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(54) METHODS FOR PRODUCING SODIUM HYPOCHLORITE WITH A THREE-COMPARTMENT APPARATUS CONTAINING A BASIC ANOLYTE

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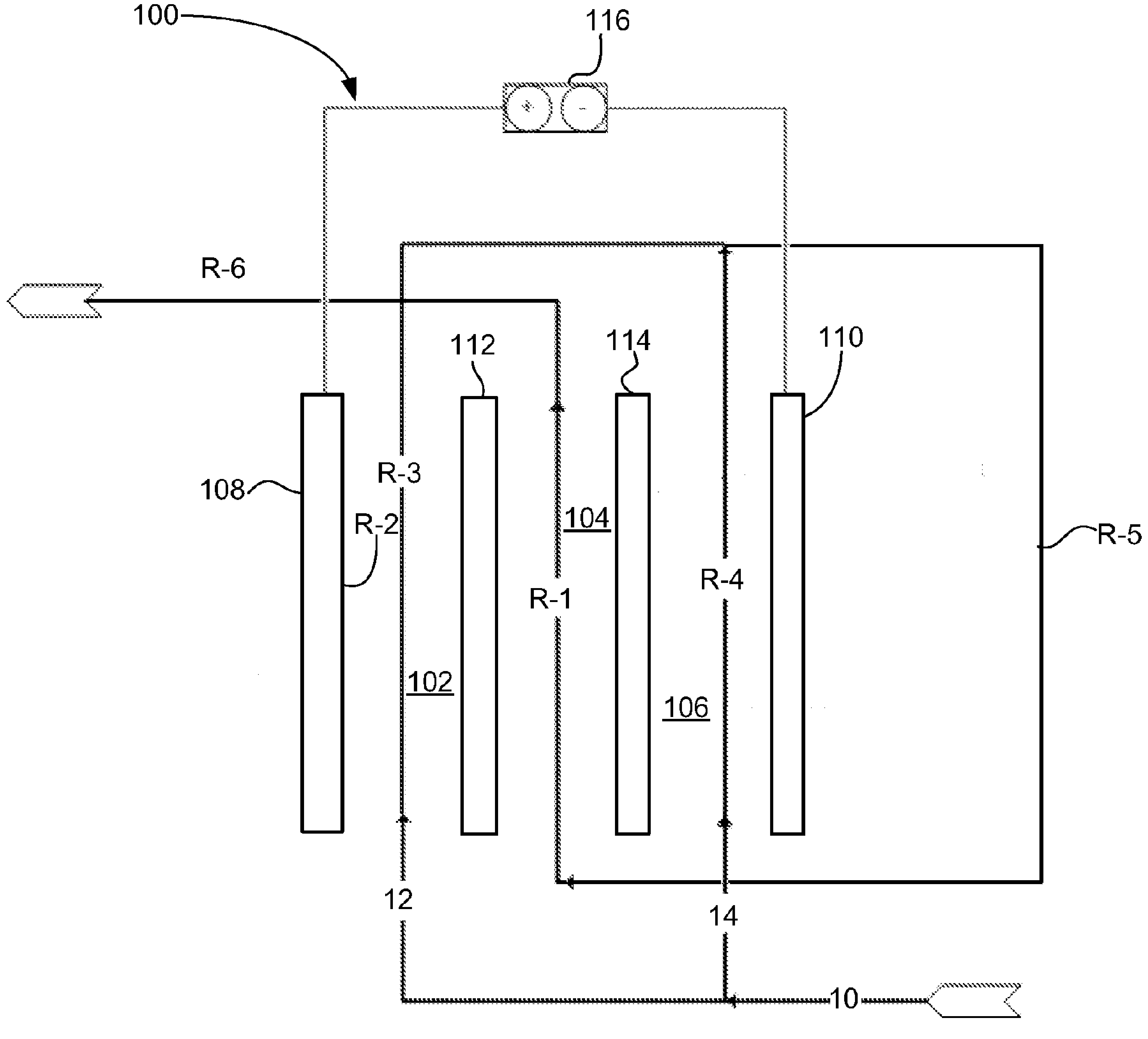
(57) ABSTRACT

An electrochemical method for the production of a chlorine-based oxidant product, such as sodium hypochlorite, is disclosed. The method may potentially be used to produce sodium hypochlorite from sea water or low purity un-softened or NaCl-based salt solutions. The method utilizes alkali cation-conductive ceramic membranes, such as membranes based on NaSICON-type materials, and organic polymer membranes in electrochemical cells to produce sodium hypochlorite. Generally, the electrochemical cell includes three compartments and the first compartment contains an anolyte having a basic pH.



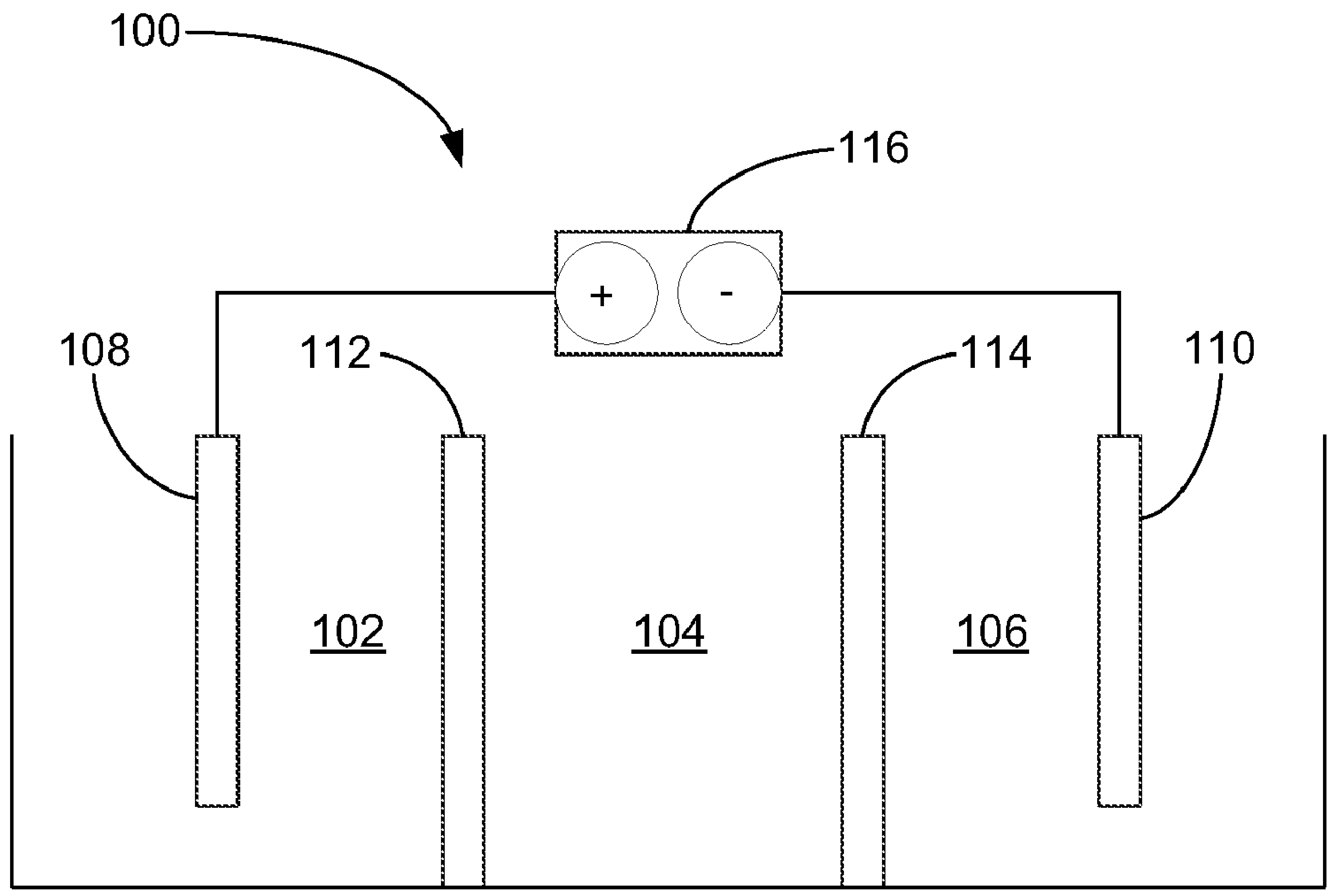


FIG. 1

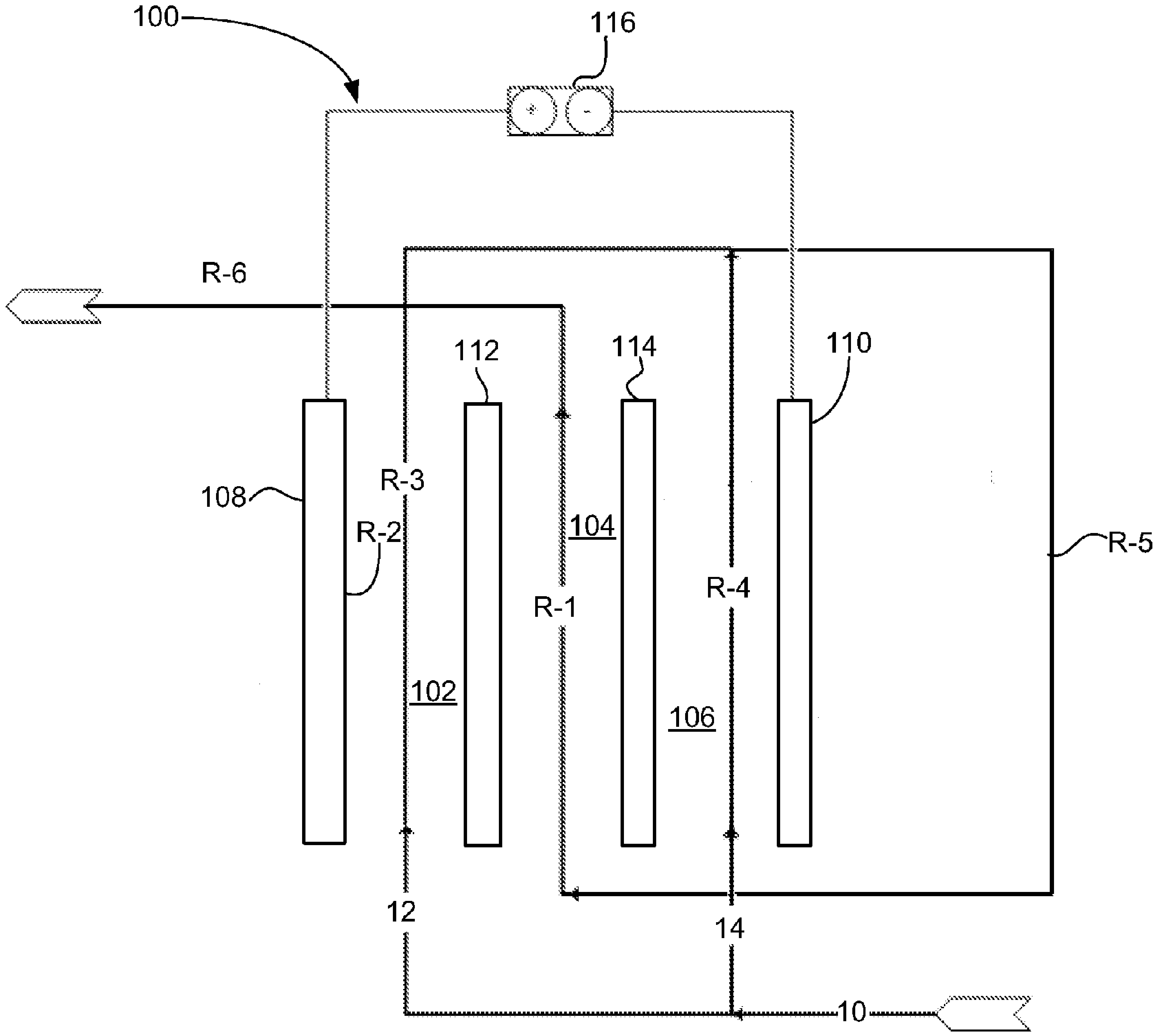


FIG. 2

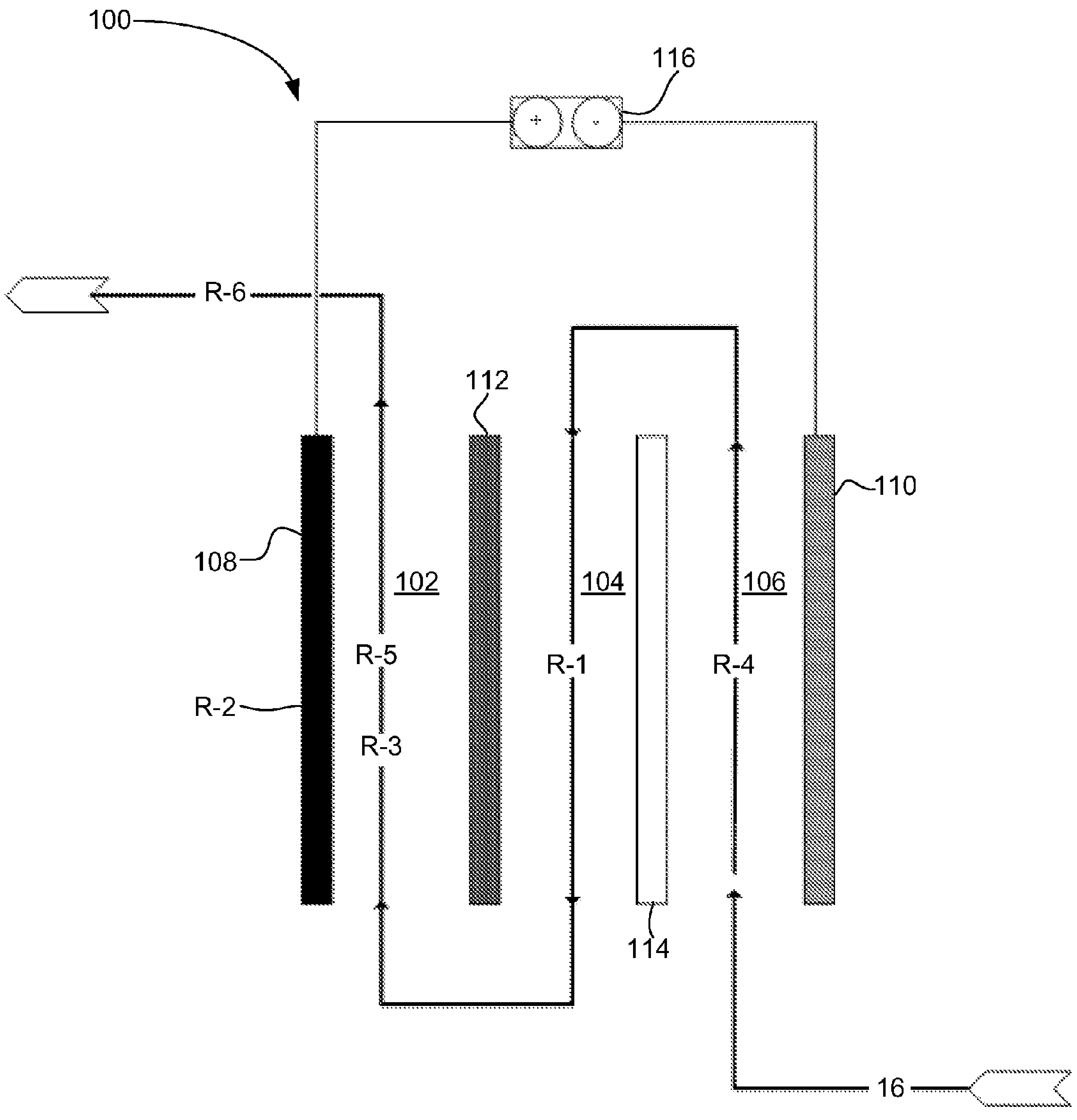


FIG. 3

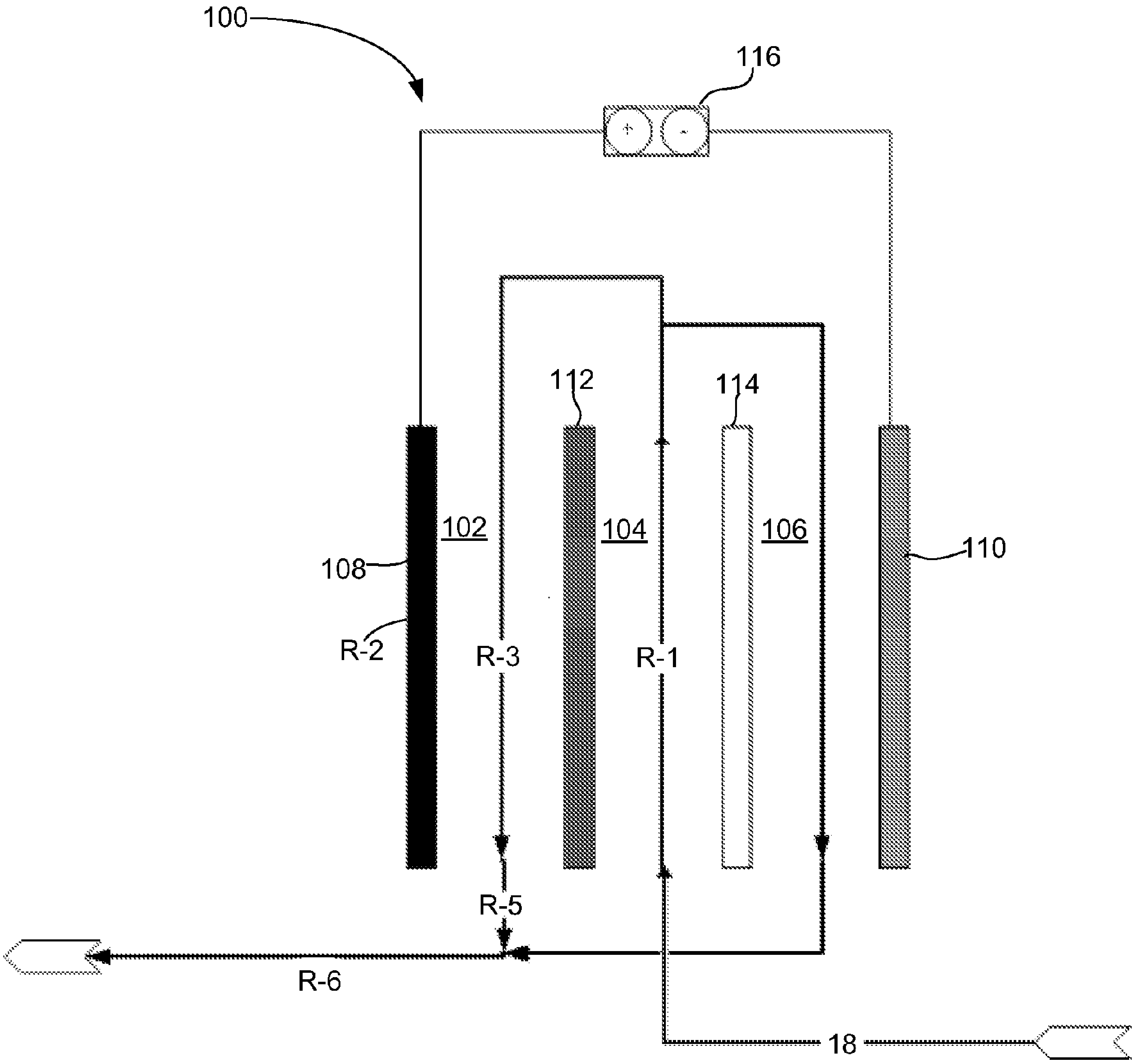


FIG. 4

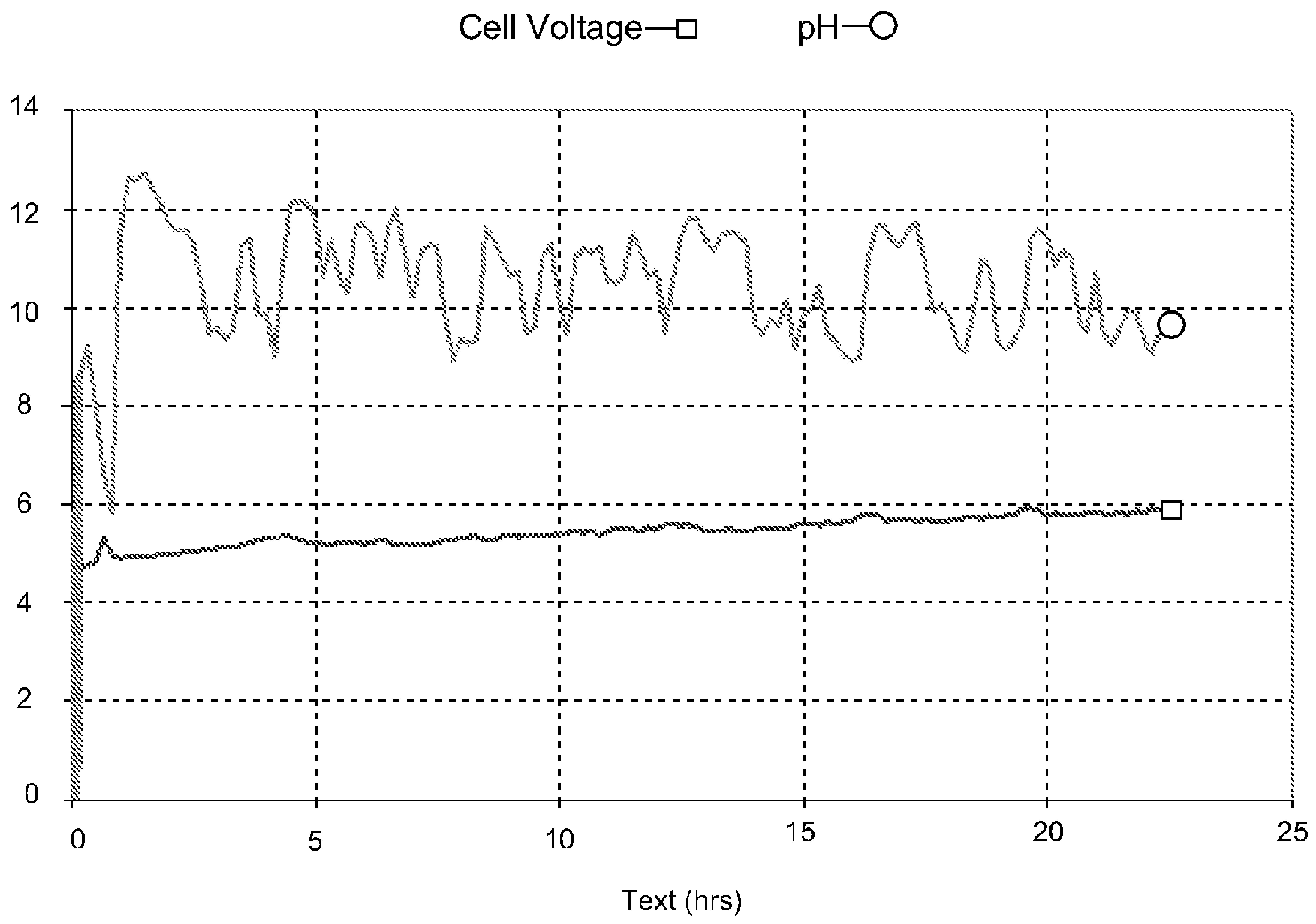


FIG. 5

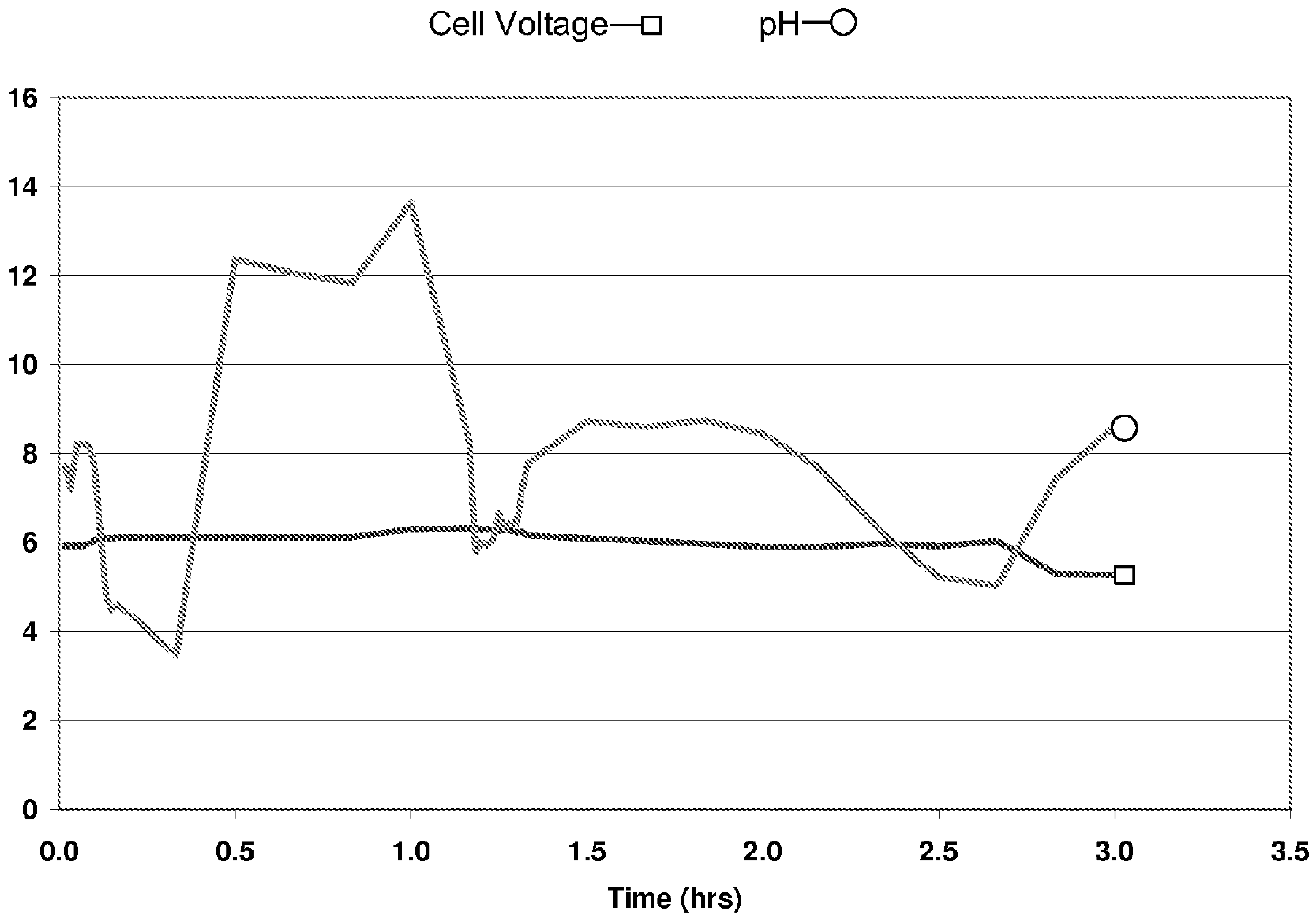


FIG. 6

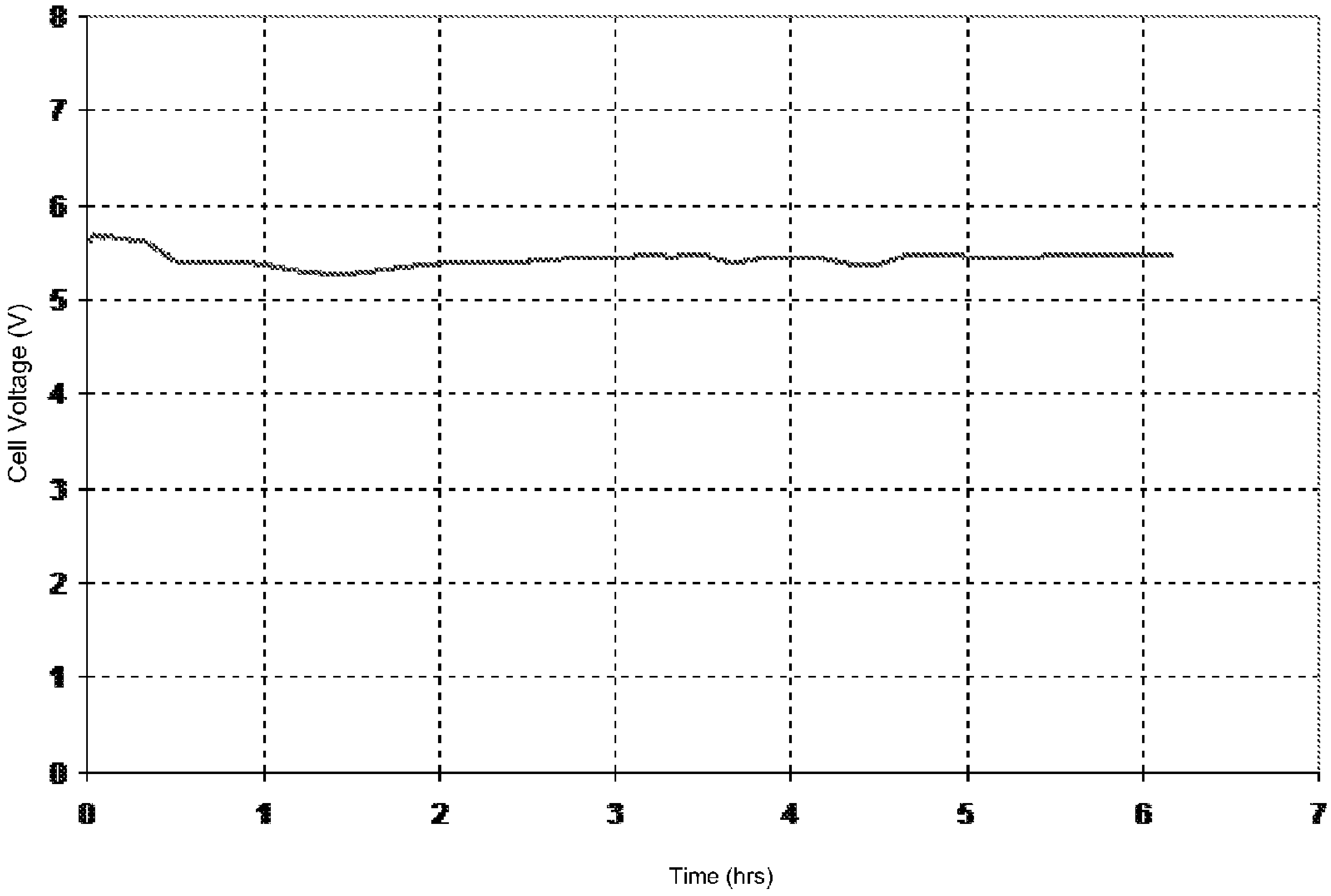


FIG. 7

METHODS FOR PRODUCING SODIUM HYPOCHLORITE WITH A THREE-COMPARTMENT APPARATUS CONTAINING A BASIC ANOLYTE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/091,627, filed Aug. 25, 2008, entitled "Three Compartment Apparatus and Method for Producing Sodium Hypochlorite" and U.S. Provisional Application No. 61/120,737, filed Dec. 5, 2008, entitled "Three Compartment Electrochemical Process for Production of Sodium Hypochlorite," the entire disclosures of which are hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates in general to electrochemical processes for the production of a chlorine-based oxidant product. More particularly, the present invention provides an electrochemical method for producing a chlorine-based oxidant product, such as sodium hypochlorite, through the use of a multi-chamber, electrolytic cell that includes an anion-conductive membrane, an alkali cation-conductive membrane, and an anolyte having a basic pH.

BACKGROUND OF THE INVENTION

[0003] Some halogen-based oxidants, such as sodium hypochlorite, are commonly used as disinfecting and bleaching agents. For example, sodium hypochlorite (NaOCl) is often used to bleach and launder cloth fabrics (e.g., clothing); to disinfect surfaces, such as floors and medical equipment in hospitals; to sanitize water in wells, waste-water treatment plants, and other water systems; and for a wide variety of other applications. In some instances, sodium hypochlorite is marketed as a 3-6 weight % (wt %) solution for use as household bleach. In other instances, stronger solutions are marketed for use in the chlorination of water (e.g., swimming pools) and for use in medical applications. The exact amount of sodium hypochlorite required for a particular application, however, depends on the quantity of water used, the water's chemistry, the water's temperature, the presence or absence of sediment in the water, contact time, and other similar factors.

[0004] Sodium hypochlorite can be produced in a variety of manners. In one example of a conventional method, sodium hypochlorite is produced as chlorine is passed into a cold and dilute solution of sodium hydroxide. In another example, sodium hypochlorite is produced through the electrolysis of brine in a double chamber electrolytic cell. In this example, the hydrolysis process produces caustic soda (sodium hydroxide) and chlorine gas, which are mixed together to form sodium hypochlorite.

[0005] While the above-mentioned production methods are used to create large amounts of sodium hypochlorite, such methods are not without their shortcomings. In one example, some methods for producing sodium hypochlorite are inefficient and expensive. For instance, some methods require large amounts of electricity to be spent for each unit of sodium hypochlorite that is produced. In still another example, certain conventional production processes are essentially immobile and thus prevent sodium hypochlorite from being produced at the site where it is to be used. In yet another example, some conventional methods expose components of an electrolytic cell, namely the cathode and anode, to relatively harsh conditions (e.g., scaling and degradation), which tend to shorten the component's lifespan.

BRIEF SUMMARY OF THE INVENTION

[0006] The present invention provides methods and apparatus for the electrochemical production of halogen-based oxidant solutions from an alkali-salt feed stream using a multi-compartment, electrolytic cell comprising alkali cation-conductive membrane technologies. The methods and apparatus of the present invention may provide the capability of continually generating alkali hypohalite from seawater, salt brine, R.O. brine or another alkali halide solution. The alkali metal could include lithium, sodium and potassium and the halogen could be fluorine, chlorine, bromine and iodine.

[0007] Generally, the multi-compartment, electrolytic cell comprises a first compartment, a second compartment, and a third compartment, which are each configured to hold an amount of fluid. The first, or anolyte, compartment includes an anode electrode that is positioned to contact an anolyte fluid within that compartment. Similarly, the third, or catholyte, compartment includes a cathode electrode that is positioned to contact a catholyte fluid within that compartment. The second, or middle compartment may be positioned intermediate to, and is in operable communication with, both the first (anolyte) and the third (catholyte) compartments. Indeed, in some implementations, the first and the second compartments are separated by an anion-conductive membrane (e.g., an ACS membrane from Astom Corp.), while the second and third compartments are separated by a cation-conductive membrane (e.g., a NaSICON membrane) that is selective to one type of material (e.g., sodium ions).

[0008] The electrolytic cell can be used in any suitable manner that allows sodium hypochlorite or another chlorine-based oxidant product to be produced through the cell's use. For example, one or more feed streams can be added to the electrolytic cell, charge can be passed between the cathode and the anode, and the fluids from the various compartments can be mixed in a variety of ways to form solutions comprising different concentrations of sodium hypochlorite.

[0009] The feed streams added to the cell can comprise any fluid or fluids that allow the cell to function properly and to produce sodium hypochlorite or another chlorine-based oxidant product. For example, water, an aqueous sodium chloride solution, an acid containing chlorine (e.g., hydrochloric acid (HCl) and/or base containing chlorine (sodium hydroxide) can be added to the first compartment. In another example, an aqueous solution of a chlorine-containing salt or alkali hydroxide (e.g., sodium chloride or sodium hydroxide) can be added to the second compartment. In still another example, water, an aqueous solution containing a chlorine-containing salt (e.g., salt brine, reverse osmosis (RO) brine, seawater, tap water containing sodium chloride, etc.), and/or an aqueous solution of an alkali-containing base (e.g., sodium hydroxide) can be added to the third compartment. In some implementations, however, an aqueous solution containing between about 1 wt % and about 26 wt % of a chlorine-containing salt (e.g., sodium chloride) is added as the only solution used as a feed stream.

[0010] The pH and concentration of the feed stream or streams added to the compartments can be controlled so the fluid in each compartment has a pH that allows the cell to function as intended. In other words, the fluids in the 3 compartments can be tailored to have any suitable pH. That said, the fluid or anolyte in the first compartment has a pH that is greater than about 2, and in some instances, greater than about 4. Indeed, in some implementations, the anolyte has a pH of between about 7 and about 12. This basic pH of the anolyte may increase the lifespan of membranes (e.g., a NaSICON membrane) used in the cell.

[0011] With reference to the fluid or electrolyte in the second compartment, the electrolyte has a pH between about 6 and about 14. Additionally, the fluid or catholyte in the third compartment has a pH between about 7 and about 14.

[0012] In some instances, the cell is configured to direct and mix fluid from one or more compartments into one or more other compartments of the cell. In this manner, the cell may mix the fluids and cause chemical reactions to occur in desired compartments.

[0013] In one example of a suitable method for producing sodium hypochlorite, a feed stream comprising an aqueous sodium chloride solution is added into the first and third compartments. As current is passed between the anode and the cathode, sodium chloride in the second compartment is split, and its anions (e.g., Cl^-) and cations (e.g., Na^+) are transported through their respective anion- and cation-conducting membranes. Additionally, as current passes between the electrodes, hypochlorous acid and hydrochloric acid (including ions thereof) accumulate in the first compartment and sodium hydroxide accumulates in the third compartment. To form sodium hypochlorite, an effluent from the first compartment and an effluent from the third compartment are mixed together and added to the second (middle) compartment.

[0014] In a second example, a feed stream comprising an aqueous sodium chloride solution is added to the third compartment in which sodium hydroxide is formed. An effluent from the third compartment is then fed from the third compartment to the second compartment in which sodium chloride splitting occurs. An effluent from the second compartment is then fed into the first compartment, in which hypochlorous acid and hydrochloric acid are both produced. As sodium hydroxide from the second compartment is introduced into the first compartment, the sodium hydroxide reacts with the hypochlorous acid and hydrochloric acid in the first compartment to form sodium hypochlorite.

[0015] In a final example, a feed stream containing an aqueous sodium chloride solution is added into the second compartment where sodium chloride splitting occurs. An effluent from the second compartment is fed into both the first compartment and the third compartment. As in the first and second examples, hypochlorous acid and hydrochloric acid accumulate in the first compartment while sodium hydroxide accumulates in the third compartment. An effluent from the first compartment and an effluent from the third compartment are then mixed (e.g., in the first compartment, a separate vessel, or another suitable location) to form sodium hypochlorite.

[0016] While the described systems and methods have proven particularly useful for the production of sodium hypochlorite, the skilled artisan will recognize that the described methods may be modified to produce one or more other chlorine-based oxidant products, such as lithium hypochlorite and/or potassium hypochlorite. For example, instead of using sodium chloride and a NaSICON membrane, the described methods may use another alkali-chloride salt (e.g., LiCl, KCl, etc.) solution with a membrane (e.g., a LiSICON membrane, a KSICON membrane, etc.) that is capable of transporting selected cations from the salt solution into the third compartment.

[0017] These features and advantages of the present invention will become more fully apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL DRAWINGS

[0018] In order that the manner in which the above-recited and other features and advantages of the invention are obtained and will be readily understood, a more particular description of the invention briefly described above will be rendered by reference to specific embodiments thereof that are illustrated in the appended drawings. Understanding that the drawings depict only typical embodiments of the invention and are not therefore to be considered to be limiting of its scope, the invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

[0019] FIG. **1** depicts a schematic diagram of a representative embodiment of a 3-compartment electrolytic cell;

[0020] FIGS. **2** through **4** contain schematic diagrams illustrating some representative embodiments of systems and methods for producing sodium hypochlorite;

[0021] FIG. **5** contains a graph depicting representative results indicating cell operation voltage and pH for the system shown in FIG. **2**;

[0022] FIG. **6** contains a graph depicting representative results indicating cell operation voltage and pH for the system shown in FIG. **3**; and

[0023] FIG. **7** contains a graph depicting representative results indicating cell operation voltage for the system shown in FIG. **4**.

DETAILED DESCRIPTION OF THE INVENTION

[0024] Reference throughout this specification to "one embodiment," "an embodiment," or similar language means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment," "in an embodiment," and similar language throughout this specification may, but do not necessarily, all refer to the same embodiment.

[0025] Furthermore, the described features, structures, or characteristics of the invention may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided, such as examples of suitable ion-conducting membranes, feed streams, methods for mixing fluids within an electrolytic cell, etc., to provide a thorough understanding of embodiments of the invention. One having ordinary skill in the relevant art will recognize, however, that the invention may be practiced without one or more of the specific details, or with other methods, components, materials, and so forth. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the invention.

[0026] The present invention relates to systems and methods for producing a halogen-based oxidant, such as alkali hypohalide, through the use of a multi-compartment electrolytic cell comprising alkali cation-conductive and anion-conductive membrane technologies. In one embodiment, the use of the electrolytic cell, both pure and impure sodium-chloride-containing solutions, such as seawater, salt brine, RO brine, tap water comprising sodium chloride, and mixtures thereof, can be used to produce sodium hypochlorite. To provide a better understanding of the described systems and methods, the multi-compartment, electrolytic cell is first described, followed by a description of a variety of methods for using the cell.

[0027] FIG. **1** illustrates a representative embodiment of the electrolytic cell **100**. Specifically, FIG. **1** shows that the cell **100** comprises a first compartment **102** (an anolyte compartment), a second compartment **104** (a middle compartment), and a third compartment **106** (a catholyte compartment), which are each configured to contain a quantity of liquid. As illustrated, the first compartment **102** comprises an anode electrode **108** that is disposed within that compartment so as to contact an anolyte solution (not shown). Similarly, FIG. **1** shows that the third compartment **106** comprises a cathode electrode **110** that is disposed within that compartment to contact a catholyte solution (not shown).

[0028] The anode electrode can comprise one or more of a variety of materials that allow it to evolve chlorine when it is contact with an anolyte solution comprising chlorine ions (e.g., Cl^-) and when current is running between the electrodes. Some non-limiting examples of suitable anode materials comprise dimensionally stabilized anode-platinum on titanium (DSA), platinized titanium, ruthenium IV dioxide (RuO_2), and other suitable anode materials that are well known in the art.

[0029] The cathode electrode can comprise one or more of a variety of suitable materials that allow it to evolve hydrogen when the current is run between the cathode and the electrode, and when the cathode is disposed in a catholyte solution. Some non-limiting examples of suitable cathode materials include nickel, stainless steel, and other conventional cathode materials that are stable in a caustic pH.

[0030] FIG. **1** illustrates a power supply **116** connected to the anode electrode **108** and to the cathode electrode **110** to apply a voltage and current between the two electrodes to drive reactions within the electrolytic cell **100**. This power supply can be any known or novel power supply suitable for use with electrolytic cell.

[0031] FIG. **1** also shows the second (middle) compartment **104** is operatively connected to the first (anolyte) compartment **102** and the third (catholyte) compartment **106**. In particular, FIG. **1** shows the first compartment **102** is separated from the second compartment **104** by an anionic membrane **112** that is capable of selectively transporting anions (e.g., Cl^-) from the second compartment **104** into the first compartment **102** during use of the electrolytic cell **100**. Some examples of suitable anionic membranes include, but are not limited to, an ACS membrane from Astom Corp., an AMI membrane from Membranes Int'l, and other known or novel polymer anion-conductive membranes.

[0032] FIG. **1** also shows the second compartment **104** is separated from the third compartment **106** by a cation-conductive membrane **114**, which is capable of selectively transporting specific cations (e.g., Na^+) from the second compartment **104** to the third compartment **106**. Some non-limiting examples of cation-conducting membranes that are suitable for use with the described systems and methods may include any known or novel type of NaSICON membranes (including, but not limited to, NaSICON-type membranes produced by Ceramatec Corp.), LiSICON membranes, KSICON membranes, and polymer cation-conducting membranes (such as NAFION® membranes produced by DuPont). The cation-conductive ceramic membranes may be referred to as MSICON where M is chosen from lithium (Li), sodium (Na), and potassium (K). MSICON could be generally described as a super ion conducting membrane capable of transporting M^+ ions where M includes those elements descried above. In some embodiments in which the chlorine-based oxidant product comprises sodium hypochlorite, the cation-conducting membrane comprises a membrane, such as a NaSICON membrane, which is capable of selectively transporting sodium ions.

[0033] In some specific embodiments, the alkali-ion conducting ceramic membrane compositions comprising NaSICON materials may include at least one of the following: materials of general formula $M_{1+x}M^{I}_{2}Si_{x}P_{3-x}O_{12}$ where $0 \leqq x \leqq 3$, where M is selected from the group consisting of Li, Na, K, or Ag, or mixture thereof, and where MI is selected from the group consisting of Zr, Ge, Ti, Sn, or Hf, or mixtures thereof; materials of general formula $Na_{1+z}L_{z}Zr_{2-z}P_{3}O_{12}$ where $0 \leqq z \leqq 2.0$, and where L is selected from the group consisting of Cr, Yb, Er, Dy, Sc, Fe, In, or Y, or mixtures or combinations thereof; materials of general formula $M^{II}_{5}RESi_{4}O_{12}$, where M^{II} may be Li, Na, or Ag, or any mixture or combination thereof, and where RE is Y or any rare earth element. In some specific embodiments, the NaSICON materials may include at least one of the following: non-stoichiometric materials, zirconium-deficient (or sodium rich) materials of general formula $Na_{1+x}Zr_{2-x/3}Si_{x}P_{3-x}O_{12-2x/3}$ where $1.55 \leqq x \leqq 3$. In some specific embodiments, the alkali-ion conducting ceramic membrane compositions comprising NASICON materials may include at least one of the following: non-stoichiometric materials, sodium-deficient materials of general formula $Na_{1+x}(A_{y}Zr_{2-y})(Si_{z}P_{3-z})O_{12-\delta}$ where A is selected from the group consisting of Yb, Er, Dy, Sc, In, or Y, or mixtures or combinations thereof, $1.8 \leqq x \leqq 2.6$, $0 \leqq y \leqq 0.2$, $x<z$, and δ is selected to maintain charge neutrality. In some embodiments of the present invention it may be advantageous to employ polymeric anion-conductive membranes that are substantially impermeable to at least the solvent components of the anolyte solution in the first compartment.

[0034] A variety of polymeric anion-conductive membrane materials are known in the art and would be suitable for constructing the polymeric anion-conductive membrane of the present invention, as would be understood by one of ordinary skill in the art. In some specific embodiments, the polymeric anion-conductive membranes may include at least one of the following: NEOSEPTA® anion exchange membranes (from Astom Corp.) such as grades NEOSEPTA® AM-1, NEOSEPTA® AM-3, NEOSEPTA® AMX, NEOSEPTA® AHA, NEOSEPTA® ACM, NEOSEPTA® ACS, NEOSEPTA® AFN, or NEOSEPTA® AFX; Ionac® MA-3475 or MA-7500 anion membranes (Sybron Chemicals Inc, NJ); ULTREX™ AMI-7001 anion membrane (Socada LLC, NJ); and PC-SA, PC-SA/HD, PC 100 D, PC 200 D, PC Acid 60, or PC Acid 100 anion membranes (PCA GmbH, Germany).

[0035] While not shown in FIG. **1**, the various compartments of the electrolytic cell may also comprise one or more fluid inlets and outlets. In some embodiments, these inlets and outlets are used to interconnect one or more of the cell's compartments. By interconnecting the cell's compartments, effluents from one or more compartments may be mixed with the contents of one more other compartments in the cell. As used herein, the term effluent and variants thereof may refer to one or more amounts of fluid that are channeled out of one of the electrolytic cell's compartments. Because the contents of one or more compartments can be fed into one or more other compartments, the contents of one compartment can be used to change the pH of another compartment and/or to cause various desired chemical reactions to occur in a specific compartment.

[0036] The cell may be used with any suitable feed stream or streams that allow a halogen-based oxidant product (e.g., sodium hypochlorite) to be produced when the cell is operated. In one example, the feed stream that is initially added to the first compartment is selected from water, an aqueous solution comprising a salt made from an alkali-chloride salt, or a salt containing an alkali-metal and chlorine (e.g., sodium chloride, lithium chloride, potassium chloride, etc.), and/or hydrochloric acid. In another example, the feed stream that is initially introduced into the second compartment comprises an aqueous solution that includes a salt containing an alkali-metal and chlorine (e.g., sodium chloride, lithium chloride, potassium chloride, etc.). In still another example, the feed stream that is initially fed into the third compartment comprises water, an aqueous solution that includes a salt containing an alkali-metal and chlorine (e.g., sodium chloride, lithium chloride, potassium chloride, etc.), and/or an aqueous solution containing an alkali base (e.g., sodium hydroxide, lithium hydroxide, potassium hydroxide, etc.).

[0037] In some presently embodiments, the feed streams added to the first, second, and/or third compartments comprise an aqueous solution that includes a salt containing an alkali-metal and chlorine (e.g., sodium chloride, lithium chloride, potassium chloride, etc.). Indeed, where the described methods are used to produce sodium hypochlorite, the feed streams added to the first, second, and/or third compartments may comprise an aqueous solution that includes sodium chloride.

[0038] Where the feed stream comprises an aqueous sodium chloride solution (e.g., a brine, seawater, tap water solution containing sodium chloride, etc.), the stream may comprise any suitable concentration of sodium chloride. In some embodiments, the concentration of sodium chloride in the feed stream is between about 0.2 wt % and about 26 wt %. In other embodiments, the concentration of sodium chloride in the feed stream is between about 5 wt % and about 20 wt %. In still other embodiments, the sodium chloride concentration in the feed stream is between about 6 wt % and about 14 wt % (e.g., about 10 wt %±2 wt %).

[0039] In order to better explain how the electrolytic cell can be used to produce a chlorine-based oxidant, several representative embodiments of suitable methods and systems are described with reference to FIGS. **2** through **4**. While the described systems and methods may be used to produce other chlorine-based oxidant products, for the sake of simplicity, the following examples discuss methods for using the electrolytic cell to produce sodium hypochlorite.

[0040] FIG. **2** depicts a first representative method (Scheme A) for producing sodium hypochlorite. Specifically, FIG. **2** shows that a first feed solution **10** comprising an aqueous solution of sodium chloride (e.g., an aqueous solution containing between about 1 and about 26 wt % sodium chloride) is split into a first stream **12** and a second stream **14**, which are respectively fed into the cell's first (anolyte) **102** and the third (catholyte) **106** compartments. While FIG. **2** depicts one embodiment in which the first stream **12** and the second stream **14** come directly from the same feed solution **10** and, therefore, have the same chemical characteristics, in other embodiments, the first and the second stream may be modified to have chemical characteristics that vary from each other. For instance, each stream can independently comprise an aqueous sodium chloride solution having a different concentration of sodium chloride.

[0041] As shown in FIG. **2** as well as in Table 1 below, as current from the power supply **116** passes between the anode **108** and the cathode **110**, sodium chloride is split at reaction R-1 in the second (middle) compartment **104** to form chlorine anions (Cl^-) and sodium cations (Na^+), which are respectively transported through the anion-conducting membrane **112** (e.g., a DSA membrane) and the cation-conducting membrane **114** (e.g., a NaSICON membrane). In the first compartment **102**, at reaction R-2, chlorine gas (Cl_2) is evolved at the anode **108** and chlorine gas and water in the anolyte react at reaction R-3 to form hypochlorous acid (HOCl) and hydrochloric acid, including ions thereof. In the third compartment **106**, another reaction occurs. In particular, at reaction R-4, sodium cations (Na^+) react with water under the cell's electrolytic charge to form sodium hydroxide and hydrogen (H^2).

[0042] As illustrated in FIG. **2**, an effluent from the first compartment **102** and an effluent from the third **106** compartment are mixed together (e.g., at reaction R-5) to form sodium hypochlorite, sodium chloride, and water. While this reaction may occur in any suitable location, FIG. **2** shows that this reaction can occur as the effluent from the first compartment **102** is mixed with the effluent from the third compartment **106** within the second chamber **104**. Finally, R-6 shows that an effluent from the second compartment **104** comprises sodium hypochlorite, sodium chloride, hydrogen gas, and/or water.

TABLE 1

Chemical Equations for the Reactions in the Cell Shown in FIG. 2

Reaction Name/ Example of Suitable Location	Reaction Description
R-1/ Second compartment	$Na^+ + Cl^-$ Transported through membranes
R-2/Anode 108	$2Cl^- \rightarrow Cl_2 + 2e^-$
R-3/Anolyte in First Compartment 102	$Cl_2 + H_2O \rightarrow HOCl + HCl$
R-4/Cathode 110	$2H_2O + 2e^- + 2Na^+ \rightarrow 2NaOH + H_2$
R-5/Second4 Compartment 10	$HOCl + HCl + 2NaOH \rightarrow NaOCl + NaCl + H_2O$
R-6 (Overall Reaction)/ Electrolytic Cell 100	$2H_2O + 2NaCl \rightarrow NaOCl + NaCl + H_2 + H_2O$

[0043] It should be noted that throughout this disclosure, the reaction names (e.g., R-1, R-2, . . . Rn) are used for the sake of simplicity and not to identify any particular order in which specific chemical reactions occur. Additionally, while examples of suitable locations for the reactions are discussed, the discussed locations are provided for example only and are not intended to limit the scope of the invention.

[0044] FIG. **3** depicts a second embodiment (Scheme B) of a system and method for producing sodium hypochlorite with the electrolytic cell. Specifically, FIG. **3** illustrates that a sodium chloride feed stream **16** (e.g., a solution with between about 1 and about 26% sodium chloride) flows into the third compartment **106**.

[0045] As shown in FIG. **3** and in Table 2, current flowing from the power source to the cathode **110** generates hydrogen gas and sodium hydroxide in the third compartment **106**, as shown at reaction R-4. While the hydrogen gas can be handled in any suitable manner, in some embodiments, the hydrogen gas produced in the third compartment is vented of collected from that compartment.

[0046] FIG. **3** shows that an effluent from the third compartment **106** is fed into the second compartment **104**, where sodium chloride splitting occurs at reaction R-1. As shown, an effluent from the second compartment **104** is introduced into the first compartment **102** where, at reaction R-5, the sodium hydroxide produced in the first compartment reacts with the hypochlorous acid and hydrochloric acid produced in the first compartment **102** (according to reaction R-3) to form sodium hypochlorite. As shown at reaction R-6, the final effluent from the first compartment **102** comprises sodium hypochlorite, sodium chloride, and/or water. Additionally, as shown below at R-5 in Table 2, the sodium hypochlorite formed in Scheme B can be formed directly in the first compartment **102**.

TABLE 2

Chemical Equations for the Reactions in the Cell Shown in FIG. 3

Reaction Name/ Example of Suitable Location	Reaction Description
R-1/ Second compartment	$Na^+ + Cl^-$ Transported through membranes
R-2/Anode 108	$2Cl^- \rightarrow Cl_2 + 2e^-$
R-3/Anolyte in First Compartment 102	$Cl_2 + H_2O \rightarrow HOCl + HCl$
R-4/ Cathode 110 (Third Compartment 106)	$2H_2O + 2e^- + 2Na^+ \rightarrow 2NaOH + H_2$
R-5/ First Compartment 102	$HOCl + HCl + 2NaOH \rightarrow NaOCl + NaCl + H_2O$
R-6 (Overall Reaction)/Electrolytic Cell 100	$2H_2O + 2NaCl \rightarrow NaOCl + NaCl + H_2 + H_2O$

[0047] FIG. **4** depicts a third embodiment (Scheme C) of a system and method for producing sodium hypochlorite with the electrolytic cell. In particular, FIG. **4** shows that a sodium-chloride-containing feed stream **18** (e.g., an aqueous solution with a concentration of between about 1 and about 26 wt % sodium chloride) is fed into the second compartment **104** where sodium chloride splitting occurs according to reaction R-1. As shown in FIG. **4**, an effluent from the second compartment **104** is split and fed into both the first **102** and the third **104** compartments. In the third compartment, sodium hydroxide and hydrogen gas are produced according to reaction R-4. Moreover, hypochlorous acid and hydrochloric acid are produced in the first compartment **102** according to reactions R-2 and R-3. FIG. **4** shows that the sodium-hydroxide-containing effluent from the third compartment **106** is mixed with the hypochlorous-acid-containing effluent from the first compartment **102** according to reaction R-5 to produce the final sodium hypochlorite product through the overall reaction illustrated at reaction R-6. This mixing of the effluents from the first and the third compartments may occur in any suitable location, such as within tubing between the compartments, in a vessel outside the cell, etc. For instance, FIG. **4** shows the mixing can occur in the first compartment or external to the cell.

TABLE 3

Chemical Equations for the Reactions in the Cell Shown in FIG. 4

Reaction Name/ Example of Suitable Location	Reaction Description
R-1/ Second compartment	$Na^+ + Cl^-$ Transported through membranes
R-2/Anode 108	$2Cl^- \rightarrow Cl_2 + 2e^-$
R-3/Anolyte in First Compartment 102	$Cl_2 + H_2O \rightarrow HOCl + HCl$
R-4/Catholyte in Third Compartment 106	$2H_2O + 2e^- + 2Na^+ \rightarrow 2NaOH + H_2$
R-5/ First Compartment 104 or Separate Vessel	$HOCl + HCl + 2NaOH \rightarrow NaOCl + NaCl + H_2O$
R-6 (Overall Reaction)/Electrolytic Cell 100	$2H_2O + 2NaCl \rightarrow NaOCl + NaCl + H_2 + H_2O$

[0048] In the described methods, the pH values of the various compartments can be controlled in any suitable manner, including, but not limited to: controlling the pH of the various feed streams and/or effluents (e.g., by controlling the feed streams' and effluents' sodium-chloride concentrations, hydroxide concentrations, etc.), changing effluent mixing schemes, and through other methods for controlling pH.

[0049] The fluids (e.g., the anolyte, electrolyte, and catholyte) in each compartment can comprise any suitable pH. In some embodiments, the pH of the anolyte in the first compartment is maintained at a basic pH, or at a pH greater than about 7 (e.g., between about 7 and about 12). Indeed, in some embodiments, the pH of the anolyte is maintained at a pH above about 9 (e.g., between about 9 and about 12). This basic anolyte pH may serve several purposes, including preventing one or more membranes (e.g., a NaSICON membrane) from being exposed to acidic conditions. By so doing the basic anolyte can improve the useful lifespan of one or more of the membranes (e.g., a NaSICON membrane), which may be damaged at lower pHs. Despite the previously mentioned embodiments, in some other embodiments, an acid concentration (e.g., of HOCl and/or HCl) between about 1% and about 10% is also maintained in the cell (e.g., in the anolyte in the first compartment **102**).

[0050] In some embodiments, the pH of the fluid (electrolyte) in the second chamber is maintained at a pH between about 6 and about 13. Additionally, the pH of the fluid (catholyte) in the third chamber is maintained at a pH between about 7 and about 14. In one embodiment, to control the pHs of the second and third compartments, voltage is applied to the electrodes to allow a plurality of alkali ions in the second compartment to pass through the cation-conductive membrane into the third compartment. In another embodiment, the concentration of sodium hydroxide in the third compartment is controlled so as to be maintained between about 1 and about 26 wt %

[0051] In the described methods, the power supply can provide any suitable voltage that allows the cell to produce a chlorine-based oxidant product, such as sodium hypochlorite. In some embodiments, the power supply provides the cell with between about 1 and about 15 volts. In other embodiments, the power supply causes between about 2 and about 10 volts to pass between the anode and cathode. In still other non-limiting embodiments, the power supply causes between about 4 and about 6 volts to pass between the electrodes.

[0052] The power supply can also provide any suitable current density to the cell. Indeed, in some embodiments, the power supply provides between about 20 and about 100 mA/cm^2. In other embodiments, the power supply is used to provide a current density between about 30 and about 38 mA/cm^2. In still other embodiments, the power supply provides a current density between about 32 and about 75 mA/cm^2.

[0053] The final effluent produced by the cell may flow at any suitable rate that provides the final effluent with a suitable concentration of the chlorine-based oxidant product. Different flow rates can alter the pH and/or concentration of the final effluent. The skilled artisan will recognize that the actual flow rate of the final effluent from the cell can depend on several factors, including, but not limited cell size, temperature, ambient pressure, etc. In one embodiment, the flow rate of the final effluent is between about 2 and about 30 ml/min. In another embodiment, the flow rate of the final effluent is between about 5 and about 20 ml/min. In still another non-limiting embodiment, the flow rate of the final effluent is between about 8 and about 16 ml/min.

[0054] Where the described systems and methods are used to produce sodium hypochlorite, the electrolytic cell may produce any suitable concentration of sodium hypochlorite. In one example, the described systems and methods produce solutions comprising between about 0.5 and about 15 wt % sodium hypochlorite. In another example, the described systems and methods produce solutions comprising between about 0.8 and about 4 wt % sodium hypochlorite. In still another example, the described systems and methods produce solutions comprising between about 1 and about 2.4 wt % sodium hypochlorite.

[0055] The described systems and methods can be varied in any suitable manner. For instance, in addition to the described components, the electrochemical cell may comprise any other suitable component, such as a coolant system, a conventional pH controlling system, etc. Indeed, because the described systems and methods may function best between about 15° and about 30° Celsius, in some embodiments, the described cell is used with a coolant system. In another example, additional chemical ingredients are added to the cell for any suitable purpose (e.g., to modify fluid pH, to combat scaling on the electrodes, etc.). In still another example, effluents from one or more compartments are fed into a desired compartment or compartments at any suitable time (e.g., any suitable time after the introduction of a feed stream into the cell) and in any suitable amount.

[0056] The described systems and methods may have several beneficial characteristics. In one example, because the described methods can use a basic anolyte, the useful life of one or more of the membranes (e.g., the NaSICON membrane) in the cell can be increased over the lifespan that similar membranes would likely have in acidic environments. In another example, the described methods are able to produce usable amounts of sodium hypochlorite with relatively small amounts of energy (e.g., a current density between about 20 and about 50 mA/cm^2). In still another example, the described methods may use inexpensive ingredients, such as seawater, brine, tap water with sodium chloride, etc. In still another example, the described methods may be used to produce chlorine-based oxidants, such as sodium hypochlorite, on demand and continuously, as desired. In still another example, some embodiments of the electrolytic cell may be portable and, thereby, allow sodium hypochlorite or another chlorine-based oxidant product to be produced at the site where it will be used.

[0057] The following examples are given to illustrate various embodiments within the scope of the present invention. These are given by way of example only, and it is understood that the following examples are not comprehensive or exhaustive of the many types of embodiments of the present invention that can be prepared in accordance with the present invention.

Examples

Example 1

[0058] In one example of how the electrolytic cell functions, a cell was prepared and operated according to the systems and methods shown in FIG. **2**. Specifically, the first and second incoming feed streams **12** and **14** were prepared to have a concentration of about 10 wt % sodium chloride in water. After the feed streams were introduced into the cell, the cell was operated at a current density of about 34 mA/cm^2. FIG. **5** shows the voltage applied to the cell was between about 4 and about 6 volts and the measured pH of the final effluent from the second compartment was generally between about 8.5 and about 13. As a result of this experiment, the sodium hypochlorite current efficiency measured for the process was about 98.52% and the final concentration of sodium hypochlorite produced from the cell in R-6 was about 2 g/L.

Example 2

[0059] In a second example of how the electrolytic cell functions, a cell was prepared and operated according to the systems and methods shown in FIG. **3**. Specifically, the feed stream **16** was prepared to have a concentration of about 10 wt % sodium chloride in water. After the feed solution was introduced into the cell, the cell was operated at a current density of about 34 mA/cm^2. FIG. **6** shows the voltage applied to the cell was between about 5 and about 5.5 volts and the measured pH of the final effluent was between about 4 and about 13. As a result of this experiment, the cell sodium hypochlorite current efficiency measured for the process was about 40% and the final concentration of sodium hypochlorite produced from the cell was about 1 g/L at a solution flow rate of about 12.13 ml/min.

Example 3

[0060] In a third example of how the electrolytic cell functions, a cell was prepared and operated according to the systems and methods shown in FIG. **4**. Specifically, the feed stream **18** was prepared to have a concentration of about 10 wt % sodium chloride in water. After the feed solution was introduced into the cell, the cell was operated at a current density of about 34 mA/cm^2. FIG. **7** shows the voltage applied to the cell was between about 5 and about 6 volts. As a result of this experiment, the cell sodium hypochlorite current efficiency measured for the process was about 60% and the final concentration of sodium hypochlorite produced from the cell was about 1.2 g/L at a solution flow rate of about 8 ml/min. Additionally, while not shown, the pH of the final effluent from the cell was in the range of about 4 to about 14.

[0061] The examples provided herein show that various methods (e.g., Schemes A, B, and C) for mixing the effluents from the various compartments have different effects on final sodium hypochlorite concentrations and the current efficiencies of the cell. In particular, the experimental results from examples 1 through 3 show that of the schemes presented, Scheme A is the most efficient and produces the highest yield of sodium hypochlorite while Scheme B is the least efficient and produces the lowest yield of sodium hypochlorite.

[0062] While specific embodiments and examples of the present invention have been illustrated and described, numerous modifications come to mind without significantly departing from the spirit of the invention, and the scope of protection is only limited by the scope of the accompanying claims.

1. An electrolytic cell, comprising:

an anolyte compartment holding an anolyte, the anolyte compartment comprising an anode in contact with the anolyte;

a catholyte compartment containing a catholyte, the catholyte compartment comprising a cathode in contact with the catholyte;

a middle compartment in operative communication with the anolyte compartment and the catholyte compartment, the middle compartment further comprising an electrolyte;

a polymeric anion-conducting membrane positioned between the anolyte compartment and the middle compartment; and

an alkali cation-conductive ceramic membrane selective to one type of cation, the cation-conductive membrane positioned between the middle compartment and the catholyte compartment, and

wherein the anolyte comprises a pH greater than about 6, such that the electrolytic cell produces a halogen-based oxidant product.

2. The electrolytic cell of claim **1**, wherein the alkali cation-conductive ceramic membrane comprises a MSICON membrane selective to M^+ ions, wherein M comprises one or more of lithium, sodium, and potassium.

3. The electrolytic cell of claim **1**, wherein the alkali cation-conductive ceramic membrane comprises NaSICON.

4. The electrolytic cell of claim **1**, wherein the electrolyte comprises a pH greater than about 5.5.

5. The electrolytic cell of claim **1**, wherein the anolyte comprises alkali-chloride salt solution.

6. The electrolytic cell of claim **1**, wherein the anolyte comprises a pH between about 6 and about 12, the electrolyte comprises a pH between about 6 and about 13, and the catholyte comprises a pH between about 5.5 and about 14.

7. The electrolytic cell of claim **1**, wherein the halogen-based oxidant product comprises alkali hypohalite.

8. The electrolytic cell of claim **7**, wherein the catholyte comprise alkali hydroxide and/or alkali halide.

9. An electrolytic cell for producing sodium hypochlorite, comprising:

an anolyte compartment holding an anolyte, the anolyte compartment comprising an anode in contact with the anolyte;

a catholyte compartment containing a catholyte, the catholyte compartment comprising a cathode in contact with the catholyte;

a middle compartment in operative communication with the anolyte compartment and the catholyte compartment, the middle compartment comprising an electrolyte;

a polymeric anion-conducting membrane positioned between the anolyte compartment and the middle compartment; and

a NaSICON alkali cation-conductive ceramic membrane selective to sodium ions, the NaSICON membrane positioned between the middle compartment and the catholyte compartment,

wherein the anolyte comprises aqueous sodium chloride solution having a concentration of between about 1 wt % and about 25 wt % sodium chloride, and has a pH greater than about 7, and

wherein the catholyte comprises an aqueous sodium chloride solution having a concentration of between about 1 wt % and about 25 wt % sodium chloride, and

wherein the catholyte further comprises sodium hydroxide at a concentration of between about 1 wt % and about 26 wt %.

10. The electrolytic cell of claim **9**, wherein the anolyte comprises a pH between about 7 and about 12, the electrolyte comprises a pH between about 5.5 and about 13, and the catholyte comprises a pH between about 5.5 and about 14.

11. A method for creating sodium hypochlorite, the method comprising:

providing an electrolytic cell having:

an anolyte compartment for holding an anolyte, the anolyte compartment comprising an anode positioned to contact the anolyte;

a catholyte compartment for containing a catholyte, the catholyte compartment comprising a cathode positioned to contact the catholyte;

a middle compartment for holding an electrolyte, the middle compartment being in operative communication with the anolyte compartment and the catholyte compartment;

a polymeric anion-conducting membrane positioned between the anolyte compartment and the middle compartment; and

an alkali cation-conductive ceramic membrane selective to one type of material, the cation-conductive membrane positioned between the middle compartment and the catholyte compartment,

introducing an aqueous, sodium chloride solution into the electrolytic cell;

applying a current between the anode and the cathode;

maintaining a pH of the first aqueous fluid greater than about 7; and

producing a product comprising sodium hypochlorite in the anolyte.

12. The method of claim **11**, wherein the aqueous sodium chloride solution is selected from brine, sea water, another solution comprising water and sodium chloride, and mixtures thereof.

13. The method of claim **11**, further comprising operating the electrochemical cell at a temperature between about 5° C. and about 30° C.

14. The method of claim **11**, further comprising producing the solution comprising sodium hypochlorite, wherein the solution comprises sodium hypochlorite at a concentration between about 0.1 and about 30 wt %.

15. The method of claim **11**, wherein the product comprises sodium hypochlorite present at a concentration between about 0.1 wt. % and about 15 wt. %.

16. The method of claim **10**, wherein the product comprises sodium hypochlorite present at a concentration between about 0.1 wt. % and about 8 wt. %.

17. The method of claim **11**, wherein the pH of the anolyte is maintained above 7 by addition of sodium hydroxide from either catholyte or external supply

18. The method of claim **11**, wherein the introducing the aqueous sodium chloride solution comprises introducing the sodium chloride solution into the anolyte compartment and the catholyte compartment, and wherein the method further comprises feeding effluent from the anolyte in the anolyte compartment and effluent from the catholyte in the catholyte compartment into the middle compartment.

19. The method of claim **11**, wherein the introducing the aqueous sodium chloride solution comprises introducing the sodium chloride solution into the catholyte compartment, and wherein the method further comprises:

feeding effluent from the catholyte in the catholyte compartment into the middle compartment; and

feeding effluent from the electrolyte in the middle compartment into the anolyte compartment.

20. The method of claim **11**, wherein the introducing the aqueous sodium chloride solution comprises introducing the sodium chloride solution into the middle compartment, and wherein the method further comprises:

feeding an effluent from the electrolyte in the middle compartment into the anolyte compartment and the catholyte compartment; and

mixing an effluent from the anolyte compartment and an effluent from the catholyte compartment to form the solution comprising sodium hypochlorite.

21. The method of claim **11**, further comprising:

maintaining a pH of the anolyte between about 7 and about 12;

maintaining a pH of the electrolyte between about 5.5 and about 13; and

maintaining a pH of the catholyte between about 5.5 and about 14.

22. The method of claim **21**, wherein the usage of anolyte of pH above about 5.5 will prevent precipitation of scale forming salts present in the electrolyte onto the cationic membrane.

23. The method of claim **11**, wherein the aqueous sodium chloride solution comprises sodium chloride at a concentration between about 1% and about 25%.

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