



(86) Date de dépôt PCT/PCT Filing Date: 2009/06/24
(87) Date publication PCT/PCT Publication Date: 2010/01/21
(85) Entrée phase nationale/National Entry: 2010/03/24
(86) N° demande PCT/PCT Application No.: US 2009/048511
(87) N° publication PCT/PCT Publication No.: 2010/008896
(30) Priorités/Priorities: 2008/07/16 (US61/081,299);
2008/08/25 (US61/091,729);
2008/12/23 (USPCT/US2008/088242);
2009/01/28 (USPCT/US2009/032301)

(51) Cl.Int./Int.Cl. *B05D 5/12* (2006.01),
C25B 1/00 (2006.01)

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(54) Titre : SYSTÈME ELECTROCHIMIQUE A 4 CELLULES BASSE ENERGIE COMPORTANT DU DIOXYDE DE
CARBONE GAZEUX

(54) Title: LOW-ENERGY 4-CELL ELECTROCHEMICAL SYSTEM WITH CARBON DIOXIDE GAS

(57) **Abrégé/Abstract:**

A low-voltage, low-energy electrochemical system and method of producing hydroxide ions and/or bicarbonate ions and/or carbonate ions utilizing significantly less than the typical 3V used across the conventional anode and cathode to produce the ions; consequently, carbon dioxide emissions attributable to the present system and method are significantly reduced.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 January 2010 (21.01.2010)



(10) International Publication Number
WO 2010/008896 A1

(51) International Patent Classification:
B05D 5/12 (2006.01) **C25B 1/00** (2006.01)

(21) International Application Number:
PCT/US2009/048511

(22) International Filing Date:
24 June 2009 (24.06.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/081,299 16 July 2008 (16.07.2008) US
61/091,729 25 August 2008 (25.08.2008) US
PCT/US2008/088242
23 December 2008 (23.12.2008) US
PCT/US2009/032301
28 January 2009 (28.01.2009) US

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

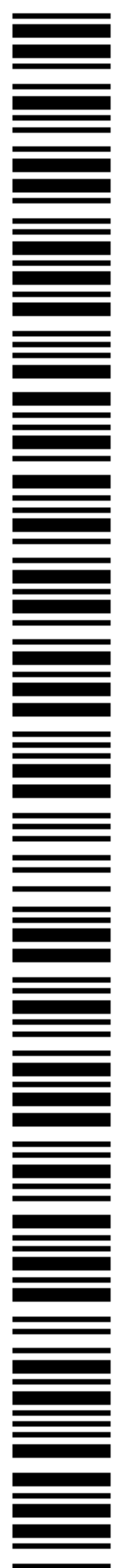
(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: LOW-ENERGY 4-CELL ELECTROCHEMICAL SYSTEM WITH CARBON DIOXIDE GAS

(57) Abstract: A low-voltage, low-energy electrochemical system and method of producing hydroxide ions and/or bicarbonate ions and/or carbonate ions utilizing significantly less than the typical 3V used across the conventional anode and cathode to produce the ions; consequently, carbon dioxide emissions attributable to the present system and method are significantly reduced.



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LOW-ENERGY 4-CELL ELECTROCHEMICAL SYSTEM WITH CARBON DIOXIDE GAS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Under 35 U.S.C. §119 (e), this application claims priority to
5 commonly assigned US Provisional Patent Application no. 61/081,299
filed July 16, 2008, title: “Low Energy pH Modulation for Carbon
Sequestration Using Hydrogen Absorptive Metal Catalysts”; and
commonly assigned US Provisional Patent Application no. 61/091,729
filed August 25, 2008, title: “Low Energy Absorption of Hydrogen Ion
10 from an Electrolyte Solution into a Solid Material”, both of which are
herein incorporated by reference in their entirety.

[0002] Under 35 U.S.C. §119 (a) and under 35 U.S.C. §365, this
application claims priority to commonly assigned PCT Patent
Application no. PCT/US08/88242, titled “Low-energy Electrochemical
15 Hydroxide System and Method” filed on December 23, 2008; and
commonly assigned PCT Patent Application no. PCT/US09/32301 titled
“Low-energy Electrochemical Bicarbonate Ion Solution” filed on January
28, 2009, both of which are herein incorporated by reference in their
entirety.

BACKGROUND

20 [0003] A solution of hydroxide ions, carbonate ions and/or bicarbonate
ions is often required to remove protons from a solution, or buffer the
pH of a solution, or precipitate an insoluble hydroxide and/or carbonate
and/or bicarbonate from a solution. Conventionally, hydroxide ions can
25 be produced by hydrolyzing a base, e.g., slaking quicklime; or, by
electrolyzing a salt solution, e.g., electrolyzing an aqueous sodium

chloride solution as in the Chlor-alkali process. Conventionally, carbonate ions or bicarbonate ions can be produced by dissolving carbon dioxide gas in water or by dissolving a soluble carbonate or bicarbonate salt, e.g., sodium bicarbonate, in water.

5 [0004] Although hydrolyzing a base or electrolyzing a salt solution can produce hydroxide ions, the conventional production of hydroxide ions consumes large amounts of energy; the conventional methods also release large amounts of carbon dioxide into the environment. Thus, for example, in producing quicklime, large amounts of fossil fuels are
10 burned to calcine and convert limestone to calcium oxide, with the consequential release of large amounts of carbon dioxide into environment. Similarly, in producing hydroxide ions by the Chlor-alkali process, since typically at least 3V is required across the anode and cathode to drive the reaction, large amounts of energy are utilized. As
15 this energy is derived typically from fossil fuelled power generating plants, this process also causes release of large amounts of carbon dioxide into the environment. Similarly, in producing carbonate ions and bicarbonate ions by dissolving carbon dioxide in aqueous solutions, a significant amount of energy is required to pressurize the gas for
20 improved solubility, with the consequential release of large amounts of carbon dioxide into the environment attributable to the energy used. Thus, an energy efficient production of hydroxide ions, carbonate ions and bicarbonate ions is highly desirable.

25 SUMMARY

[0005] In various embodiments, the present system and method pertain to a low-voltage, low-energy electrochemical system and

method of producing hydroxide ions and/or bicarbonate ions and/or carbonate ions. In various embodiments, the system and method utilize significantly less than the typical 3V used across the conventional anode and cathode to produce the ions; consequently, the carbon dioxide emissions attributable to the present system and method are significantly reduced.

[0006] In one embodiment, the system comprises: a first electrolyte in contact with a cathode; a second electrolyte in contact with an anode; a third electrolyte separated from the first electrolyte by a first ion-exchange membrane; a fourth electrolyte separated from the second electrolyte by a second ion-exchange membrane; and a third-ion exchange membrane separating the third and fourth electrolytes.

[0007] In one embodiment, the method comprises: placing a first electrolyte in contact with a cathode; placing a second electrolyte in contact with an anode; placing a third electrolyte such that it is separated from the first electrolyte by a first ion-exchange membrane; placing a fourth electrolyte such that it is separated from the third electrolyte by an third ion-exchange membrane and is separated from the second electrolyte by a second ion-exchange membrane; and forming hydroxide ions in the first electrolyte by applying a voltage across the anode and cathode.

[0008] In another embodiment, the method comprises: placing a first electrolyte in contact with a cathode; placing second electrolyte in contact with an anode; placing a third electrolyte such that it is separated from the first electrolyte by a first ion-exchange membrane; placing a fourth electrolyte such that it is separated from the third electrolyte by an third ion-exchange membrane and is separated from

the second electrolyte by a second ion- exchange membrane; and supplying carbon dioxide gas to the first electrolyte.

[0009] In various embodiments, the first ion-exchange membrane comprises a cation exchange membrane; the second ion-exchange
5 membrane comprises a cation exchange membrane; and the third ion-exchange membrane comprises an anion exchange membrane. In various embodiments, the first electrolyte is a cathode electrolyte in contact with the cathode, and the second electrolyte is an anode electrolyte in contact with an anode.

10 [0010] In various embodiments, the system and method are adapted to withdraw some or all of the cathode electrolyte via an outflow stream, and/or replenishing this electrolyte via an inflow stream to the cathode electrolyte compartment. In various embodiments, the system and method are adapted to withdraw some or all of the fourth electrolyte
15 from an outflow stream and replenishing this electrolyte via an inflow stream of the fourth electrolyte compartment. In various embodiments, the system and method are adapted for batch, semi-batch or continuous flow operation, with or without withdrawing and replenishing the electrolytes in the system.

20 [0011] In various embodiments, the system includes a hydrogen gas transfer system adapted for directing hydrogen gas generated at the cathode to the anode. In another embodiment, the system includes a carbon dioxide delivery system adapted for delivering carbon dioxide gas into the cathode electrolyte where it dissolves and may form
25 bicarbonate and/or carbonate ions, depending on the pH of the electrolyte. In embodiments in which carbon dioxide is supplied to the cathode electrolyte by dissolving the gas into the cathode electrolyte,

the dissolution may in some embodiments occur in one or more compartments located in the outflow stream, or in an inflow stream or in between them. In various embodiments, the system is operably connected to an industrial waste gas stream comprising combustion gases for supplying gases, e.g., carbon dioxide, to the cathode electrolyte. In various embodiments, the waste gas stream includes combustion gases from fossil fuelled electrical power generating plants, cement manufacturing plants and/or other industrial plants. In various embodiments, the waste gas includes acidic gases, e.g., oxides of nitrogen (nitrous oxide, nitric oxide) and sulfur gases (sulfur dioxide, hydrogen sulfide) that dissolve in the cathode electrolyte to form anions. In some embodiments the waste gas is treated to remove some or all of its non-carbon dioxide components before contact with the cathode electrolyte.

[0012] In various embodiments, the products of the system and method including the hydroxide ions, bicarbonate ions, carbonate ions, hydrochloric acid and a partially desalinated water from which certain cation and anions have been removed are utilized to sequester carbon dioxide and other constituents of industrial waste gases, e.g., sulfur gases, nitrogen oxide gases and other combustion gases, by contacting the waste gas with a solution comprising divalent cations and the hydroxide, bicarbonate and/or carbonate ions to precipitate divalent cation carbonates and bicarbonates as described in commonly assigned U.S. Patent Application no. 12/344,019 filed on December 24, 2008, herein incorporated by reference in its entirety. The precipitates, comprising, e.g., calcium and magnesium carbonates and bicarbonates in various embodiments are utilized as building materials, e.g., as

cements and aggregates, as described in commonly assigned U.S. Patent Application no. 12/126,776 filed on May 23, 2008, herein incorporated by reference in its entirety.

[0013] In another application, the partially desalinated water from which cation and anions have been removed, e.g., a partially desalinated water formed by removing sodium and chloride ions from the third electrolyte, is used as feed water in a desalination system where the water is further processed as described in commonly assigned U.S. Patent Application no. 12/163,205 filed on June 27, 2008, herein incorporated by reference in its entirety.

[0014] In another embodiment, the acid produced in the fourth electrolyte and/or the base solution produced in the cathode electrolyte are utilized to dissolve minerals and waste materials comprising divalent cations, e.g., Ca^{++} and Mg^{++} to produce divalent cation solutions that are utilized in producing divalent metal ion carbonate precipitates using the present cathode electrolyte. In various embodiments, the precipitates are used as building materials e.g. cement and aggregates as described in commonly assigned U.S. Patent application no. 12/126,776, herein incorporated by reference in its entirety.

BRIEF DESCRIPTION OF THE DRAWINGS

The following drawings illustrate by way of examples and not by limitation embodiments of the present system and method.

[0015] Fig. 1 is an illustration of an embodiment of the present system.

[0016] Fig. 2 is a flow chart of an embodiment of the present method.

[0017] Fig. 3 is a flow chart of an embodiment of the present method.

DETAILED DESCRIPTION

[0018] Before the present methods and systems are described in
5 detail, it is should be understood that the present system and method
are not limited to particular embodiments described and illustrated
herein, as such may vary. It is also to be understood that the
terminology used herein is for the purpose of describing particular
embodiments only, and is not limiting, since the scope are limited only
10 by the appended claims.

[0019] Herein, where a range of values is provided, it is should
understood that each intervening value, to the tenth of the unit of the
lower limit (unless the context clearly dictates otherwise) between the
upper and lower limit of that range and any other stated or intervening
15 value in that stated range, is encompassed within the present system
and method. The upper and lower limits of these smaller ranges may
independently be included in the smaller ranges and are also
encompassed within the system and method, subject to any specifically
excluded limit in the stated range. Where the stated range includes one
20 or both of the limits, ranges excluding either or both of those included
limits are also included in the system and method.

[0020] Herein, ranges are presented with numerical values being
preceded by the term "about." Herein, the term "about" is used to
provide literal support for the exact number that it precedes, as well as
25 a number that is near to or approximately the number that the term
precedes. In determining whether a number is near to or approximately
a specifically recited number, the near or approximating un-recited

number may be a number, which, in the context in which it is presented, provides the substantial equivalent of the specifically recited number.

[0021] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods, systems and materials similar or equivalent to those described herein can also be used in practicing the present system and method, only representative methods, systems and materials are herein described.

[0022] All publications and patents cited in this specification are herein incorporated by reference as if each individual publication or patent were specifically and individually indicated to be incorporated by reference and are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided may differ from the actual publication dates that may need to be independently confirmed.

[0023] As used herein and in the appended claims, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Also, the claims may be drafted to exclude any optional element. As such, this statement is intended to serve as antecedent basis for use of such exclusive terminology as “solely,” “only” and the like in connection with the recitation of claim elements, or use of a “negative” limitation.

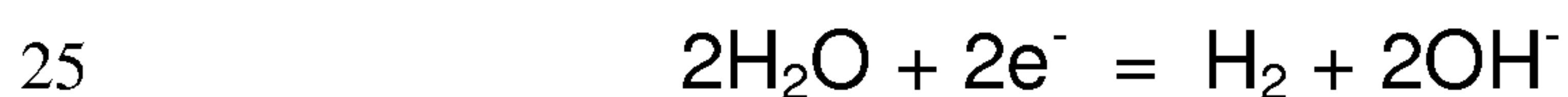
[0024] As will be apparent to those of skill in the art, each of the embodiments described and illustrated herein comprise discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope of the present invention. Any recited method can be carried out in the order of events recited or in any possible logical order.

[0025] In various embodiments, the present system and method pertain to producing hydroxide and/or bicarbonate and/or carbonate ions in an aqueous solution by a low-voltage, low-energy electrochemical process. In one embodiment, and with reference to Fig.1, hydroxide ions are produced in a cathode electrolyte 102 by applying a voltage of less than 3V across the cathode 104 and anode 108, while: i) oxidizing hydrogen gas at the anode 108 to produce protons; ii) migrating protons from the anode 108 through the anode electrolyte 106 and across a second cation exchange membrane 118 to a fourth electrolyte 116; iii) holding the voltage across the anode 108 and cathode 104 to a level such that a gas does not form at the anode 108; iv) reducing water at the cathode 104 to form hydroxide ions and hydrogen gas; v) preventing hydroxide ions in the cathode electrolyte 102 from migrating from the cathode electrolyte 102 to the adjacent third electrolyte 110 by positioning a first cation exchange membrane 112 between the cathode electrolyte 102 and the third electrolyte 110; vi) migrating sodium ions from the third electrolyte 110 to the cathode electrolyte 102 where they combine with hydroxide ions to form sodium hydroxide in the cathode electrolyte 102; vii) migrating chloride ions from the third electrolyte 110 across an anion exchange membrane

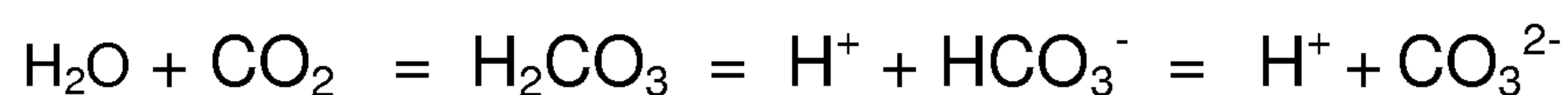
120 to the fourth electrolyte 116 where they combine with protons migrated from the anode 108 to form hydrochloric acid; and vii) separating the anode electrolyte 106 from the fourth electrolyte 116 by a second cation exchange membrane 118.

5 [0026] In various embodiments, hydrogen gas obtained at the cathode is directed to the anode where the gas is oxidized. In various embodiments, sodium hydroxide produced in the cathode electrolyte and hydrochloric acid produced in the fourth electrolyte are continually removed from the system, while the cathode electrolyte and sodium
10 chloride in the third electrolyte are continually replenished with water to maintain a continuous production operation of the system. In other embodiments, the system and method are adapted for other modes of operation, e.g., batch or semi-batch flows.

[0027] In another embodiment, bicarbonate ions and/or carbonate
15 ions are produced in the cathode electrolyte by dissolving carbon dioxide gas in the cathode electrolyte and applying a voltage of less than 3V across the anode and cathode. The carbon dioxide gas may be dissolved in the cathode electrolyte or may be dissolved in a separate carbon dioxide compartment 152 connected to the cathode electrolyte
20 compartment 122 to provide carbon dioxide, dissolved in a solution, to the cathode electrolyte compartment. In this embodiment, since carbon dioxide is dissolved in the cathode electrolyte, three reactions occur as follows:

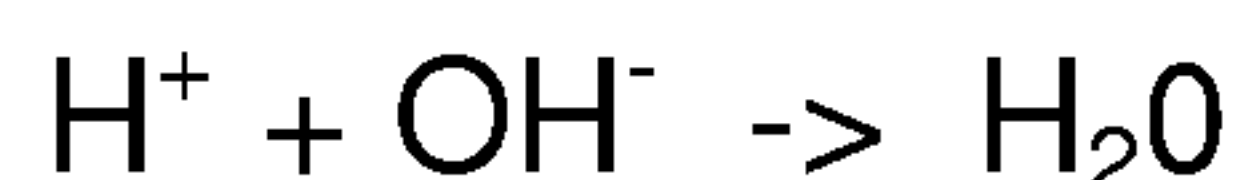


(water is reduced at the cathode),



(carbonate and/or bicarbonate ions are formed in the cathode electrolyte, depending on the pH of the electrolyte), and

5



As these reactions are pH dependent, the overall cathode reaction is:



10



or a combination of both reactions, depending on the pH of the cathode electrolyte.

15 [0028] In this embodiment, and with reference to Fig. 1, bicarbonate ions and/or carbonate ions are produced in a cathode electrolyte 102 by applying a voltage of less than 3V across the cathode 104 and anode 108, while: i) oxidizing hydrogen gas at the anode 108 to produce protons at the anode 108; ii) allowing protons formed at the anode 108
20 to migrate from the anode 108 through the anode electrolyte 106 and across the second cation exchange membrane 118 to the fourth electrolyte 116; iii) applying a voltage across the anode 108 and cathode 104 such that a gas does not form at the anode 108; iv) producing hydrogen gas at the cathode 104 and optionally circulating
25 the gas to the anode 108; v) preventing carbonate ions and/or bicarbonate anions produced in the cathode electrolyte 102 from migrating to the adjacent third electrolyte 110 by positioning the first

cation exchange membrane 112 between the cathode electrolyte 102 and the third electrolyte 110, wherein the cation exchange membrane is selected to block migration of anions from the cathode electrolyte 102; vi) migrating sodium ions from the third electrolyte 110 to the cathode electrolyte 102 through the first cation exchange membrane 112; vii) in the cathode electrolyte 102, combining sodium ions with carbonate ions and/or bicarbonate ions to form sodium carbonate and/or sodium bicarbonate in the cathode electrolyte 102; viii) migrating chloride ions from the third electrolyte 110 across the anion exchange membrane 120 to the fourth electrolyte 116; ix) in the fourth electrolyte 116, combining chloride ions with protons migrated from the anode electrolyte 106 to form hydrochloric acid; and x) preventing chloride ions from migrating from the fourth electrolyte 116 to the anode electrolyte 106 by positioning the second cation exchange membrane between the fourth electrolyte 116 and the anode electrolyte 106, wherein the second cation exchange membrane 118 is selected to block migration of anions from the fourth electrolyte 116 to the anode electrolyte 106.

[0029] In this embodiment of the system, as with the embodiment that produces hydroxide ions described above, hydrogen gas produced at the cathode is optionally directed to the anode where it is oxidized, or the gas is vented. In embodiments where the hydrogen gas is vented, another source of hydrogen gas provides the hydrogen gas to the anode. In various embodiments of this system, as with the production of hydroxide ions, the carbonate ions and/or bicarbonate ions produced in the cathode electrolyte are continually removed from the system while the cathode electrolyte and sodium chloride in the third electrolyte are

continually replenished with water to maintain continuous operation of the system. In various embodiments, the system and method are adaptable for other modes of operation, e.g., batch or semi-batch flows.

[0030] In various embodiments, as will be appreciated by one
ordinarily skilled in the art, the voltage across the anode and cathode is
dependent on the pH of the anode electrolyte and cathode electrolyte,
as well as the pH difference between these electrolytes. Thus, in
various embodiments, hydroxide ions, carbonate ions and/or
bicarbonate ions are produced in the cathode electrolyte when the
voltage applied across the anode and cathode is less than 3, 2.9 2.8,
2.7, 2.6 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2,
1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V or less, while the
pH of difference between the anode electrolyte and the cathode
electrolyte, is 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 pH units or
greater; and while the pH of the anode electrolyte varies from 1 to 7 pH
units and the pH of the cathode electrolytes varies from 7 to 14 pH units
or greater.

[0031] In various embodiments, and with reference to Fig.1, by
selectively placing the second cation exchange membrane 118
between the anode electrolyte 106 and the fourth electrolyte 116, and
on applying the present voltage across the anode 108 and cathode 104,
protons formed by oxidation of hydrogen gas at the anode 108 migrate
into the anode electrolyte 106 from where they migrate to the fourth
electrolyte 116 through the second cation exchange membrane 118.
However, since the fourth electrolyte 116 is separated from the third
electrolyte 110 by the anion exchange membrane 120, further migration
of the protons from the fourth electrolyte 116 towards the cathode

through the third electrolyte 110 is blocked; thus, protons accumulate in the fourth electrolyte 116 to form an acid, e.g., hydrochloric acid.

[0032] Similarly, and with reference to Fig. 1, by selectively placing the first cation exchange membrane 112 between cathode electrolyte 102 and the third electrolyte 110, and on applying the low voltage across the anode 108 and cathode 104, hydroxide ions or carbonate ions or bicarbonate ions form in the cathode electrolyte 102 from where their migration to the third electrolyte 110 is blocked by the first cation exchange membrane 112. Consequently, hydroxide ions, or carbonate ions or bicarbonate ions are contained in the cathode electrolyte 102. At the same time, hydrogen gas formed at the cathode 104 from reduction of water at the cathode 104 is vented or is directed to the anode for oxidation of the gas at the anode. If the hydrogen is vented, then an alternative exogenous source of hydrogen is utilized to provide the hydrogen gas to the anode.

[0033] In various embodiments, and with reference to Fig. 1, since the first cation exchange membrane 112 allows migration of cations from the third electrolyte 110 to the cathode electrolyte 102, and the anion exchange membrane 120 allows migration of anions from the third electrolyte 110 to the fourth electrolyte 116, on application of the voltage across the anode and cathode, cations, e.g., sodium ions, will migrate from the third electrolyte 110 to the cathode electrolyte 102, and anions, e.g., chloride ions will migrate from the third electrolyte 110 to the fourth electrolyte 116.

[0034] Thus, in embodiments where the third electrolyte 110 is initially charged with sodium chloride, sodium ions will migrate from the third electrolyte to the cathode electrolyte 102 to form sodium hydroxide or

sodium bicarbonate or sodium carbonate, depending on the pH of the cathode electrolyte 102. Similarly, chloride ions will migrate from the third electrolyte 110 to the fourth electrolyte to form hydrochloric acid 148 with protons that migrate from the anode electrolyte 106.

5 Consequently, in various embodiments, a partially desalinated water 150 from which sodium ions and chloride are removed is produced in the third electrolyte 110.

[0035] In various embodiments where hydrogen gas is not provided for oxidation at the anode, the system and method is adaptable to
10 produce a gas at the anode, e.g., oxygen or chlorine, while producing hydroxide, bicarbonate and carbonate ions in the cathode electrolyte and hydrogen gas at the cathode. As with other embodiments, in this embodiment the system and method are adaptable to form an acid in the fourth electrolyte and a partially desalinated water in the third
15 electrolyte, while forming a gas, e.g., oxygen or chlorine, at the anode. In this embodiment, however, since hydrogen gas is not oxidized at the anode, a higher voltage is generally required across the cathode and anode to drive the electrochemical reaction in the system.

[0036] In various embodiments, and with reference to Fig. 1, with the
20 voltages as described herein applied across the cathode 104 and anode 108, protons that form at the anode and migrate into the anode electrolyte 106 and to the fourth electrolyte 116 across the second cation exchange membrane 118 may cause the pH of the anode electrolyte 106 and the fourth electrolyte 116 to adjust, depending on
25 the flow of the electrolytes through the system. At the same time, as hydroxide ions, bicarbonate ions or carbonate ions that form in the cathode electrolyte 102 are prevented from migrating from the cathode

electrolyte across the first cation exchange membrane, the pH of the cathode electrolyte 102 may adjust, depending on the flow of the electrolytes through the system. Thus, in various embodiments, a pH differential is obtained between the cathode electrolyte 102 and anode electrolyte 106, e.g., a difference of at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14 pH units or more, depending on the flow of the electrolytes through the system. Similarly, due to the migration of protons to the fourth electrolyte 116 from the anode electrolyte 106, a pH differential is obtained between the fourth electrolyte 116 and the cathode electrolyte 102, e.g., a difference of at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14 pH units or more, depending on the flow of the electrolytes through the system.

[0037] In the following exemplary description of a specific embodiment of the system and method, for illustrative purposes, a system is configured as in Fig. 1 wherein a concentrated aqueous solution of sodium chloride 142 is used as the initial third electrolyte 110 between the first cation exchange membrane 112 and the anion exchange membrane 120. Also in this system, an electrically conductive water or a low concentration of sodium hydroxide solution or sodium bicarbonate solution or sodium carbonate solution is used as the initial cathode electrolyte 102; and in this system an electrically conductive water is used as the anode electrolyte 106; and further in this system a low concentration of the hydrochloric acid produced in the fourth electrolyte 116 is used as the initial fourth electrolyte.

[0038] Thus in this system, on applying a voltage across the anode 108 and cathode 104, sodium ions will migrate from the third electrolyte 110 to the cathode electrolyte 102, and chloride ions will migrate from

the third electrolyte to the fourth electrolyte 116; hydroxide ions, or carbonate ions or bicarbonate ions will be produced in the cathode electrolyte 102 (depending on whether carbon dioxide gas is added to the electrolyte); hydrogen gas will be produced at the cathode 104; hydrogen gas supplied to the anode 108 will be oxidized to protons at the anode; and the protons will migrate into the anode electrolyte 106 from where they will migrate across the second cation exchange membrane 118 to the fourth electrolyte 116 where they accumulate, as the anion exchange membrane 120 will block their further migration to the third electrolyte 110.

[0039] Consequently, in various embodiments, on applying a voltage across the anode and cathode in this system, sodium hydroxide will be produced in the cathode electrolyte; hydrochloric acid will be produced in the fourth electrolyte; the concentration of sodium chloride in the third electrolyte will decrease; hydrogen gas will be oxidized at the anode; and hydrogen gas will be generated at the cathode.

[0040] In an embodiment of this system where carbon dioxide gas is dissolved in the cathode electrolyte, the system and method additionally will produce bicarbonate and/or carbonate ions in the cathode electrolyte; hence, in this embodiment, sodium bicarbonate and/or sodium carbonate will be produced in the cathode electrolyte, depending on the pH of the cathode electrolyte. In this embodiment, as with the embodiment wherein carbon dioxide is not dissolved in the cathode electrolyte, the system and method will produce hydrochloric acid in the fourth electrolyte; the concentration of sodium chloride in the third electrolyte will decrease; hydrogen gas will be oxidized at the anode; and hydrogen gas will be generated at the anode.

[0041] As will be appreciated by one ordinarily skilled in the art, the present system and method are not limited to this exemplary use of sodium chloride solution as the third electrolyte, but are adaptable for using an equivalent ionic salt solution in the third electrolyte, e.g., a potassium sulfate. Thus, for example, if potassium sulfate were used, sulfuric acid will be produced in the fourth electrolyte and potassium hydroxide, bicarbonate and/or carbonate will be produced in the cathode electrolyte. As can be appreciated, the system and method with potassium sulfate as the third electrolyte will produce protons at the anode by oxidizing hydrogen gas supplied to the anode; hydrogen gas will form at the cathode; and the third electrolyte will be depleted of potassium and sulfate ions. In embodiments where carbon dioxide gas is dissolved in the cathode electrolyte, the system and method with potassium sulfate as the third electrolyte will produce bicarbonate and carbonate ions in the cathode electrolyte. Hence, in this equivalent system, potassium hydroxide, potassium bicarbonate and/or potassium carbonate will be produced in the cathode electrolyte, depending on the pH of the cathode electrolyte. Other electrolytes that can be used to produce the electrolytes in the present system include seawater, brackish water and brines. Such equivalent systems and methods are therefore within the scope of the present system and method.

[0042] Also as will be appreciated by one skilled in the art, in the embodiment where carbon dioxide is dissolved in the cathode electrolyte to produce bicarbonate and carbonate anions, other equivalent gases that react dissolve and ionize in water will produce equivalent results. Thus, for example, acidic gases such as sulfur dioxide and oxides of nitrogen that are soluble in the cathode electrolyte

will produce equivalent anions in the cathode electrolyte. Therefore, to the extent that an equivalent gas is dissolved in the third electrolyte to produce equivalent anions as with carbon dioxide, such systems and methods are also within by the scope of the present system and
5 method.

[0043] In various embodiments, the system and method are adapted to withdraw some or the entire cathode electrolyte from an outflow to an inflow stream of the cathode compartment. Also, the system and method are adapted to withdraw some or the entire fourth electrolyte
10 from an outflow stream to an inflow stream of the fourth electrolyte. In various embodiments, the system and method are adapted for batch, semi-batch or continuous flow operation, with or without directing hydrogen gas generated at the cathode for oxidation at the anode, and with or without withdrawing and replenishing the electrolytes in the
15 system.

[0044] In various embodiments, the system includes a hydrogen gas transfer system for circulating hydrogen gas from the cathode to the anode. In another embodiment, the system includes a carbon dioxide delivery system for dissolving carbon dioxide gas in the cathode
20 electrolyte. In various embodiments, the system is operably connected to an industrial waste gas stream comprising combustion gases for supplying gases, e.g., carbon dioxide, to the cathode electrolyte. In various embodiments, the waste gas stream includes combustion gases from fossil fuelled electrical power generating plants, cement
25 manufacturing plants and other industrial plants. In various embodiments, the waste gas includes acidic gases, e.g., oxides of nitrogen (nitrous oxide, nitric oxide) and sulfur gases (sulfur dioxide,

hydrogen sulfide) that dissolve in the cathode electrolyte to form anions analogous to the production of bicarbonate and carbonate ions when carbon dioxide is dissolved in the cathode electrolyte.

[0045] Referring to Fig.1, in one embodiment, the system 100

5 comprises: a first electrolyte that is a cathode electrolyte 102 in contact with a cathode 104; a second electrolyte that is anode electrolyte 106 contacting an anode 108; a third electrolyte 110 separated from the cathode electrolyte 102 by a first cation exchange membrane 112; a fourth electrolyte 116 separated from the anode electrolyte 106 by a
10 second cation exchange membrane 118; a third ion-exchange membrane 120 separating the third electrolyte 110 and fourth electrolytes 116. In various embodiments, the first ion-exchange membrane comprises a cation exchange membrane; the second ion-exchange membrane comprises a cation exchange membrane; and the
15 third ion-exchange membrane comprises an anion exchange membrane.

[0046] In the system illustrated in Fig. 1, cathode electrolyte 102 is in fluid contact with cathode 104 and both are contained in a first cell 122 defined by first cation exchange membrane 112 and first sidewall 124.

20 Similarly, anode electrolyte 106 is in fluid contact with anode 108 and both are contained in a second cell 126 defined by second cation exchange membrane 118 and second sidewall 128. Third cell 130 containing third electrolyte 110 is defined by first cation exchange membrane 112 and anion exchange membrane 120; and fourth cell 132
25 containing fourth electrolyte 116 is defined by anion exchange membrane 120 and second cation exchange membrane 118.

[0047] Also with reference to Fig.1, system 100 in various embodiments includes a voltage supply 134 that is capable of applying a voltage across the anode 108 and the cathode 104. In various embodiments the cathode and anode in the system are comprised of an un-reactive, conductive material such as nickel or platinum. The system includes a hydrogen gas circulating system 136 adapted for circulating hydrogen gas generated at the cathode 104 for oxidation at the anode 108. In various embodiments, the hydrogen gas is operationally connected to an external supply of hydrogen (not shown) to provide hydrogen gas to the anode, e.g., at start-up of operations when the hydrogen supply from the cathode is insufficient.

[0048] In various embodiments, the system includes a cathode electrolyte withdrawal and replenishing system 138 adapted for withdrawing all of, or a portion of, the cathode electrolyte 102 from the first cell 122 containing the cathode electrolyte. In various embodiments the system includes a fourth electrolyte withdrawal and replenishing system 140 for withdrawing and replenishing all of, or a portion of, the fourth electrolyte 116 to the fourth cell 132 containing the fourth electrolyte. In various embodiments, the system includes a salt supply system for providing a salt solution 142, e.g., concentrated sodium chloride, to the third electrolyte cell 130. In various embodiments the system includes a gas supply system 144 for providing a gas, e.g., carbon dioxide, to the cathode electrolyte 102. In various embodiments the system includes a carbon dioxide mixing system 152 in which carbon dioxide is supplied to the cathode electrolyte by dissolving the gas into the cathode in one or more compartments located in the outflow stream, or in an inflow stream or in between them. In various

embodiments, the system includes inlet ports (not shown) for introducing fluids into the cells (122, 126, 130, 132) and outlet ports (not shown) for removing fluids from the cells.

[0049] In various operating modes, e.g., continuous flow, batch flow or mixed modes, the system when charged with sodium chloride solution 142 will produce a solution of sodium hydroxide 146 in the cathode electrolyte 102, hydrochloric acid 148 in the fourth electrolyte 116, and an a partially desalinated aqueous solution 150 in which the cation and anion content is reduced. In various embodiments, the aqueous partially desalinated solution 150 is utilized feed water to a desalinated water treatment plant (not shown) for further processing to remove e.g., other ions present in the solution. In other embodiments, the aqueous solution 150 is used to prepare the initial electrolyte solutions for charging the first cell 122, second cell 126, third cell 130 and fourth cell 132 with an electrolyte.

[0050] As can be appreciated, in various embodiments and with reference to Fig. 1, although: i) the cathode electrolyte 102 is separated from the third electrolyte 110 by the first cation exchange membrane 112; and ii) the fourth electrolyte 116 is separated from the anode electrolyte 106 by the second cation exchange membrane 118; and iii) the fourth electrolyte 116 is separated from the third electrolyte 110 by the anion exchange membrane 120; nevertheless, when a voltage 134 is applied across the anode 108 and cathode 104, the negatively charged anions ions in the electrolytes will attempt to migrate towards the positive anode 108, and positively charged cations will attempt to migrate towards the negative cathode 104 through the first cation

exchange membrane 112, the second cation exchange membrane 118 and the anion exchange membrane 120 .

[0051] Thus, for example, with reference to Fig. 1, where the cathode electrolyte 102 and the anode electrolyte 106 are initially made
 5 conductive by adding a small amount of sodium hydroxide and hydrochloric acid respectively to the electrolytes; and the fourth electrolyte 116 is an aqueous solution initially made conductive by the adding a small amount of hydrochloric acid to the solution; and initially a concentrated solution of sodium chloride is placed in the third
 10 electrolyte 110; and initially a stream of hydrogen gas 136 is directed to the anode 108 through the anode electrolyte 106 for oxidation at the anode 108, on application of the voltage 134 across the anode 108 and cathode 104, protons will form at the anode 108 from oxidation of hydrogen gas 136 supplied to the anode, while hydroxide ions and
 15 hydrogen gas 138 will form at the cathode electrolyte 116 from the reduction of water, as follows:



[0052] As will be appreciated by one ordinarily skilled in the art and with reference to Fig. 1, since protons are formed at the anode 108 from hydrogen gas 136 provided to the anode 108; and since a gas such as oxygen does not form at the anode 108; and since water is
 25 electrolyzed in the cathode electrolyte to form hydroxide ions and hydrogen gas 138 at the cathode 104, therefore when a voltage is applied across the anode 108 and cathode 104, the system will produce

hydroxide ions in the cathode electrolyte 102 and protons in the anode electrolyte 106.

[0053] Further, as can be appreciated by one skilled in the art, in the present system since a gas does not form at the anode, the system will produce hydroxide ions in the cathode electrolyte and hydrogen gas at the anode when less than 3V is applied across the anode and cathode, in contrast to the higher voltage that is required in conventional systems that does generate gas, e.g., chlorine at the anode. For example, in various embodiments, hydroxide ions are produced when less than 2.0, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 V or less is applied across the anode and cathode.

[0054] Further, as will be appreciated by those ordinarily skilled in the art and with reference to Fig. 1, on applying a voltage across the anode 108 and cathode 104, the positively charged protons formed at the anode will attempt to migrate to the cathode 104 through the anode electrolyte 106, while the negatively charged hydroxide ions formed at the cathode 104 will attempt to migrate to the anode 108 through the cathode electrolyte 102.

[0055] However, as is illustrated in Fig. 1 and with reference to the hydroxide ions in the cathode electrolyte 102, since the first cation exchange membrane 112 will contain the cathode electrolyte 102 within first cell 122, and since the first cation exchange membrane 112 will prevent the migration of anions from the cathode electrolyte 102 to the third electrolyte 110, the hydroxide ions generated in the cathode electrolyte 102 will be prevented from migrating out of the cathode electrolyte through the first cation exchange membrane 112.

Consequently, on applying the voltage 134 across the anode and

cathode, the hydroxide ions produced at the cathode will be contained in the cathode electrolyte 102. Thus, depending on the flow rate of fluids into and out of the cathode electrolyte, the pH of the cathode electrolyte will adjust, e.g., the pH may increase, decrease or remain the same.

[0056] Similarly with reference to protons generated at the anode 108, under the applied voltage 134 across the cathode 104 and anode 108, the protons will enter the anode electrolyte 106 and migrate to the fourth electrolyte through the second cation exchange membrane 118. However, since the anion exchange membrane 120 between the fourth electrolyte 116 and the third electrolyte 110 will block the movement of cations from the fourth electrolyte 116 to the third electrolyte 116, consequently, protons in the fourth electrolyte 116 will be prevented from migrating from the fourth electrolyte to the third electrolyte 110. Consequently, on applying the voltage 134 across the anode and cathode, the protons produced at the anode will be contained in the fourth electrolyte 116. Thus, depending on the flow rate of fluids into and out of the fourth electrolyte the pH of the fourth electrolyte will adjust, e.g., the pH may increase, decrease or remain the same.

[0057] With reference to the third electrolyte 110 that is initially charged with a concentrated solution of sodium and chloride ions and contained in the third cell 130 by the anion exchange membrane 120 and the first cation exchange membrane 112, on applying a voltage across the anode 108 and cathode 104, anions in the third electrolyte 110, e.g., chloride ions, will attempt to migrate to the anode 108, while cations, e.g., sodium ions in the third electrolyte, will attempt to migrate to the cathode 104. Since the anion exchange membrane 120 will allow

the migration of anions from the third electrolyte 110 to the fourth electrolyte 116, chloride ions present in the third electrolyte 110 will migrate to the fourth electrolyte where they will form an acid, e.g., hydrochloric acid, with the protons from the anode.

- 5 [0058] Further, since the first cation exchange membrane 112 will allow the migration of cations from the third electrolyte 110 to the cathode electrolyte 102, sodium ions present in the third electrolyte 110 will migrate to the cathode electrolyte 102 where they will form sodium hydroxide with the hydroxide ions generated at the cathode 104.
- 10 Consequently, as is illustrated in Fig. 1, on application of a voltage across the anode 108 and cathode 104, the cations, e.g., sodium ions, and anions, e.g., chloride ions will migrate out of the third electrolyte 110, thereby forming a desalinated water in the third electrolyte.

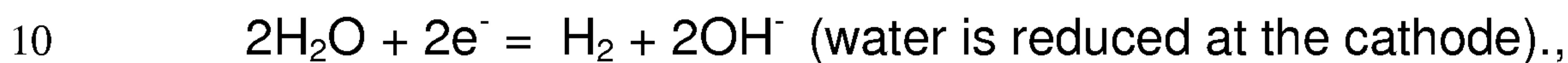
- [0059] In various embodiments and as is illustrated in Fig.1, hydrogen
- 15 gas 120 is generated at the cathode 104 from reduction of water in the cathode electrolyte. This gas can be vented from the cathode or directed to the anode 108 where it is oxidized to protons as described herein.

- [0060] In other embodiments, depending on the ionic species desired,
- 20 alternative reactants can be dissolved in the cathode electrolyte to produce the desired ions. Thus, for example, in various embodiments, carbon dioxide is added to the cathode electrolyte to produce carbonate and bicarbonate ions. The carbon dioxide gas can be added to the electrolyte by bubbling it directly into the electrolyte; alternatively, the
- 25 carbon dioxide gas may be dissolved in the cathode electrolyte or may be dissolved in a separate compartment 152 connected to the cathode

compartment by a conduit to feed the solution with carbon dioxide dissolved into the cathode compartment as noted above.

[0061] In embodiments where carbon dioxide is dissolved in the cathode electrolyte, as discussed above and with reference to Fig. 1, on
 5 applying the voltage across the anode 108 and cathode 104, the system 100 will produce hydroxide ions, bicarbonate ions, carbonate ions and hydrogen gas as follows:

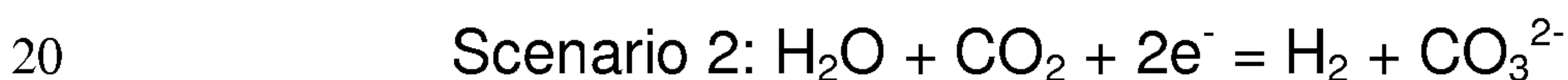
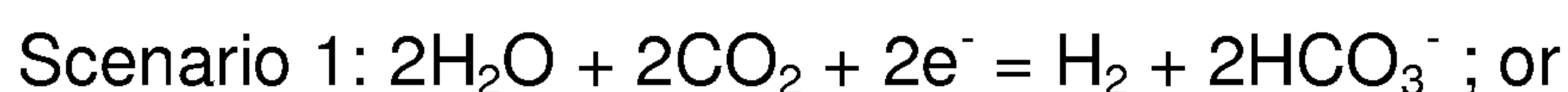
At the cathode 104, water is reduced to hydroxide ions and hydrogen gas as follows:



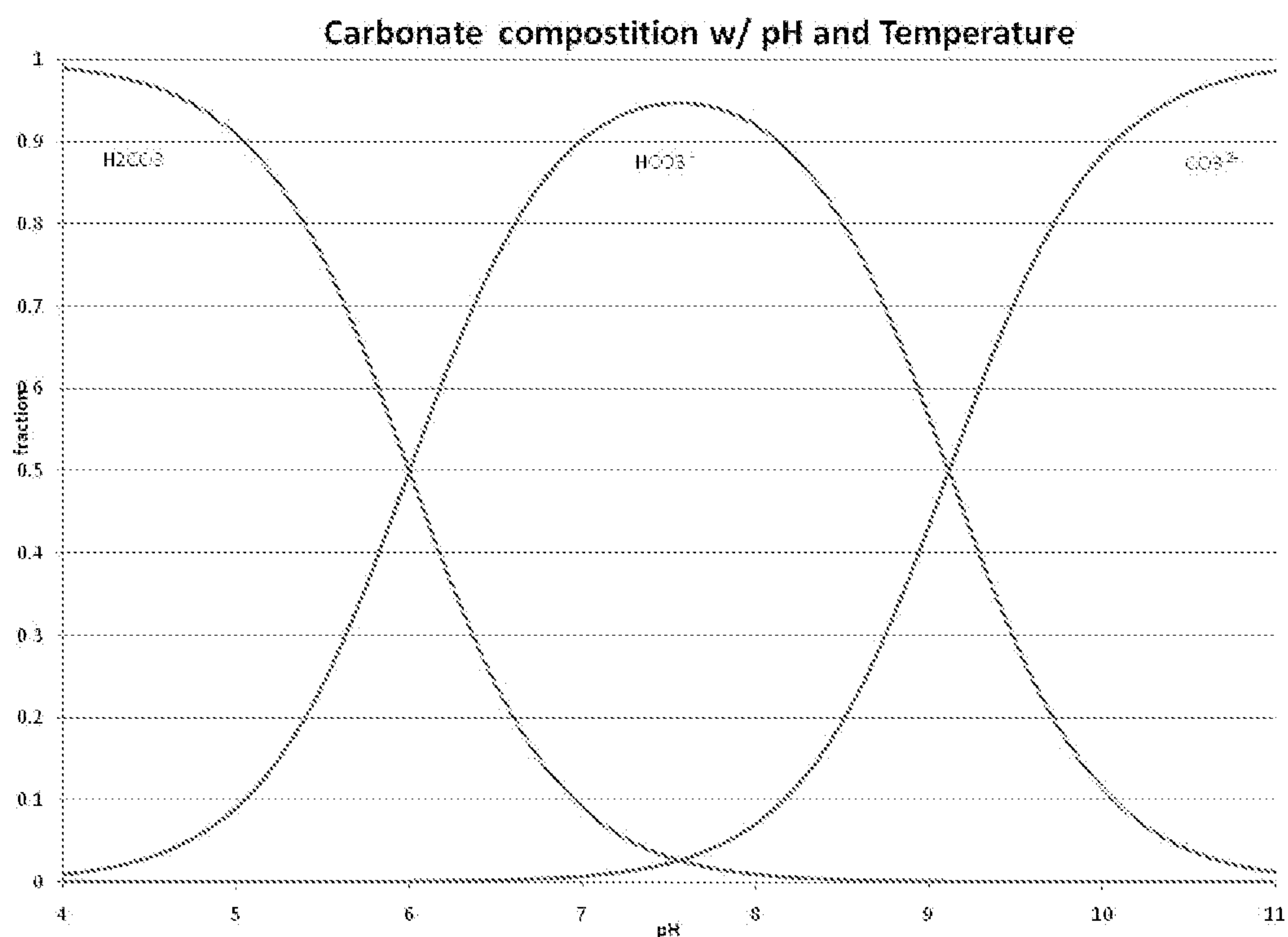
In the cathode electrolyte 102, the carbon dioxide gas will dissolve to form carbonic acid, protons, bicarbonate ions, and carbonate ions, depending on the pH of the electrolyte, as follows:



As the dissolution of carbon dioxide and the concentration of bicarbonate and carbonate ions in the cathode electrolyte 102 are pH dependant, the overall reaction in the first (cathode) cell 122 is either:



or a combination of both, depending on the pH of the cathode electrolyte 102, as is illustrated in the following carbonate speciation diagram:



Carbonate/Bicarbonate speciation in H₂O v. pH at 25 °C.

[0062] For either scenario the overall cell potential can be determined through the Gibbs energy change of the reaction by the formula:

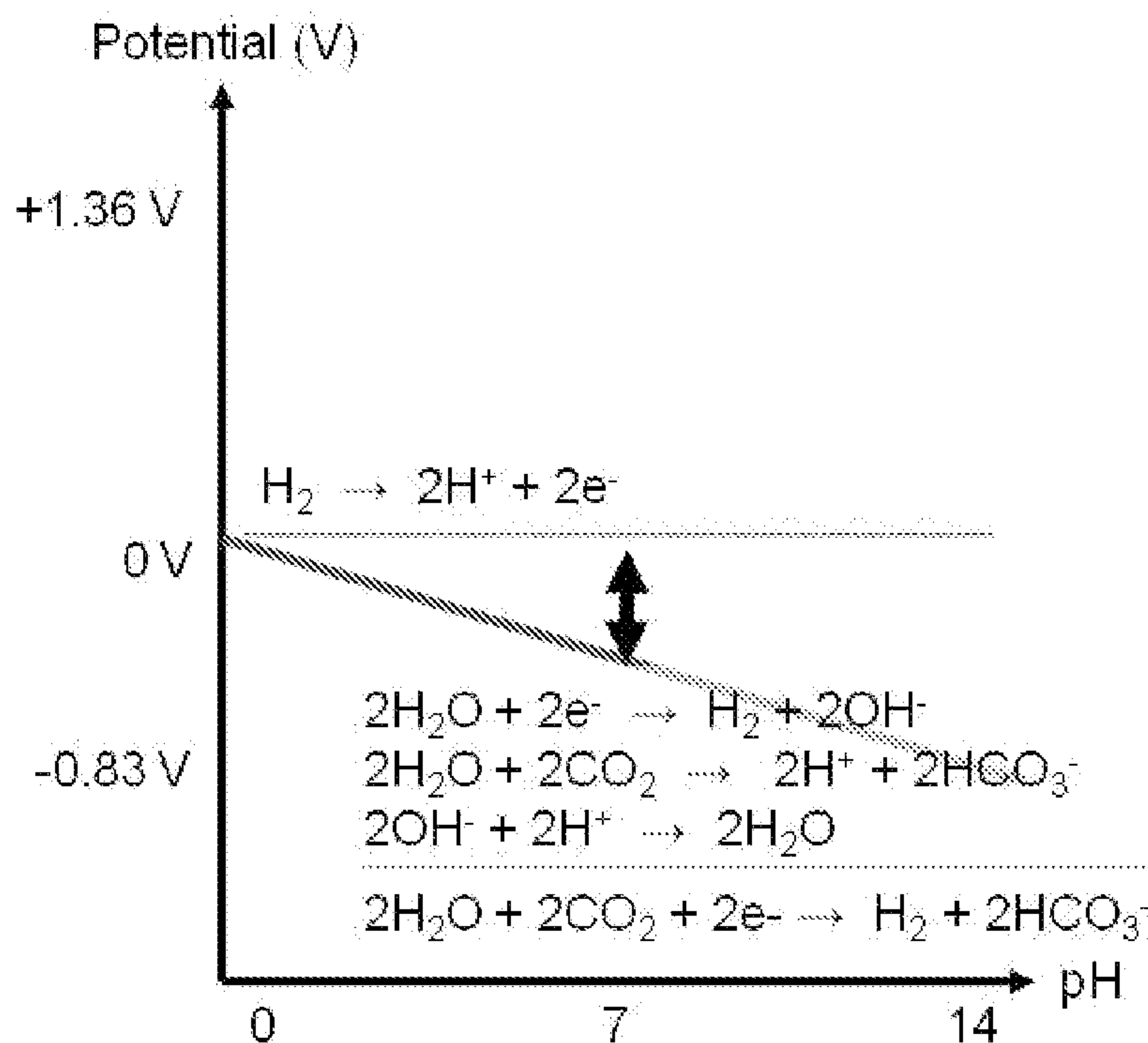
$$E_{\text{cell}} = -\Delta G/nF$$

Or, at standard temperature and pressure conditions:

$$E^{\circ}_{\text{cell}} = -\Delta G^{\circ}/nF$$

where, E_{cell} is the cell voltage, ΔG is the Gibbs energy of reaction, n is the number of electrons transferred, and F is the Faraday constant

(96485 J/Vmol). The E_{cell} of each of these reactions is pH dependent based on the Nernst equation as demonstrated for Scenario 1, below:



Scenario 1: Bicarbonate Ion Generation in the Cathode Electrolyte

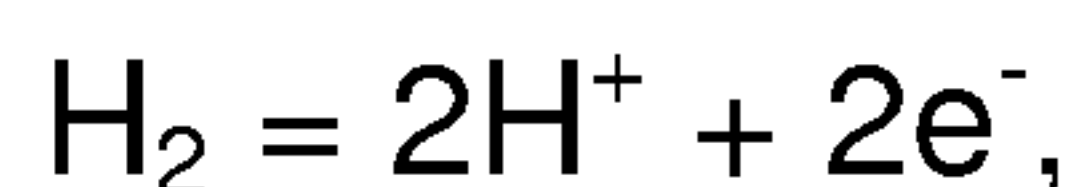
[0063] For either scenario the overall cell potential can be determined
 5 through the combination of Nernst equations for each half cell reaction:

$$E = E^{\circ} - R T \ln(Q) / n F$$

where, E° is the standard reduction potential, R is the universal gas constant, (8.314 J/mol K) T is the absolute temperature, n is the number of electrons involved in the half cell reaction, F is Faraday's
 10 constant (96485 J/V mol), and Q is the reaction quotient so that:

$$E_{\text{total}} = E_{\text{cathode}} + E_{\text{anode}}.$$

When hydrogen is oxidized to protons at the anode as follows:

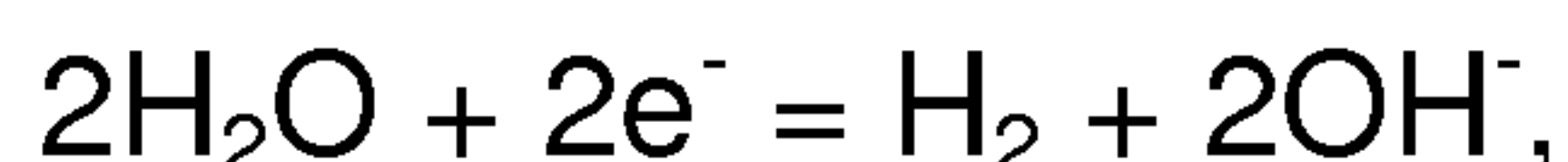


E° is 0.00 V, n is 2, and Q is the square of the activity of H^+ so that:

$$E_{\text{anode}} = -0.059 \text{ pH}_a,$$

where pH_a is the pH of the anode electrolyte.

When water is reduced to hydroxide ions and hydrogen gas at the cathode as follows:



E° is -0.83 V, n is 2, and Q is the square of the activity of OH^- so that:

$$E_{\text{cathode}} = -0.059 \text{ pH}_c,$$

where pH_c is the pH of the cathode electrolyte.

[0064] For either Scenario, the E for the cathode and anode reactions varies with the pH of the anode and cathode electrolytes. Thus, for Scenario 1 if the anode reaction, which is occurring in an acidic

environment, is at a pH of 0, then the E of the reaction is 0 V for the half cell reaction. For the cathode reaction, if the generation of bicarbonate ions occur at a pH of 7, then the theoretical E is $7 \times (0.059 \text{ V}) = 0.413 \text{ V}$ for the half cell reaction where a negative E means energy is needed to be input into the half cell or full cell for the reaction to proceed. Thus, if the anode pH is 0 and the cathode pH is 7 then the overall cell potential would be 0.413 V, where:

$$E_{\text{total}} = 0.059 (\text{pH}_a - \text{pH}_c) = 0.059 \Delta\text{pH}.$$

[0065] For Scenario 2 in which carbonate ions are produced, if the anode pH is 0 and the cathode pH is 10, this would represent an E of 0.59 V.

[0066] Thus, in various embodiments, an effect of directing CO_2 into the cathode electrolyte (to lower the pH of the cathode electrolyte and to produce bicarbonate ions and/or carbonate ions in the cathode electrolyte) is a lowering of the required voltage across the anode and cathode of the system to produce the hydroxide, carbonate and bicarbonate in the cathode electrolyte. In Scenario 1, it can be appreciated that if the cathode electrolyte was allowed to increase to a

pH of 14 or greater, the difference between the anode half-cell potential (represented as the thin dashed horizontal line) and the cathode half cell potential (represented as the thick solid sloping line) would increase to 0.83V. With increased duration of cell operation without CO₂ addition or other intervention, e.g., diluting with water, the required cell potential would continue to increase. It can thus be appreciated that operation of the electrochemical cell with the cathode pH at 7 or greater provides a significant energy savings.

[0067] Thus, as can be appreciated by one ordinarily skilled in the art, for different pH values in the cathode electrolyte and the anode electrolyte, hydroxide ions, carbonate ions and/or bicarbonate ions are produced in the cathode electrolyte when the voltage applied across the anode and cathode is less than 3, 2.9, 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V or less, while the pH difference between the anode electrolyte and the cathode electrolyte is greater 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or greater.

[0068] Also as will be appreciated by one skilled in the art, in embodiments wherein it is desired to produce bicarbonate and/or carbonate ions, the system as illustrated in Fig. 1, and as described above with reference to production of hydroxide ions, is adaptable to produce bicarbonate ions and/or carbonate ions in the cathode electrolyte 102 by dissolving carbon dioxide in the cathode electrolyte 102 and applying a voltage of less than 3V, or less than 2.5 V, or less than 2 V, or less than 1.5 V across the cathode 104 and anode 108, while: i) oxidizing hydrogen gas at the anode 108 to produce protons at the anode 108; ii) allowing protons formed at the anode 108 to migrate

from the anode 108 through the anode electrolyte 106 and across the second cation exchange membrane 118 to the fourth electrolyte 116; iii) applying a voltage across the anode 108 and cathode 104 such that a gas does not form at the anode 108; iv) producing hydrogen gas at the cathode 104 and optionally circulating the gas to the anode 108; v) preventing carbonate ions and/or bicarbonate anions produced in the cathode electrolyte 102 from migrating to the adjacent third electrolyte 110 by positioning the first cation exchange membrane 112 between the cathode electrolyte 102 and the third electrolyte 110, wherein the cation exchange membrane is selected to block migration of anions from the cathode electrolyte 102; vi) migrating sodium ions from the third electrolyte 110 to the cathode electrolyte 102 through the first cation exchange membrane 112; vii) in the cathode electrolyte 102, combining sodium ions with carbonate ions and/or bicarbonate ions to form sodium carbonate and/or sodium bicarbonate in the cathode electrolyte 102; viii) migrating chloride ions from the third electrolyte 110 across the anion exchange membrane 120 to the fourth electrolyte 116; ix) in the fourth electrolyte 116, combining chloride ions with protons migrated from the anode electrolyte 106 to form hydrochloric acid; and x) preventing chloride ions from migrating from the fourth electrolyte 116 to the anode electrolyte 106 by positioning the second cation exchange membrane between the fourth electrolyte 116 and the anode electrolyte 106, wherein the second cation exchange membrane 118 is selected to block migration of anions from the fourth electrolyte 116 to the anode electrolyte 106.

[0069] Thus, in producing carbonate/bicarbonate ions in the cathode electrolyte 102, as with the embodiment that produces hydroxide ions in

the cathode electrolyte without the addition of carbon dioxide to the cathode electrolyte as described above, the anode 108, the first cation exchange membrane 118, the anion exchange membrane 120, the first cation exchange membrane 112, the anode electrolyte, the fourth
5 electrolyte and the third electrolyte are functionally identical.

[0070] As with the production of hydroxide ions, in the production of carbonates and or bicarbonates, hydrogen gas 136 produced at the cathode 104 is optionally directed for oxidization of the hydrogen gas at the anode 108; a desalinated water 150 depleted of sodium chloride is
10 obtained from the third electrolyte 110, and hydrochloric acid 148 is produced in the fourth electrolyte. Also, in various embodiments as with the production of hydroxide ions, the carbonate ions or bicarbonate ions produced in the cathode electrolyte can be continually removed from the system while water in the cathode electrolyte and sodium chloride in
15 the third electrolyte are continually replenished to maintain a continuous operation of the system. In various embodiments, the system and method are adaptable for other modes of operation, e.g., batch or semi-batch flows.

[0071] As can be appreciated by one skilled in the art, in various
20 embodiments, the system can be configured to operate in various production modes including batch mode, semi-batch mode, continuous flow mode, with or without the option to withdraw portions of the sodium hydroxide produced in the cathode electrolyte, or withdraw all or a portions of the acid produced in the fourth electrolyte, or direct the
25 hydrogen gas produced at the cathode to the anode where it may be oxidized.

[0072] In various embodiments, the hydroxide ions, bicarbonate ions and/or carbonate ion solutions are produced in the cathode electrolyte when the voltage applied across the anode and cathode is less than 3, 2.9 or less, 2.8 or less, 2.7 or less, 2.6 or less, 2.5 or less, 2.4 or less, 2.3 or less, 2.2 or less, 2.1 or less, 2.0 or less, 1.9 or less, 1.8 or less, 1.7 or less, 1.6, or less 1.5 or less, 1.4 or less, 1.3 or less, 1.2 or less, 1.1 or less, 1.0 or less, 0.9 or less or less, 0.8 or less, 0.7 or less, 0.6 or less, 0.5 or less, 0.4 or less, 0.3 or less, 0.2 or less, or 0.1 V or less.

[0073] In another embodiment, the system and method is adaptable to allow for formation of a gas at the anode, e.g., oxygen or chlorine, while hydroxide ions, carbonate ions and bicarbonate ions are produced in the cathode electrolyte and hydrogen gas is generated at the cathode. However, in this embodiment, hydrogen gas is not supplied to the anode. While with this embodiment protons will be produced at the anode, and sodium hydroxide, sodium carbonate, and/or sodium bicarbonate will be produced in the cathode electrolyte, in general the voltage across the anode and cathode will be higher compared to the embodiment when a gas does not form at the anode but, instead, hydrogen gas is oxidized at the anode.

[0074] In various embodiments, and with reference to Fig.1, useable anion exchange membrane 120 include conventional anion exchange ion exchange membranes. Preferably, such membranes should be useable in an acidic and/or basic electrolytic solution temperatures in the range from about 0°C to about 100°C or higher. Similarly, first cation exchange membrane 112 and second cation exchange membrane 118 may be selected from conventional cation ion exchange membranes and should be useable in an acidic and/or basic electrolytic

solution temperatures in the range from about 0 °C to about 100 °C or higher.

[0075] Examples of suitable cation exchange membranes include, e.g., a TeflonTM-based membranes available from Asahi Kasei of Tokyo, Japan. In general, exemplary cation exchange membrane should be capable of use in strong basic solutions in a temperature range from about 0°C to about 120°C and higher. However, with reference to Fig. 1, as can be appreciated, due to the low voltage and low temperature operation of the present system, other low cost hydrocarbon-based cation exchange membranes can also be utilized. Such hydrocarbon-based membranes are available from e.g., Membrane International of Glen Rock, NJ, USA.

[0076] Similarly, typical hydrocarbon based anion exchange membranes are also available from Membrane International of Glen Rock, NJ, USA. In general, such anion exchange membranes should exhibit high ion selectivity, low ionic resistance, high burst strength, and high stability in an acidic electrolytic solution temperature range from about 0°C to about 100°C or higher.

[0077] As will be appreciated by one skilled in the art, since a cation exchange membrane is selective to migrating cations between two adjacent electrolytes, when a cation exchange membrane is positioned between two electrolytes in an electrochemical system as is illustrated in Fig.1, the membrane will allow migration of cations from one electrolyte to an adjacent electrolyte in the direction of the cathode.

Thus, for example, and with reference to Fig. 1, on applying a voltage across the cathode 104 and an anode 108, cations, e.g., sodium ions, will migrate from the third electrolyte 110 to the cathode electrolyte 102

across the first cation exchange membrane 112. Also as will be appreciated, at the same time, the first cation exchange membrane 112 being selective to cations will block migration of anions from the cathode electrolyte to the third electrolyte 110 in the direction of the anode 108.

[0078] Also as will be appreciated by those skilled in the art, since an anion exchange membrane is selective to migrating anions between two adjacent electrolytes, when an anion exchange membrane is positioned between two electrolytes in an electrochemical system as is illustrated in Fig.1, the membrane will allow migration of anions from one electrolyte to an adjacent electrolyte in the direction of the anode.

[0079] Thus, for example, and with reference to Fig. 1, on applying a voltage across the cathode 104 and an anode 108, anions, e.g., chloride ions, will migrate from the third electrolyte 110 to the fourth electrolyte 116 across the anion exchange membrane 120. Also as will be appreciated, at the same time, the anion exchange membrane 120 being selective to anions will block migration of cation from the fourth electrolyte 116 to the third electrolyte 110 in the direction of the cathode 104.

[0080] With reference to Figs. 1 and 2, the method 200 in one embodiment comprises a step 202 of: e.g., placing a first electrolyte that is a cathode electrolyte in contact with a cathode, and a second electrolyte that is an anode electrolyte in contact with an anode; a step 204 of e.g., placing a third electrolyte such that it is separated from the cathode electrolyte by a first cation exchange membrane; a step 206 of e.g., placing a fourth electrolyte such that it is separated from the third electrolyte by an anion exchange membrane and is separated from the

anode electrolyte by a second cation exchange membrane; and a step
208 of e.g., forming hydroxide ions in the cathode electrolyte by
applying a voltage across the anode and cathode. In various
embodiments, method 200 does not form a gas at the anode when the
5 voltage applied across the anode and cathode is less than 3 or less, 2.9
or less, 2.8 or less, 2.7 or less, 2.6 or less, 2.5 or less, 2.4 or less, 2.3
or less, 2.2 or less, 2.1 or less, 2.0 or less, 1.9 or less, 1.8 or less, 1.7
or less, 1.6 or less, 1.5 or less, 1.4 or less, 1.3 or less, 1.2 or less, 1.1
or less, 1.0 or less, 0.9 or less, 0.8 or less, 0.7 or less, 0.6 or less, 0.5
10 or less, 0.4 or less, 0.3 or less, 0.2 or less, or 0.1 V or less, while
hydrogen gas is provided to the anode where it is oxidized to protons.
As will be appreciated by one ordinarily skilled in the art, by not forming
a gas at the anode and by providing hydrogen gas to the anode for
oxidation at the anode, and by otherwise controlling the resistance in
15 the system, hydroxide ions can be produced in the cathode electrolyte
with the present lower voltages.

[0081] In various embodiments, method 200 further comprises, a step
of e.g., directing carbon dioxide 144 gas into the cathode electrolyte
102; a step of e.g., directing carbon dioxide gas 144 into the cathode
20 electrolyte before or after the cathode electrolyte is placed in contact
with the cathode 104; a step of e.g., applying a voltage 134 of less than
3 V, or less than 2V, or less than 1.5V, or less than 1V, or less than
0.5V across the cathode 104 and anode 108; a step of e.g., forming
hydrogen gas 136 at the cathode; a step of e.g., forming oxidizing
25 hydrogen to form protons at the anode 108; e.g., a step of forming a pH
differential of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 pH units or
greater between the anode and cathode electrolytes without forming a

gas at the anode by applying a voltage of less than 3 V, or less than 2V, or less than 1.5V, or less than 1V, or less than 0.5V across the anode and the cathode; a step of forming pH differential of between 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 pH units or greater between the fourth electrolyte 116 and the cathode electrolyte 102 by applying a voltage of 3V or less, or less than 2V, or less than 1.5V, or less than 1.0V, or less than 0.5V across the anode and the cathode; a step of e.g., forming hydroxide ions, bicarbonate ions, carbonate ions and/or a combination thereof in the cathode electrolyte 102; a step of e.g., forming sodium hydroxide, sodium bicarbonate or sodium carbonate in the cathode electrolyte 102; a step of e.g., migrating protons from the anode electrolyte 106 across the second cation exchange membrane 118 to the fourth electrolyte 116; a step of e.g., a step of migrating anions from the third electrolyte 110 across the anion exchange membrane 120 to the fourth electrolyte 116; a step of e.g., migrating chloride ions from the third electrolyte 110 across the anion exchange membrane 120 to the fourth electrolyte 116; a step of e.g., forming an acid 148 in the fourth electrolyte; a step of e.g., forming hydrochloric acid 148 in the fourth electrolyte; a step of e.g., migrating cations from the third electrolyte 110 across the first cation exchange membrane 112 to the cathode 104; a step of e.g., migrating sodium ions from the third electrolyte 110 across the first cation exchange membrane 112 to the cathode electrolyte 102; a step of e.g., directing hydrogen gas formed at the cathode 104 for oxidation of the gas at the anode 108; a step of e.g., removing cathode electrolyte 102 via an outflow and replenishing cathode electrolyte via an inflow stream to the cathode electrolyte; a step of e.g., removing fourth cathode electrolyte 116 via an outflow

stream and replenishing the fourth electrolyte via an inflow stream of the fourth electrolyte.

[0082] With reference to Figs. 3 and 1, in another embodiment, the method 300 comprises a step of 302 of e.g., placing a cathode electrolyte 102 in contact with a cathode 104, and an anode electrolyte 106 in contact with an anode 108; a step 304 of e.g., placing a third electrolyte 110 such that it is separated from the cathode electrolyte 102 by a first cation exchange membrane 112; a step 306 of e.g., placing a fourth electrolyte 116 such that it is separated from the third electrolyte 110 by an anion exchange membrane 120 and is separated from the anode electrolyte 106 by a second cation exchange membrane 118; and a step 308 of e.g., forming hydroxide ions in the cathode electrolyte 102 by applying a voltage across the anode and cathode.

[0083] In various embodiments, method 300 as with method 200 does not form a gas at the anode 108 when the voltage applied across the anode and cathode is less than 3, 2.9, 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V or less, while hydrogen gas is provided to the anode where it is oxidized to protons. As will be appreciated by one ordinarily skilled in the art, by not forming a gas at the anode and by providing hydrogen gas to the anode for oxidation at the anode, hydroxide ions are produced in the cathode electrolyte with the present voltages. In various embodiments, method 300 in conjunction with the system of Fig. 1 further comprises a step of: e.g., applying a voltage across the anode 108 and cathode 104 such that a gas, e.g., oxygen or chlorine, is prevented from forming at the anode; a step of e.g., forming

bicarbonate ions, carbonate ions or a mixture of bicarbonate and carbonate ions in the cathode electrolyte 102; a step of e.g., supplying and oxidizing hydrogen gas at the anode 108; applying a voltage of 3, 2.9, 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V or less across the cathode and anode; e.g., forming hydrogen gas the cathode 104; a step of e.g., oxidizing hydrogen gas at the anode to form protons at the anode; a step of e.g., forming a pH differential of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 pH units or greater between the anode electrolyte and cathode electrolyte without forming a gas at the anode; a step of e.g., forming a pH gradient of pH differential of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 pH units or greater between the fourth electrolyte and cathode electrolyte without forming a gas at the anode; a step of e.g., forming sodium carbonate, sodium bicarbonate or mixture of sodium carbonate and sodium bicarbonate in the cathode electrolyte 102; a step of e.g., migrating protons from the anode electrolyte 106 across the second cation exchange membrane 118 to the fourth electrolyte 116; a step of migrating anions from the third electrolyte 110 across the anion exchange membrane to the fourth electrolyte 116; a step of e.g., migrating chloride ions from the third electrolyte 110 across the anion exchange membrane 120 to the fourth electrolyte 116; a step of e.g., forming an acid 148 in the fourth electrolyte; a step of e.g., forming hydrochloric acid 148 in the fourth electrolyte; a step of e.g., migrating cations from the third electrolyte 110 across the first cation exchange membrane 112 to the cathode electrolyte 102; a step of e.g., migrating sodium ions from the third electrolyte 110 across the first cation exchange membrane 112 to the

cathode electrolyte 102; a step of e.g., circulating hydrogen gas 136 formed at the cathode 104 for oxidation at the anode 108; a step of e.g., circulating at least a portion of the cathode electrolyte 102 from an outflow to an inflow stream of the cathode electrolyte; and a step of
5 e.g., circulating a portion of the fourth electrolyte 116 from an outflow stream to an inflow stream.

[0084] In various embodiments, bicarbonate ions and carbonate ions are produced where the voltage applied across the anode and cathode is less than 3.0, 2.9, 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8,
10 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1V or less without the formation of gas at the anode. In various embodiments, the method is adapted to withdraw and replenish at least a portion of the cathode electrolyte and the acid in the fourth electrolyte back into the system in either a batch, semi-batch or continuous mode
15 of operation.

[0085] With reference to Fig.1, when a voltage is applied across the anode and cathode hydroxide ions, or carbonate and/or bicarbonate ions will form in the in the cathode electrolyte and consequently cause the pH of the cathode electrolyte to be adjusted. In one embodiment,
20 when a voltage of about 0.1 V or less, 0.2 V or less. 0.4V or less, 0.6 V or less, 0.8 V or less, 1.0V or less, 1.5V or less, or 2.0V or less, e.g., when a voltage of 0.8V or less is applied across the anode and cathode, the pH of the cathode electrolyte solution is increased; in another embodiment, when a voltage of 0.01 to 2.5 V, or 0.01V to
25 2.0V, or 0.1V to 2.0V, or 0.1 to 2.0 V, or 0.1V to 1.5V, or 0.1 V to 1.0V, or 0.1V to 0.8V, or 0.1V to 0.6V, or 0.1V to 0.4V, or 0.1V to 0.2V, or 0.01V to 1.5V, or 0.01 V to 1.0V, or 0.01V to 0.8V, or 0.01V to 0.6V, or

0.01V to 0.4V, or 0.01V to 0.2V, or 0.01V to 0.1V, e.g., when a voltage of 0.1V to 2.0V is applied across the anode and cathode the pH of the cathode electrolyte increased; in yet another embodiment, when a voltage of about 0.1 to 1 V is applied across the anode and cathode the pH of the cathode electrolyte solution increased. Similar results are achievable with voltages of 0.1 to 0.8 V; 0.1 to 0.7 V; 0.1 to 0.6 V; 0.1 to 0.5 V; 0.1 to 0.4 V; and 0.1 to 0.3 V across the electrodes.

[0086] Exemplary results achieved with the present system are summarized in Table 1, below. Using 270 cm² 20-mesh Ni gauze for cathode and a 50cm² 100-mesh Pt gauze as anode, several 24-hr runs were done where hydrogen gas flow to the anode was controlled at a rate of 20 mL/min at room temperature while various voltages were applied across the anode and cathode. A SolartronTM potentiostat was used for electrochemical measurements, and a PC Acid and a PC SK ion exchange membrane from GMbHTM Membranes of Germany were chosen as the anion exchange membrane and cation exchange membrane, respectively.

Table 1. 24-hr Analysis Summary

Applied Voltage	Anion Exchange Membrane	Cation Exchange Membrane	Initial Anode pH	Final Anode pH	Initial Cathode pH	Final Cathode pH	Change Cathode in pH
1.0	PC Acid	PC SK	5.87	1.13	9.75	12.44	2.69
1.0	PC Acid	PC SK	4.68	2.03	9.20	12.43	3.23
1.0	PC Acid	PC SK	3.25	2.02	9.98	11.33	1.35

[0087] For example, in particular embodiments the method and system are capable of producing a pH difference of more than 0.5 pH units between the anode electrolyte solution and a cathode electrolyte

solution, and the two electrolyte solutions are separated, e.g., by one or more ion exchange membranes, when a voltage of 3V or less, 2.9 V or less or 2.5 V or less, or 2 V or less is applied across the anode and cathode. In some embodiments the method and system are capable of producing a pH difference of more than 1.0 pH units, or 2 pH units, or 4 pH units, or 6 pH units, or 8 pH units, or 10 pH units, or 12 pH units, or 14 pH units between a first electrolyte solution and a second electrolyte solution where the first electrolyte solution contacts an anode and the second electrolyte solution contacts a cathode, and the two electrolyte solutions are separated, e.g., by one or more ion exchange membranes, when a voltage of 0.1V or less is applied across the anode and cathode. In some embodiments the invention provides a system that is capable of producing a pH difference of more than 2.0 pH units between a first electrolyte solution and a second electrolyte solution where the first electrolyte solution contacts an anode and the second electrolyte solution contacts a cathode, and the two electrolyte solutions are separated, e.g., by one or more ion exchange membranes, when a voltage of 0.2V or less is applied across the anode and cathode.

[0088] In other embodiments, the method and system are capable of producing a pH difference of more than 4.0 pH units between a first electrolyte solution and a second electrolyte solution where the first electrolyte solution contacts an anode and the second electrolyte solution contacts a cathode, and the two electrolyte solutions are separated, e.g., by one or more ion exchange membranes, when a voltage of 0.4V or less is applied across the anode and cathode. In some embodiments the invention provides a system that is capable of producing a pH difference of more than 6 pH units between a first

electrolyte solution and a second electrolyte solution where the first electrolyte solution contacts an anode and the second electrolyte solution contacts a cathode, and the two electrolyte solutions are separated, e.g., by one or more ion exchange membranes, when a voltage of 0.6V or less is applied across the anode and cathode. In some embodiments the invention provides a system that is capable of producing a pH difference of more than 8 pH units between a first electrolyte solution and a second electrolyte solution where the first electrolyte solution contacts an anode and the second electrolyte solution contacts a cathode, and the two electrolyte solutions are separated, e.g., by one or more exchange membranes, when a voltage of 0.8V or less is applied across the anode and cathode. In particular embodiments the invention provides a system that is capable of producing a pH difference of more than 8 pH units between a first electrolyte solution and a second electrolyte solution where the first electrolyte solution contacts an anode and the second electrolyte solution contacts a cathode, and the two electrolyte solutions are separated, e.g., by one or more ion exchange membranes, when a voltage of 1.0 V or less is applied across the anode and cathode. In some embodiments the invention provides a system that is capable of producing a pH difference of more than 10 pH units between a first electrolyte solution and a second electrolyte solution where the first electrolyte solution contacts an anode and the second electrolyte solution contacts a cathode, and the two electrolyte solutions are separated, e.g., by one or more ion exchange membranes, when a voltage of 1.2V or less is applied across the anode and cathode.

[0089] As will be appreciated by one skilled in the art, the voltage need not be kept constant and the voltage applied across the anode and the cathode may be very low, e.g., 0.05V or less, when the two electrolytes are the same pH or close in pH, and that the voltage may
5 be increased as needed as the pH difference increases. In this way, the desired pH difference or production of hydroxide ions, carbonate ions and bicarbonate ions may be achieved with the minimum average voltage. Thus in some embodiments described in the previous paragraph, the average voltage may be less than 80%, 70%, 60%, or
10 less than 50% of the voltages given in previous paragraph for particular embodiments.

[0090] In various embodiments and with reference to Fig. 1, hydrogen gas formed at the cathode 104 is directed to the anode 108. Without being bound to any theory, it is believed that the hydrogen gas is
15 adsorbed and/or absorbed into the anode and subsequently oxidized to form protons at the anode.

[0091] In some embodiments, divalent cations are removed from the electrolyte solutions, e.g., in magnesium or calcium, during parts of the process where the electrolytes are in contact with the ion exchange
20 membranes. This is done to prevent scaling of the membranes, if necessary for that particular membrane. Thus, in various embodiments the total concentration of divalent cations in the electrolyte solutions when they are in contact with the ion exchange membrane or
membranes for any appreciable time is less than 0.06 mol/kg solution,
25 or less than 0.06 mol/kg solution, or less than 0.04 mol/kg solution, or less than 0.02 mol/kg solution, or less than 0.01 mol/kg solution, or less than 0.005 mol/kg solution, or less than 0.001 mol/kg solution, or less

than 0.0005 mol/kg solution, or less than 0.0001 mol/kg solution, or less than 0.00005 mol/kg solution.

[0092] In embodiments where carbon dioxide gas is dissolved in the cathode electrolyte, as protons are removed from the cathode

5 electrolyte more carbon dioxide may be dissolved to form bicarbonate and/or carbonate ions. Depending on the pH of the cathode electrolyte the balance is shifted toward bicarbonate or toward carbonate, as is well understood in the art and as is illustrated in the carbonate speciation diagram, above. In these embodiments the pH of the
10 cathode electrolyte solution may decrease, remain the same, or increase, depending on the rate of removal of protons compared to rate of introduction of carbon dioxide. It will be appreciated that no hydroxide, carbonate or bicarbonate ion are formed in these embodiments, or that hydroxide, carbonate, bicarbonate may not form
15 during one period but form during another period.

[0093] In another embodiment, the present system and method are integrated with a carbonate and/or bicarbonate precipitation system (not illustrated) wherein a solution of divalent cations, when added to the present cathode electrolyte, causes formation of precipitates of divalent
20 carbonate and/or bicarbonate compounds e.g., calcium carbonate or magnesium carbonate and/or their bicarbonates. In various embodiments, the precipitated divalent carbonate and/or bicarbonate compounds are utilized as building materials, e.g., cements and aggregates as described for example in commonly assigned U.S.
25 Patent Application no. 12/126,776 filed on May 23, 2008, herein incorporated by reference in its entirety.

[0094] In an alternative embodiment, the present system and method are integrated with a mineral and/or material dissolution and recovery system (not illustrated) wherein the acidic fourth electrolyte solution 116 or the basic cathode electrolyte 102 is utilized to dissolve calcium and/or magnesium-rich minerals e.g., serpentine or olivine, or waste materials e.g., fly ash, red mud and the like, to form divalent cation solutions that are utilized to precipitate carbonates and/or bicarbonates as described herein. In various embodiments, the precipitated divalent carbonate and/or bicarbonate compounds are utilized as building materials, e.g., cements and aggregates as described for example in commonly assigned U.S. Patent Application no. 12/126,776 filed on May 23, 2008, herein incorporated by reference in its entirety.

[0095] In an alternative embodiment, the present system and method are integrated with an industrial waste gas treatment system (not illustrated) for sequestering carbon dioxide and other constituents of industrial waste gases, e.g., sulfur gases, nitrogen oxide gases, metal and particulates, wherein by contacting the flue gas with a solution comprising divalent cations and the present cathode electrolyte comprising hydroxide, bicarbonate and/or carbonate ions, divalent cation carbonates and/or bicarbonates are precipitated as described in commonly assigned U.S. Patent Application no. 12/344,019 filed on December 24, 2008, herein incorporated by reference in its entirety. The precipitates, comprising, e.g., calcium and/or magnesium carbonates and bicarbonates in various embodiments are utilized as building materials, e.g., as cements and aggregates, as described in commonly assigned U.S. Patent Application no. 12/126,776 filed on May 23, 2008, herein incorporated by reference in its entirety.

[0096] In another embodiment, the present system and method are integrated with an aqueous desalination system (not illustrated) wherein the partially desalinated water 150 of the third electrolyte of the present system is used as feed-water for the desalination system, as described
5 in commonly assigned U.S. Patent Application no. 12/163,205 filed on June 27, 2008, herein incorporated by reference in its entirety.

[0097] In an alternative embodiment, the present system and method are integrated with a carbonate and/or bicarbonate solution disposal system (not illustrated) wherein, rather than producing precipitates by
10 contacting a solution of divalent cations with the first electrolyte solution to form precipitates, the system produces a slurry or suspension comprising carbonates and/or bicarbonates. In various embodiments, the slurry/suspension is disposed of in a location where it is held stable for an extended periods of time, e.g., the slurry/suspension is disposed
15 in an ocean at a depth where the temperature and pressure are sufficient to keep the slurry stable indefinitely, as described in U.S. Patent Application no. 12/344,019 filed on December 24, 2008, herein incorporated by reference in its entirety.

[0098] While several embodiments of the system and method have
20 been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example and not by limitation. Thus, variations, changes, and substitutions will occur to those skilled in the art that are within the scope of the appended claims.

CLAIMS:

1. An electrochemical system comprising:
a first electrolyte that is a cathode electrolyte in contact with a
5 cathode;
a second electrolyte that is an anode electrolyte in contact with an
anode;
a third electrolyte separated from the cathode electrolyte by a first
ion-exchange membrane;
10 a fourth electrolyte separated from the anode electrolyte by a
second ion-exchange membrane; and
a third-ion exchange membrane separating the third and fourth
electrolytes.
- 15 2. The system of claim 1, wherein the first ion-exchange membrane
comprises a cation exchange membrane; the second ion-exchange
membrane comprises a cation exchange membrane; and the third ion-
exchange membrane comprises an anion exchange membrane.
- 20 3. The system of claim 1, further comprising a gas transfer system
configured to direct a gas to the anode.
4. The system of claim 3, wherein the gas comprises hydrogen.
- 25 5. The system of claim 3, wherein the gas transfer system is
configured to direct gas from the cathode to the anode.

6. The system of claim 5, wherein the gas comprises hydrogen.

7. The system of claims 3 or 4, wherein the gas transfer system is configured to direct hydrogen gas into the anode electrolyte, or onto the anode, or a combination thereof, for oxidation of the gas at the anode.

8. The system of claim 1, further comprising an exogenous gas delivery system configured to deliver an exogenous gas into an electrolyte of the electrochemical system.

10

9. The system of claim 8, wherein the exogenous gas comprises carbon dioxide.

15

10. The system of claim 8, wherein the exogenous gas delivery system is configured to deliver the gas into the cathode electrolyte.

11. The system of claim 1, further comprising a gas absorption system operatively configured to absorb carbon dioxide into the cathode electrolyte.

20

12. The system of claim 8, wherein the exogenous gas delivery system is operably connected to an industrial waste gas stream system comprising combustion gases.

25

13. The system of claim 8, wherein the exogenous gas delivery system is operably connected to a fossil fuelled power plant or a cement plant gas exhaust system.

14. The system of claims 1 or 5, wherein the system is capable of forming hydroxide ions in the cathode electrolyte without forming a gas at the anode on applying a voltage across the electrodes.

5

15. The system of claim 14, where hydroxide ions are formed on applying a voltage of less than 3V across the anode and cathode.

16. The system of claim 14, wherein the hydroxide ions are formed while oxidizing hydrogen gas at the anode.

10

17. The system of claim 14, wherein the system is capable of forming a pH differential of between 7 and 14 pH units or greater between the anode and cathode electrolytes.

15

18. The system of claim 17, wherein the pH differential is formed while hydrogen gas is oxidized at the anode.

19. The system of claims 1 or 5, wherein the system is capable of forming hydroxide ions, bicarbonate ions and/or carbonate ions in the cathode electrolyte without forming a gas at the anode on applying a voltage across the electrodes.

20

20. The system of claims 14 or 19, wherein the voltage across the electrodes is less than 3V.

25

21. The system of claims 20, wherein the hydroxide ions, bicarbonate ions and/or carbonate ions are formed while the system is oxidizing hydrogen gas at the anode.

5 22. The system of claims 1 or 5, wherein the system is capable of forming protons in the anode electrolyte on applying a voltage of less than 3 V across the anode and cathode.

23. The system of claims 1 or 5, wherein the system is capable of
10 forming hydrogen gas at the cathode without generating a gas at the anode on applying a voltage of less than 3V across the anode and cathode.

24. The system of claims 1 or 5, wherein the system is capable of
15 removing sodium ions and chloride ions from the third electrolyte without forming a gas at the anode on applying a voltage of less than 3 V across the anode and cathode.

25. The system of claims 1 or 5, wherein the system is capable of
20 forming an acid solution in the fourth electrolyte without forming a gas at the anode on applying a voltage of less than 3 V across the anode and cathode.

26. The system of claims 1 or 5, further comprising a circulating
25 system adapted for circulating a portion of the cathode electrolyte from an outflow to an inflow stream of the cathode electrolyte.

27. The system of claims 1 or 5, further comprising a circulating system for circulating a portion of the fourth electrolyte from an outflow stream to an inflow stream of the fourth electrolyte.

5 28. The system of claim 1, wherein the system is adapted for batch, semi-batch or continuous flow operation.

29. The system of claim 1, wherein the system is adapted for continuous flow operation.

10

30. The system of claim 1, wherein the cathode electrolyte comprises dissolved carbon dioxide.

15

31. The system of claim 30, wherein the cathode electrolyte comprises hydroxide, bicarbonate ions and/or carbonate ions.

32. The system of claim 30, wherein the cathode electrolyte comprises sodium bicarbonate, sodium carbonate or a combination thereof.

20

33. The system of claim 1, wherein the fourth electrolyte comprises protons and chloride ions.

25

34. The system of claim 1, wherein the anode electrolyte comprises protons.

35. An electrochemical method comprising:

placing a first electrolyte that is a cathode electrolyte in contact with a cathode;

placing a second electrolyte that is an anode electrolyte in contact with an anode;

5 placing a third electrolyte such that it is separated from the cathode electrolyte by a first ion-exchange membrane;

placing a fourth electrolyte such that it is separated from the third electrolyte by an third ion-exchange membrane and is separated from the anode electrolyte by a second ion-exchange membrane; and

10 forming hydroxide ions in the cathode electrolyte by applying a voltage across the anode and cathode.

36. The method of claim 35, wherein the first ion-exchange membrane comprises a cation exchange membrane; the second ion-exchange membrane comprises a cation exchange membrane; and the
15 third ion-exchange membrane comprises an anion exchange membrane.

37. The method of claim 35, wherein a gas does not form at the
20 anode.

38. The method of claim 37, further comprising oxidizing hydrogen gas at the anode.

25 39. The method of claim 35, further comprising directing carbon dioxide gas into the cathode electrolyte.

40. The method of claim 39, wherein the carbon dioxide is directed into the cathode electrolyte before or after the cathode electrolyte is placed in contact with the cathode.

5 41. The method of claims 35, comprising applying a voltage of less than 3 V across the cathode and anode.

42. The methods of claims 35, comprising forming hydrogen gas at the cathode.

10

43. The method of claims 35, comprising forming protons at the anode.

15

44. The method of claims 35, comprising forming a pH differential of between 7 and 14 pH units or greater between the anode and cathode electrolytes without forming a gas at the anode by applying a voltage of less than 3V is across the anode and the cathode.

20

45. The method of claim 39, comprising forming hydroxide ions, bicarbonate ions, carbonate ions and/or a combination thereof in the cathode electrolyte.

25

46. The method of claim 39, comprising forming sodium hydroxide, sodium bicarbonate or sodium carbonate in the cathode electrolyte.

47. The method of claim 35, comprising migrating protons from the anode electrolyte across the second cation exchange membrane to the fourth electrolyte.

5 48. The method of claim 47, comprising migrating anions from the third electrolyte across the anion exchange membrane to the fourth electrolyte.

49. The method of claim 48, comprising migrating chloride ions from
10 the third electrolyte across the anion exchange membrane to the fourth electrolyte.

50. The method of claim 49, comprising forming an acid in the fourth electrolyte.

15

51. The method of claim 49, comprising forming hydrochloric acid in the fourth electrolyte.

52. The method of claim 48, comprising migrating cations from the
20 third electrolyte across the first cation exchange membrane to the cathode.

53. The method of claim 35, comprising migrating sodium ions from the third electrolyte across the first cation exchange membrane to the
25 cathode electrolyte.

54. The method of claim 42, comprising circulating hydrogen gas formed at the cathode for oxidation of the gas at the anode.

55. The method of claim 35, comprising circulating cathode electrolyte from an outflow to an inflow stream of the cathode electrolyte.

56. The method of claim 35, comprising circulating fourth cathode electrolyte from an outflow stream to an inflow stream of the fourth electrolyte.

57. An electrochemical method comprising:

placing a first electrolyte that is a cathode electrolyte in contact with a cathode;

15 placing second electrolyte that is an anode electrolyte in contact with an anode;

placing a third electrolyte such that it is separated from the cathode electrolyte by a first ion-exchange membrane;

20 placing a fourth electrolyte such that it is separated from the third electrolyte by an third ion-exchange membrane and is separated from the anode electrolyte by a second ion- exchange membrane; and
supplying carbon dioxide gas to the cathode electrolyte.

58. The method of claim 57, wherein the first ion-exchange membrane comprises a cation exchange membrane; the second ion-exchange membrane comprises a cation exchange membrane; and the

third ion-exchange membrane comprises an anion exchange membrane.

59. The methods of claim 57, wherein a gas does not form at the
5 anode.

60. The methods of claim 57, comprising forming bicarbonate ions, carbonate ions or a mixture of bicarbonate and carbonate ions in the cathode electrolyte.

10

61. The method of claim 57, further comprising oxidizing hydrogen gas at the anode.

15

62. The method of claim 57, comprising applying a voltage of less than 3 V across the cathode and anode.

63. The method of claim 57, comprising forming hydrogen gas the cathode.

20

64. The method of claim 57, comprising forming protons at the anode and the anode electrolyte.

25

65. The method of claim 64, comprising forming a pH gradient of between 7 to 14 pH units or greater between the anode electrolyte and cathode electrolyte without forming a gas at the anode.

66. The method of claim 57, comprising forming sodium carbonate, sodium bicarbonate or mixture of sodium carbonate and sodium bicarbonate in the cathode electrolyte.

5 67. The method of claim 57, comprising migrating protons from the anode electrolyte across the second cation exchange membrane to the fourth electrolyte.

68. The method of claim 57, comprising migrating anions from the
10 third electrolyte across the anion exchange membrane to the fourth electrolyte.

69. The method of claim 57, comprising migrating chloride ions from the third electrolyte across the anion exchange membrane to the fourth
15 electrolyte.

70. The method of claim 57, comprising forming an acid in the fourth electrolyte.

20 71. The method of claim 57, comprising forming hydrochloric acid in the fourth electrolyte.

72. The method of claim 57, comprising migrating cations from the third electrolyte across the first cation exchange membrane to the
25 cathode electrolyte.

73. The method of claim 57, comprising migrating sodium ions from the third electrolyte across the first cation exchange membrane to the cathode electrolyte.

5 74. The method of claim 57, comprising circulating hydrogen gas formed at the cathode for oxidation at the anode.

75. The method of claim 57, comprising circulating at least a portion of the cathode electrolyte from an outflow to an inflow stream of the
10 cathode electrolyte.

76. The method of claim 57, comprising circulating a portion of the fourth cathode electrolyte from an outflow stream to an inflow stream of the fourth electrolyte.

15

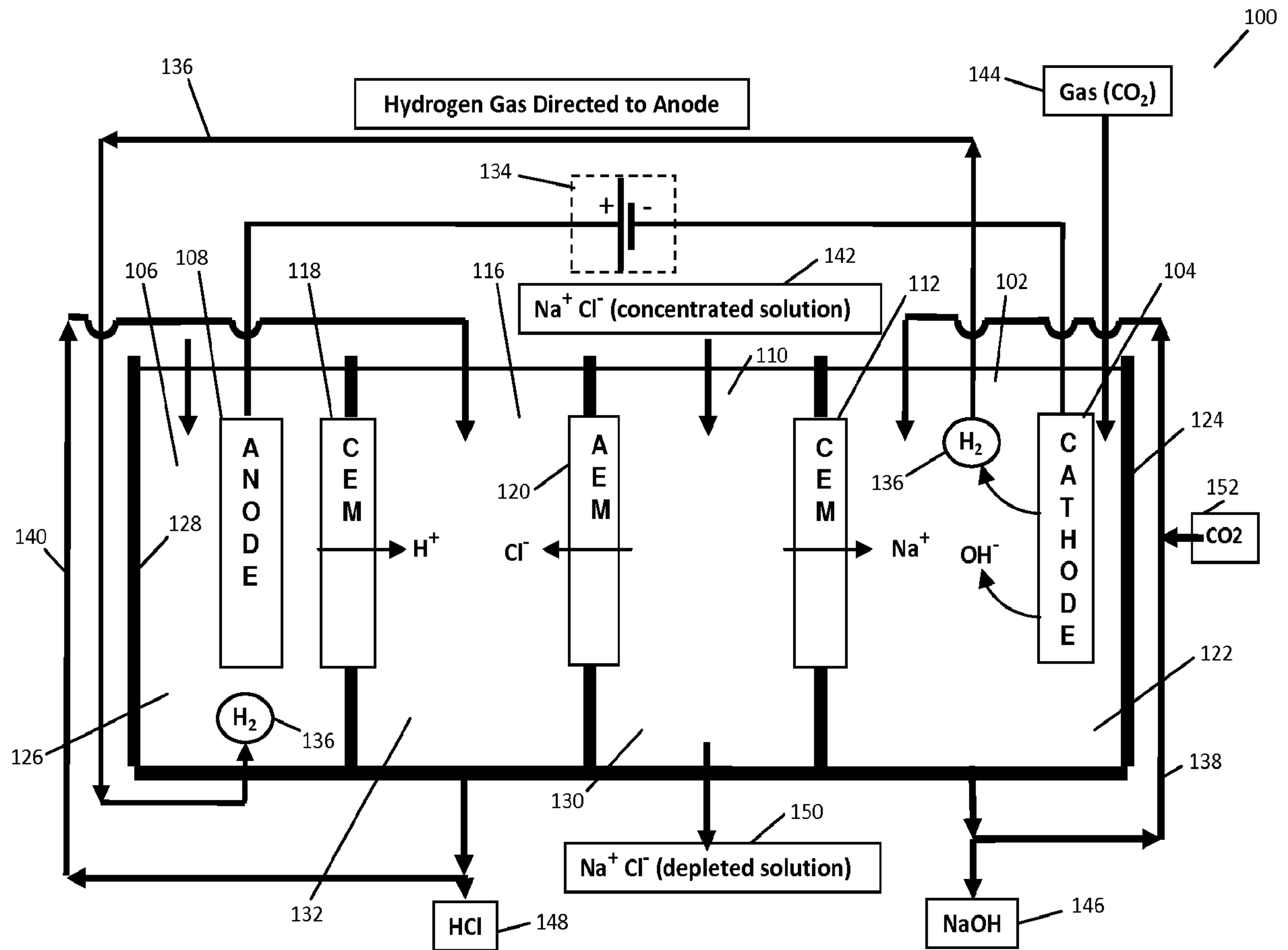


Fig. 1

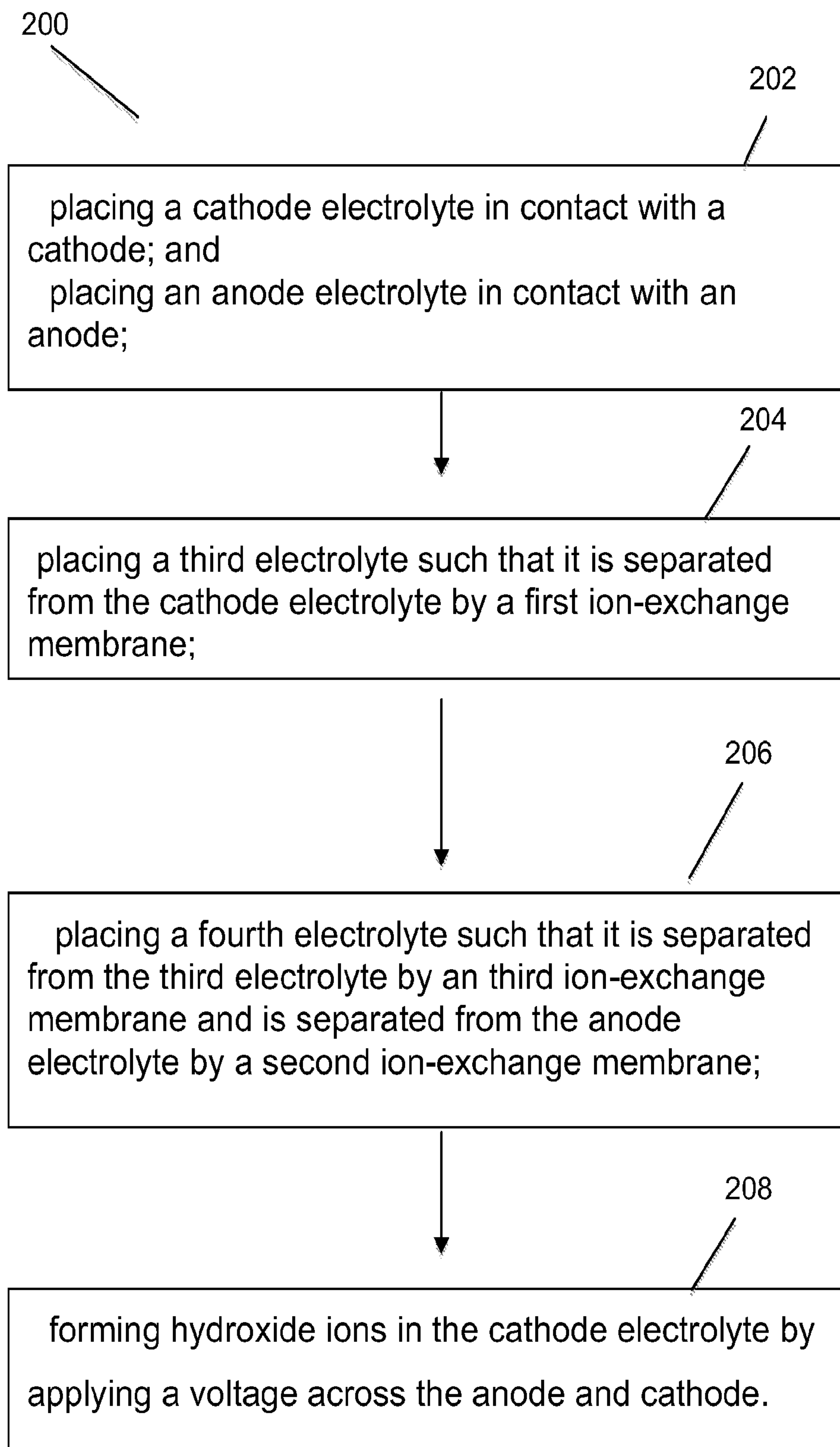


Fig. 2

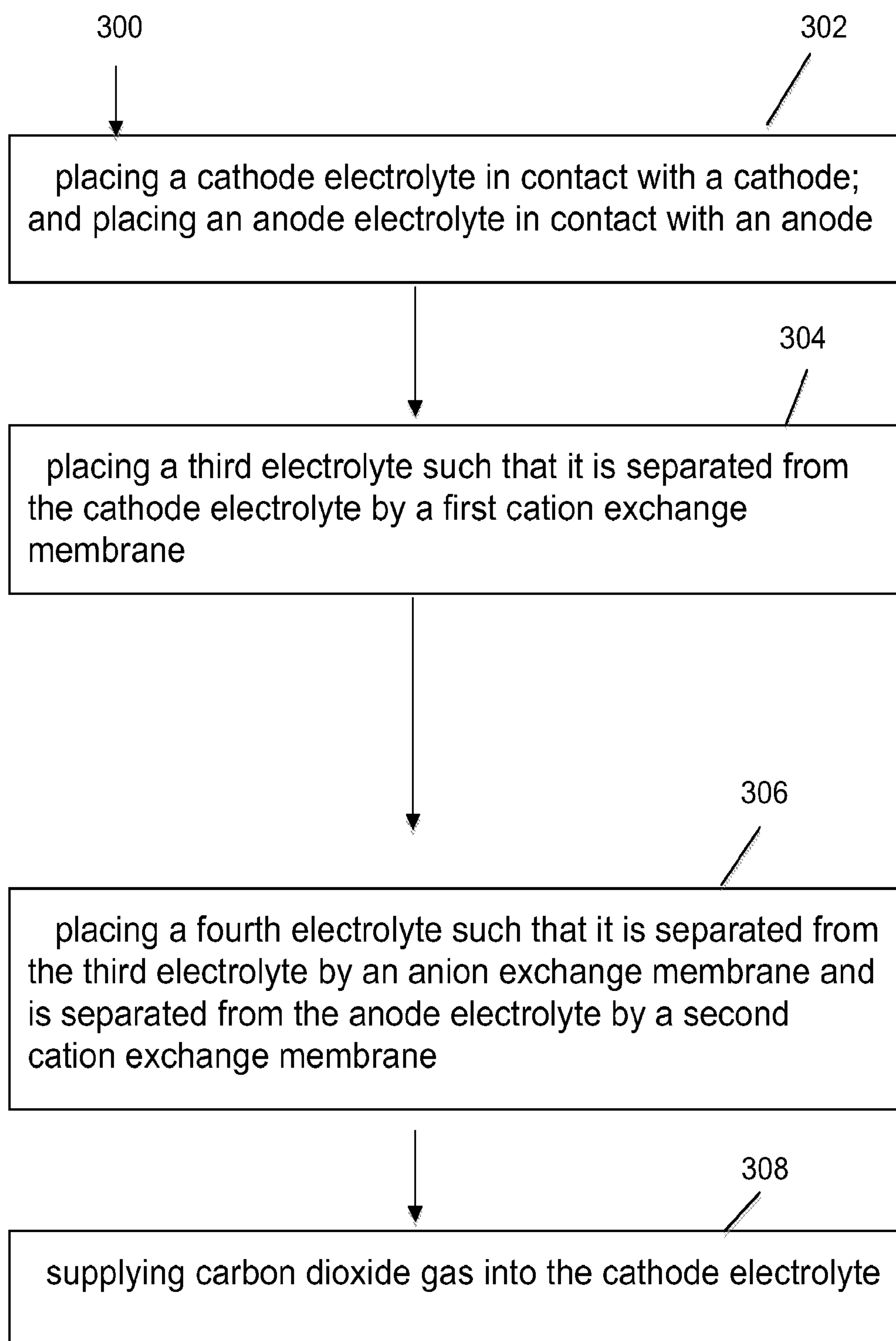


Fig. 3