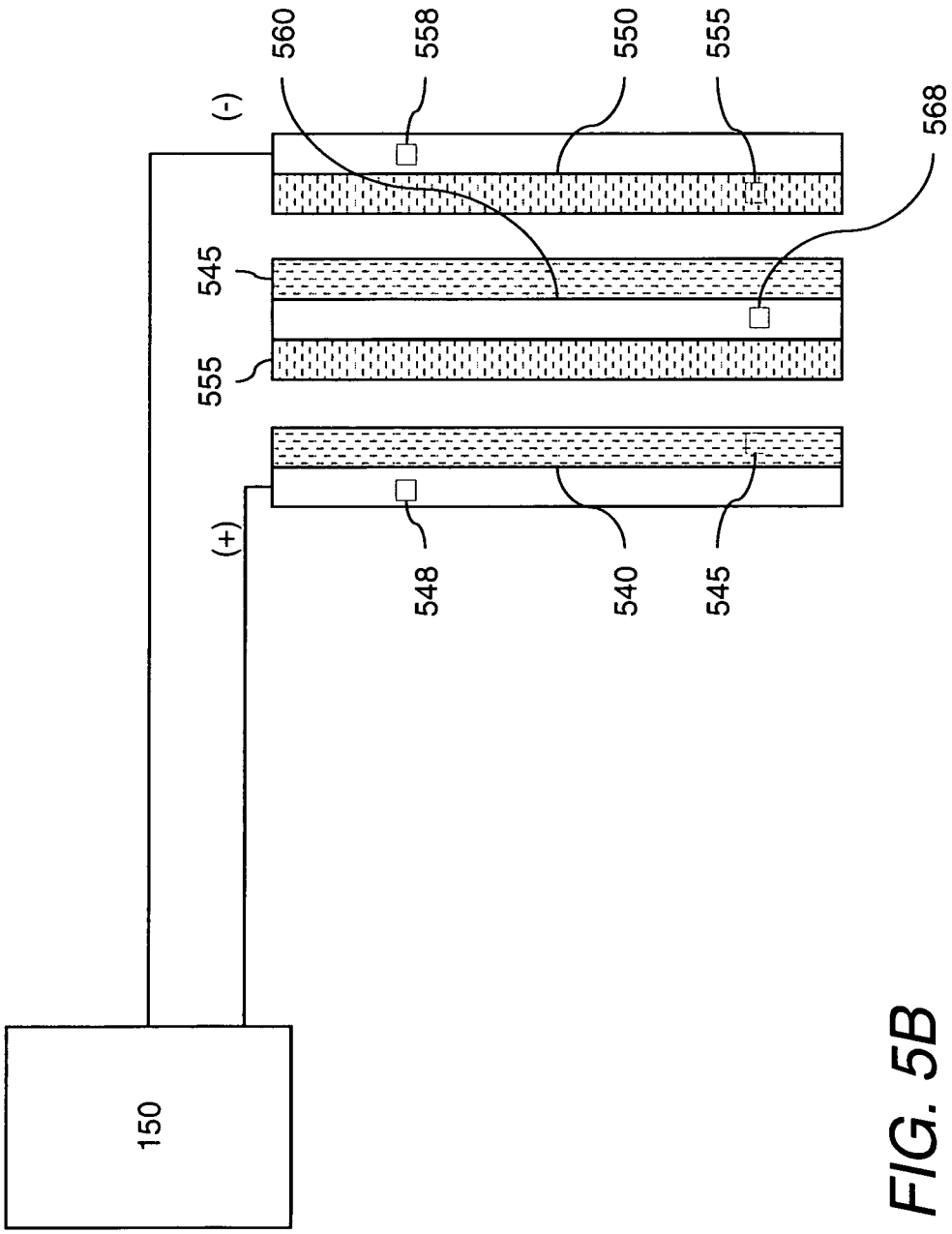

FIG. 5B

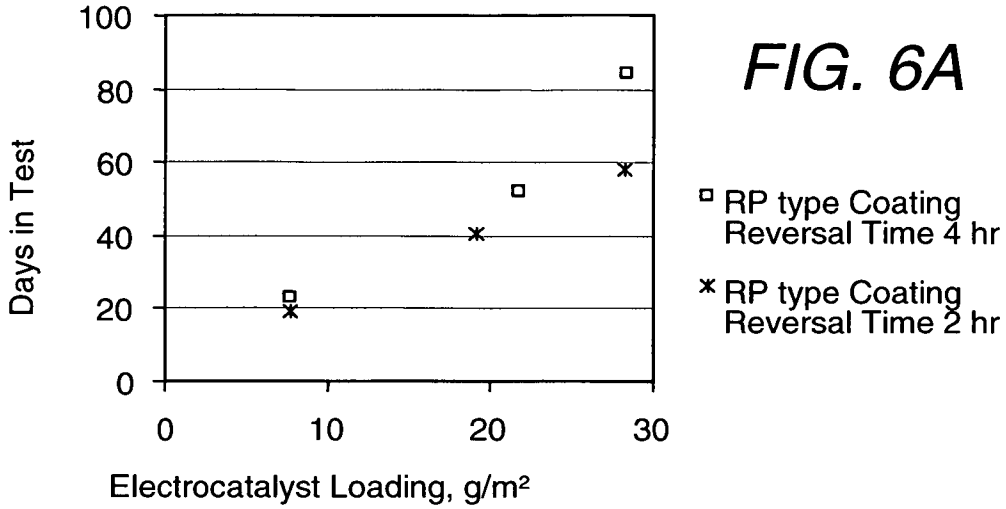
100
80
60
40
20
0
Days in Test
0
10
20
30
Electrocatalyst Loading, g/m²
RP type Coating Reversal Time 4 hr
RP type Coating Reversal Time 2 hr

FIG. 6A

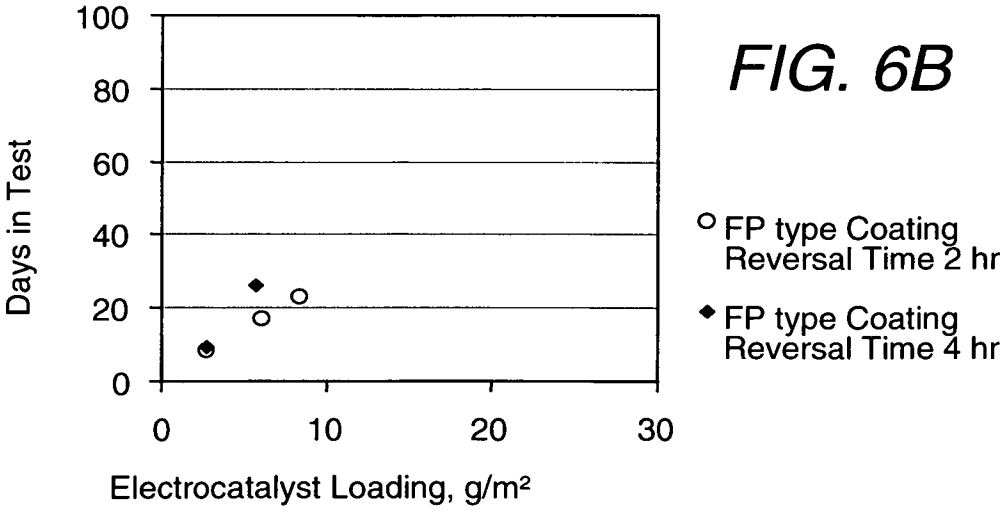
100
80
60
40
20
0
Days in Test
0
10
20
30
Electrocatalyst Loading, g/m²
FP type Coating Reversal Time 2 hr
FP type Coating Reversal Time 4 hr

FIG. 6B

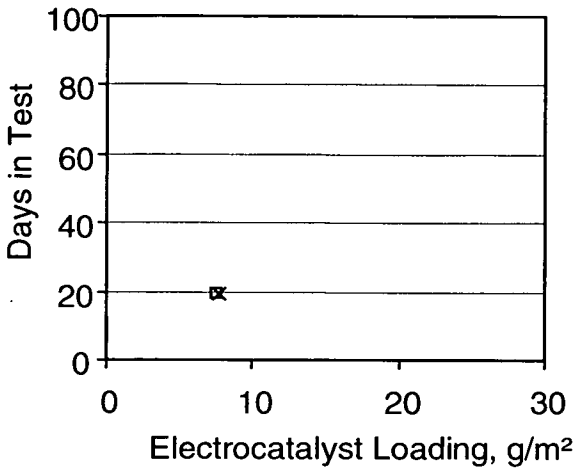

FIG. 6C

□ RP type Coating
Production Time 4 hr
Asymmetric time 10 min

× RP type Coating
Production Time 2 hr
Asymmetric time 10 min

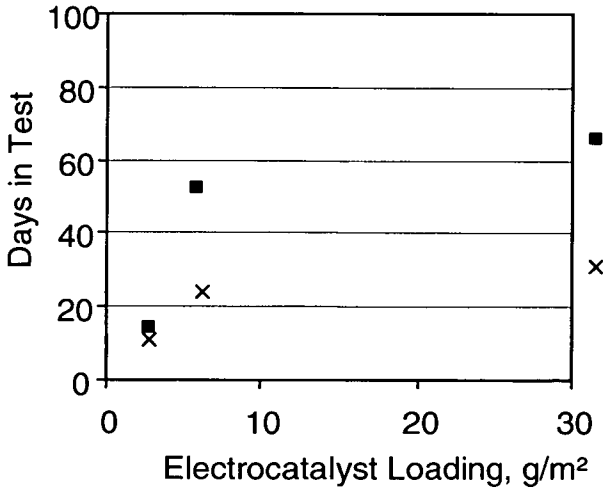

FIG. 6D

■ Anode - FP type Coating
Cathode – RP type coating
Production Time 4 hr
Asymmetric time 10 min

× Anode – FP type Coating
Cathode – RP type coating
Production Time 2 hr
Asymmetric time 10 min

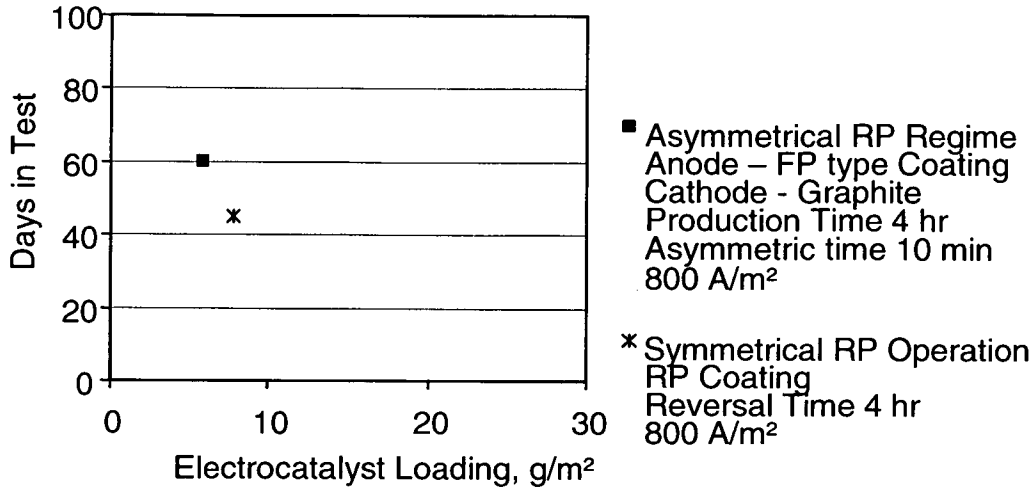
100
80
60
40
20
0
Days in Test
0
10
20
30
Electrocatalyst Loading, g/m²
Asymmetrical RP Regime
Anode – FP type Coating
Cathode - Graphite
Production Time 4 hr
Asymmetric time 10 min
800 A/m²
Symmetrical RP Operation
RP Coating
Reversal Time 4 hr
800 A/m²

FIG. 6E

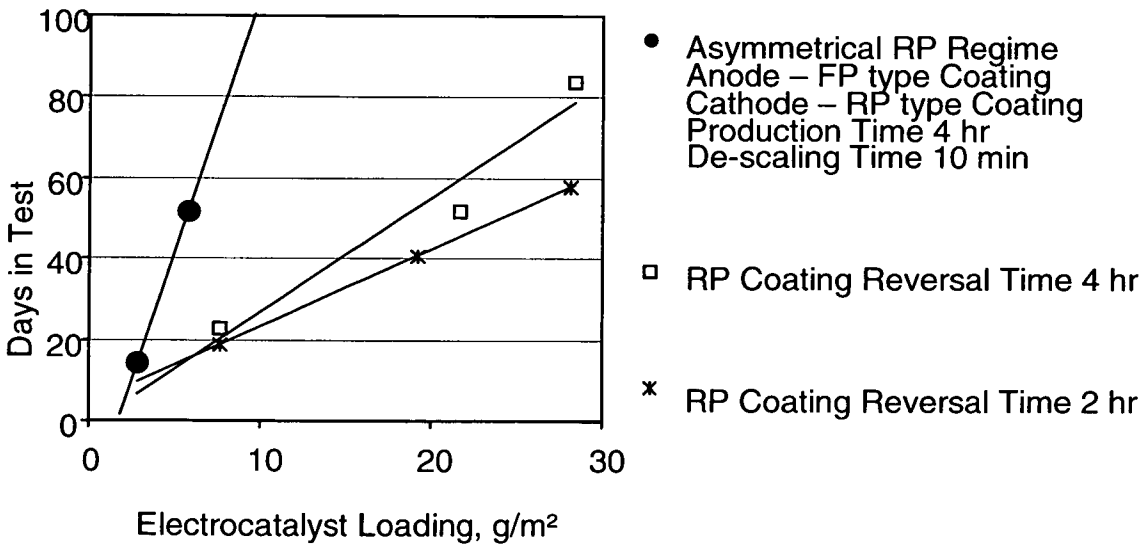
100
80
60
40
20
0
Days in Test
0
10
20
30
Electrocatalyst Loading, g/m²
Asymmetrical RP Regime
Anode – FP type Coating
Cathode – RP type Coating
Production Time 4 hr
De-scaling Time 10 min
RP Coating Reversal Time 4 hr
RP Coating Reversal Time 2 hr

FIG. 7

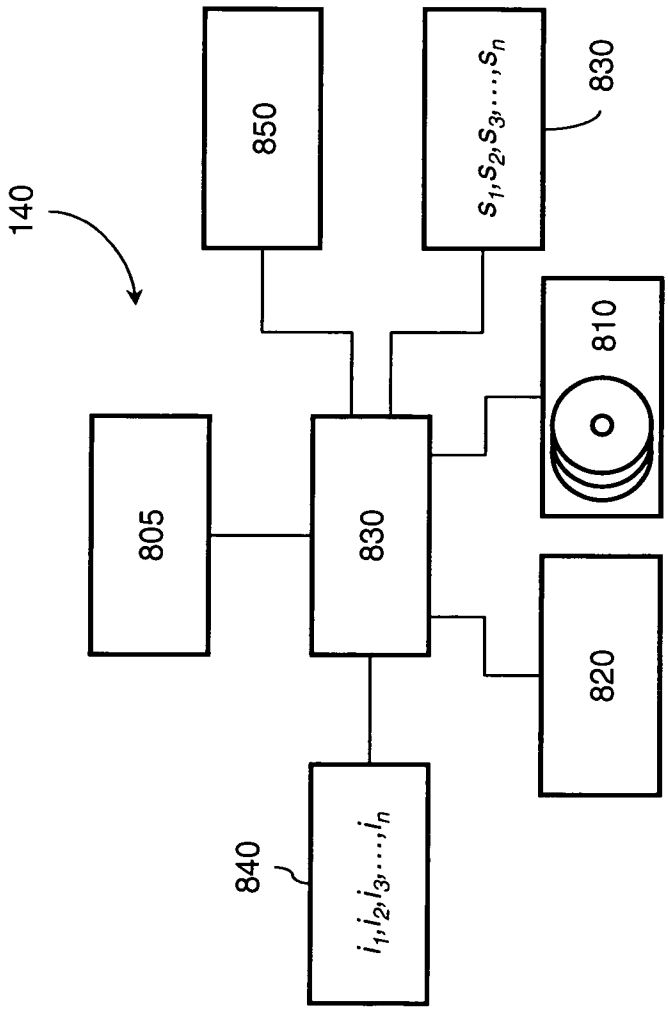
140
850
$s_1,s_2,s_3,\ldots,s_n$
830
810
805
830
820
840
$i_1,i_2,i_3,\ldots,i_n$

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 08/04525

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C02F 1/461, 1/467 (2008.04)
USPC - 205/742; 204/225
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC - 205/742; 204/225

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 205/742, $; 204/225, $
Search Terms Below

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (USPT, PGPB, EPAB, JPAB); google.com
Search Terms Used: electrolytic, electrolyzer, biocide, biocides, chloride, water, polymeric, carbon, graphite, polymeric, reversal, reverse, reversing, direction, opposite, second

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,059,942 A (Barnes et al.) 09 May 2000 (09.05.2000) entire document, especially Abstract; col. 1, ln. 51-55; col. 2, ln. 14-24; col. 4, ln. 5-13; col. 4, ln. 23-27	1-34
Y	US 2005/0263404 A1 (Keister) 01 December 2005 (01.12.2005) entire document, especially Abstract; paras [0015]; [0023]; [0028]; [0069]	1-34
A	US 4,361,471 A (Kosarek) 30 November 1982 (30.11.1982) entire document, especially Abstract	1-34

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 June 2008 (25.06.2008)	07 JUL 2008
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (April 2007)