

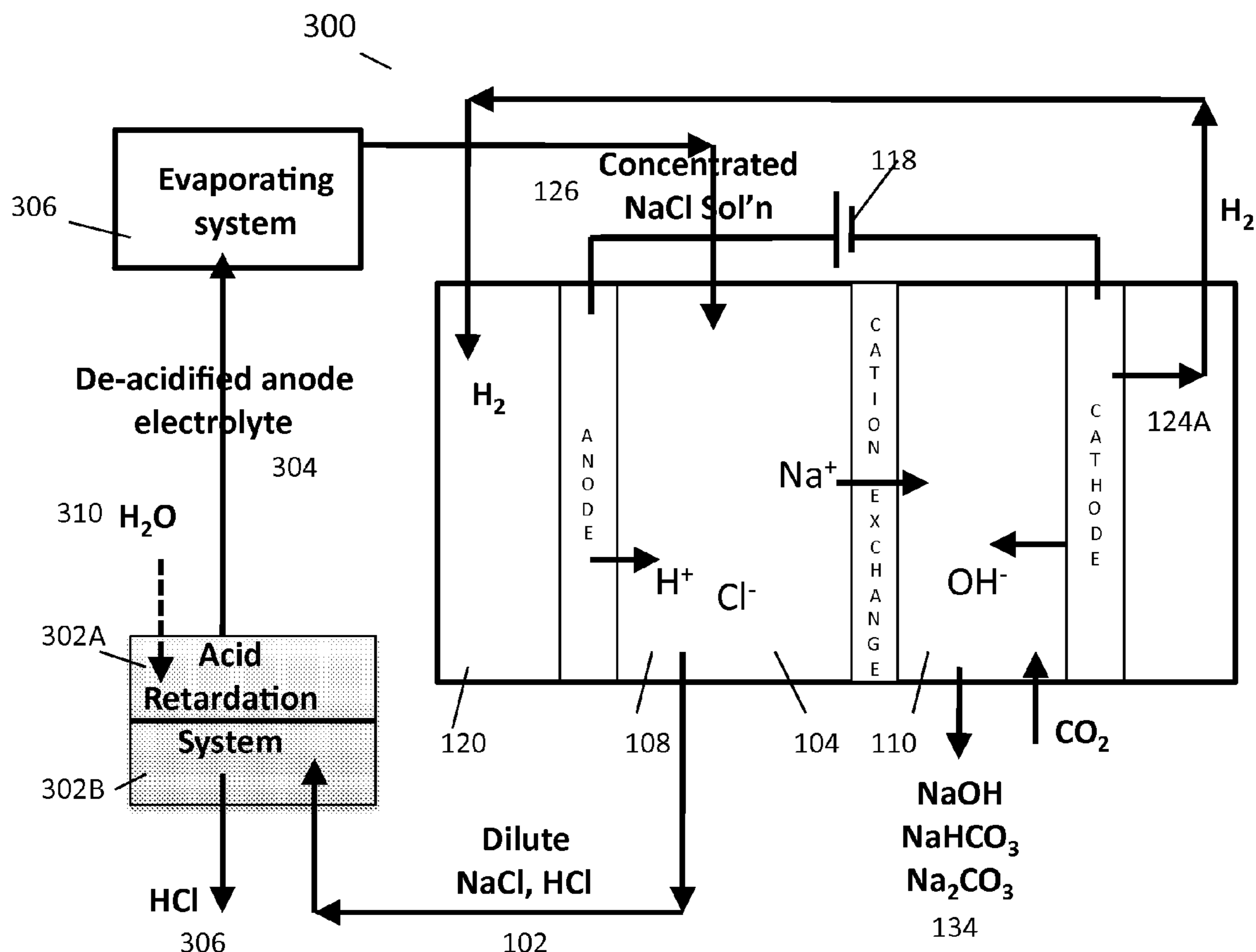
(19) **United States**(12) **Patent Application Publication**
Gilliam et al.(10) **Pub. No.: US 2011/0147227 A1**(43) **Pub. Date: Jun. 23, 2011**(54) **ACID SEPARATION BY ACID RETARDATION
ON AN ION EXCHANGE RESIN IN AN
ELECTROCHEMICAL SYSTEM**

(60) Provisional application No. 61/301,878, filed on Feb. 5, 2010.

Publication Classification(76) Inventors: **Ryan J. Gilliam**, San Jose, CA (US); **Nigel Antony Knott**, Los Gatos, CA (US); **Michael Kostowskyj**, Los Gatos, CA (US)(51) **Int. Cl.**
C25B 15/08 (2006.01)
C25B 1/00 (2006.01)
C25B 9/00 (2006.01)
C25B 15/00 (2006.01)(21) Appl. No.: **13/021,355**(52) **U.S. Cl. 205/349; 205/334; 205/464; 205/508; 205/480; 204/242; 204/234**(22) Filed: **Feb. 4, 2011**(57) **ABSTRACT****Related U.S. Application Data**

(63) Continuation-in-part of application No. 12/952,665, filed on Nov. 23, 2010, which is a continuation-in-part of application No. 12/617,005, filed on Nov. 12, 2009, which is a continuation-in-part of application No. 12/541,055, filed on Aug. 13, 2009, which is a continuation-in-part of application No. 12/503,557, filed on Jul. 15, 2009.

A method and system of separating an acid from an acid-salt solution produced in an electrochemical system using an ion exchange resin bed, by processing the acid-salt solution through the ion exchange resin bed such that the acid is retarded at the bottom of the bed and a de-acidified salt solution is recovered from the top of the bed. After removing the salt solution from the bed, the acid is recovered by back-flushing the resin bed with water.



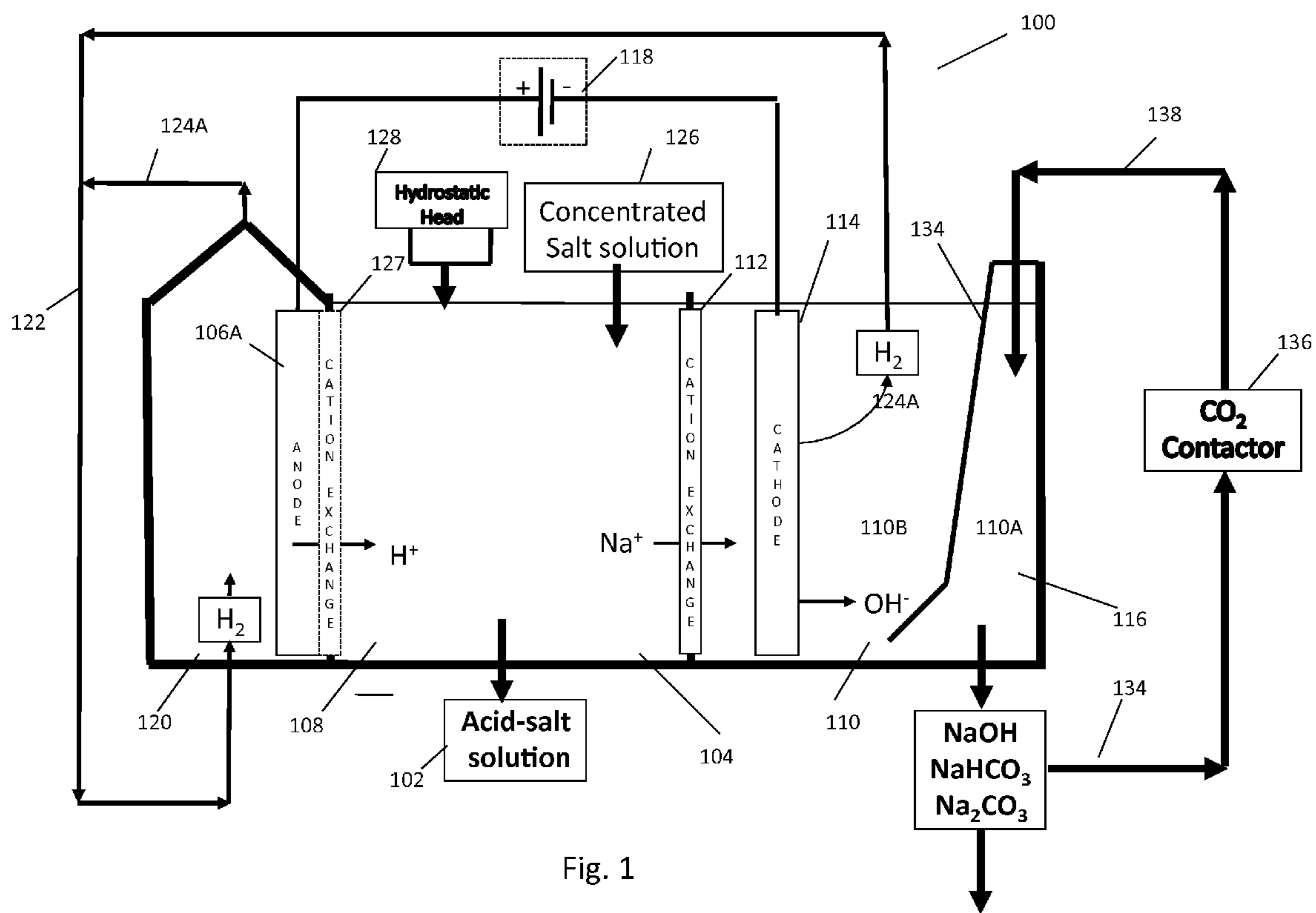


Fig. 1

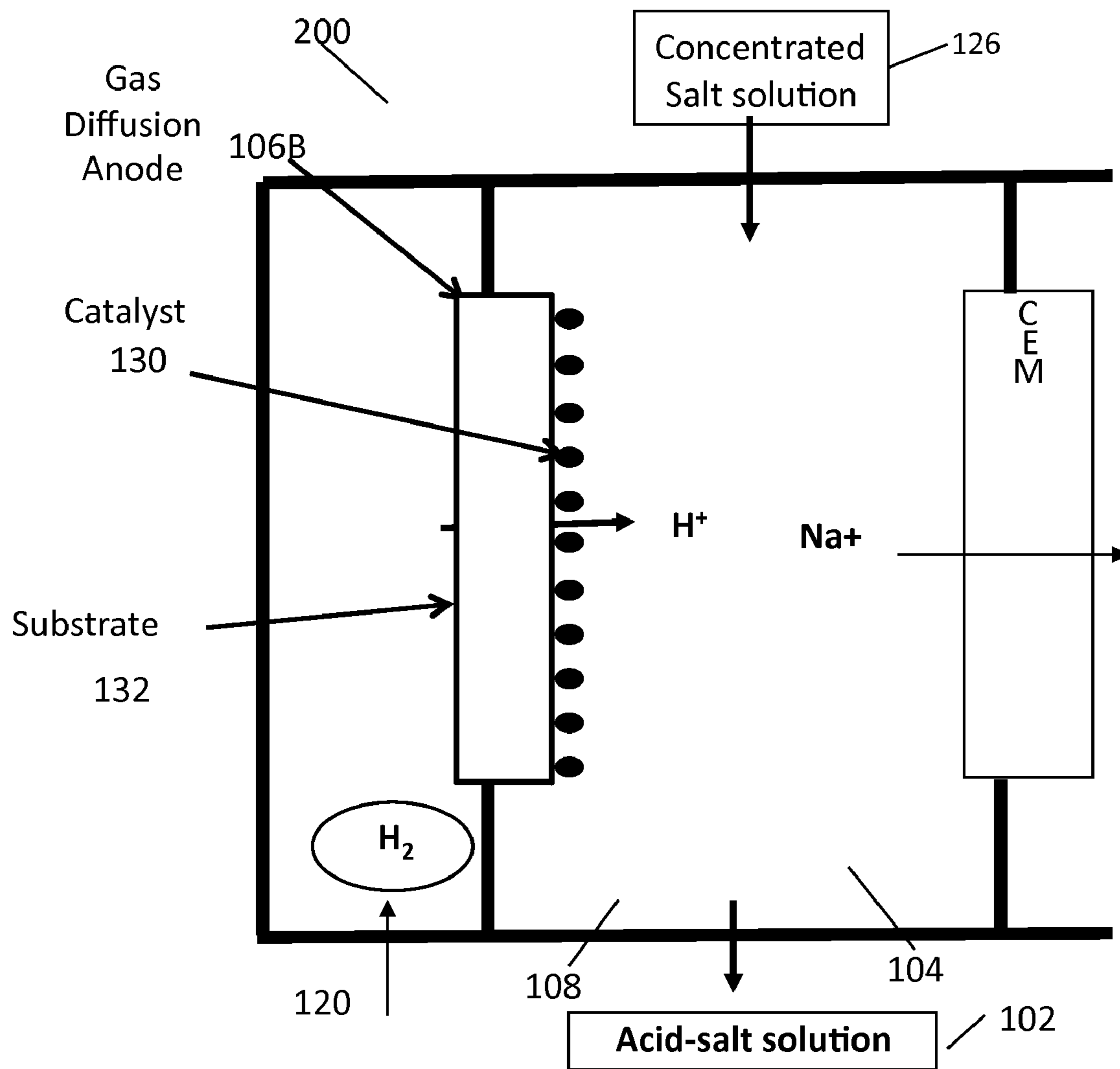


Fig. 2

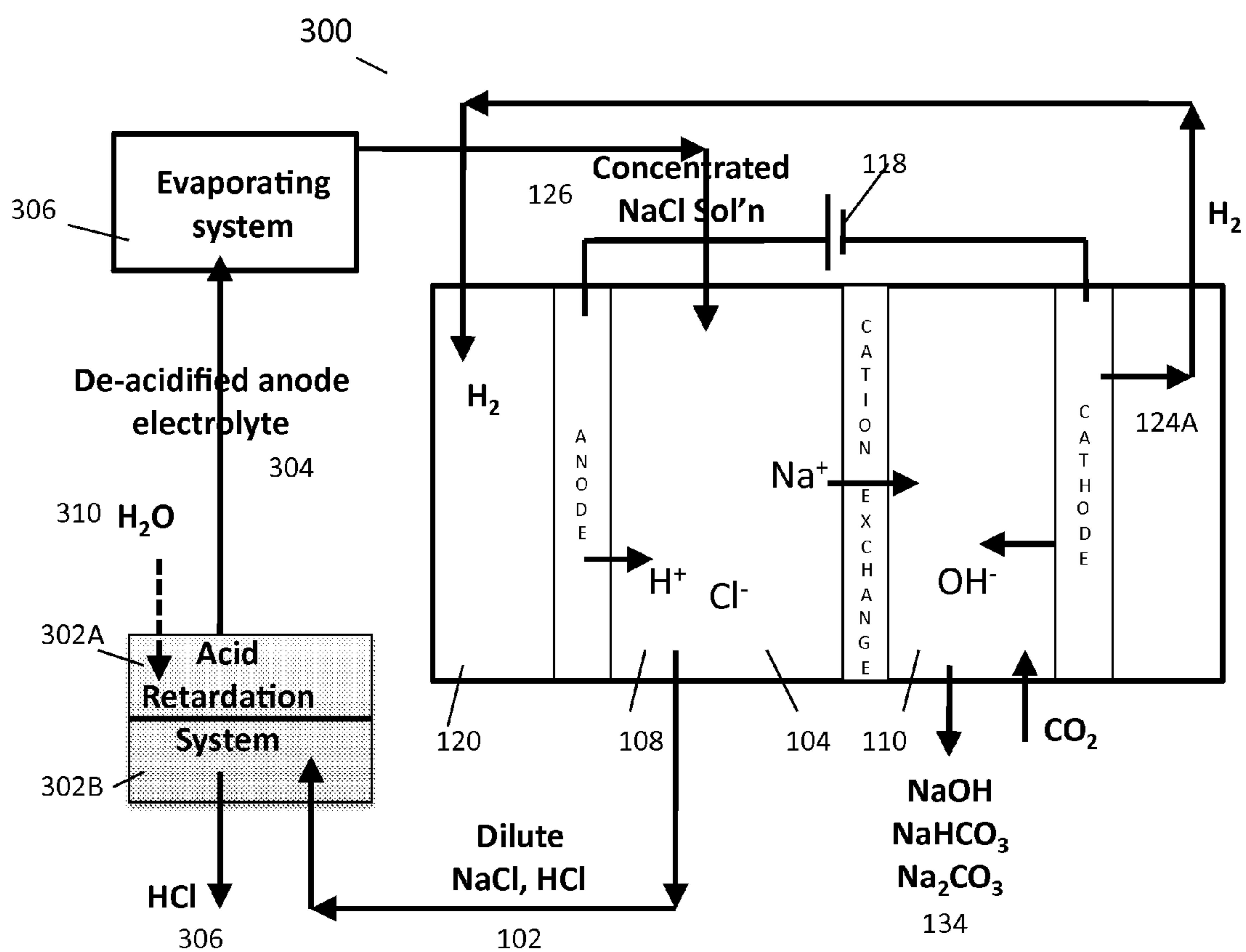


Fig. 3

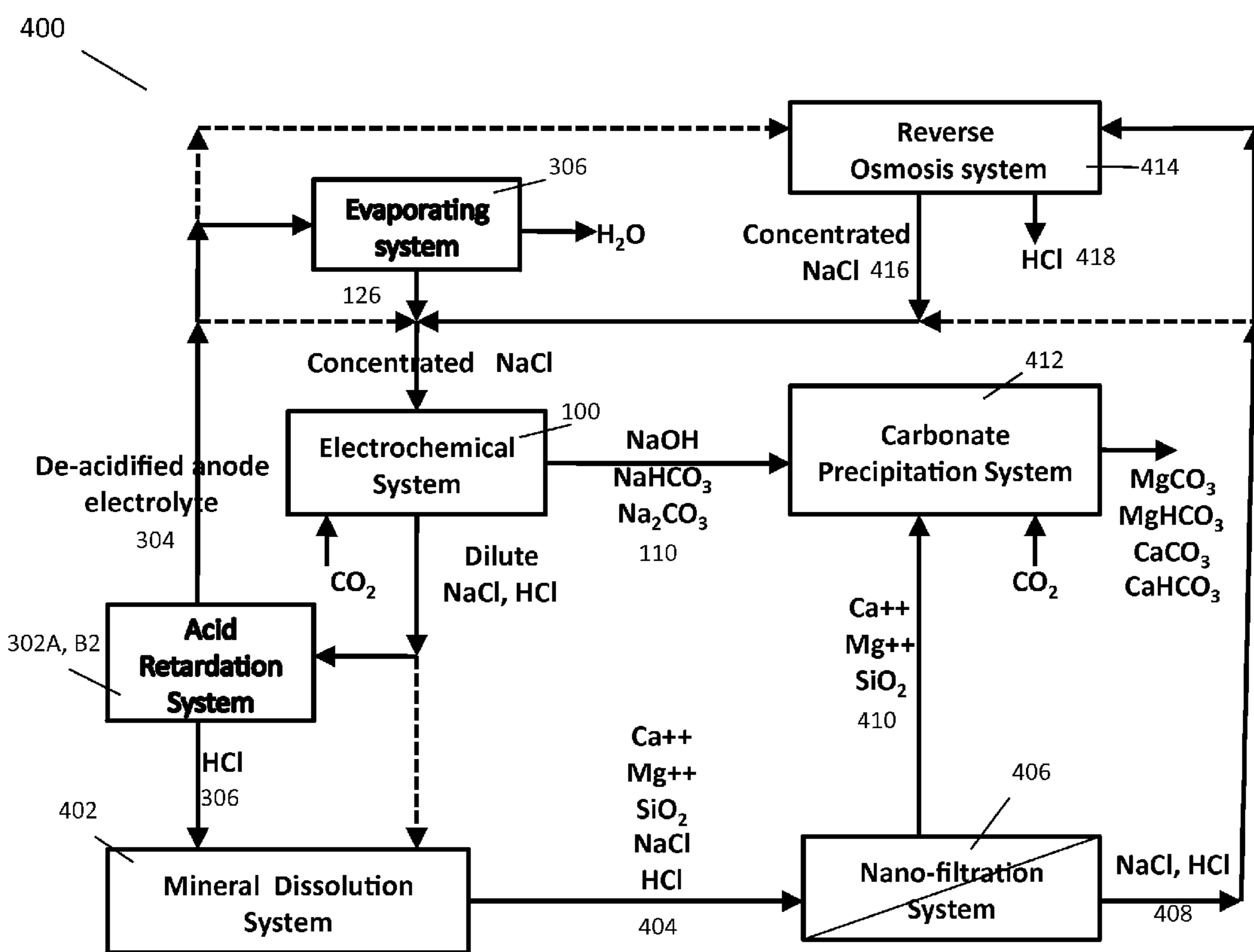


Fig. 4

**ACID SEPARATION BY ACID RETARDATION
ON AN ION EXCHANGE RESIN IN AN
ELECTROCHEMICAL SYSTEM**

CROSS-REFERENCE

[0001] This application claims priority to and the benefits of U.S. Provisional Patent Application No. 61/301,878 filed Feb. 5, 2010 herein incorporated by reference.

[0002] This application also is a continuation-in-part of, and claims priority to, commonly assigned U.S. patent application Ser. No. 12/952,665, filed Nov. 23, 2010, which is a continuation-in-part of U.S. patent application Ser. No. 12/617,005 filed Nov. 11, 2009, which is a continuation-in-part of U.S. patent application Ser. No. 12/541,055 filed Aug. 13, 2009, which is a continuation-in-part of U.S. patent application Ser. No. 12/503,557 filed Jul. 16, 2009, all of which are herein incorporated by reference in their entirety.

BACKGROUND OF THE INVENTION

[0003] In producing a hydroxide solution by an electrochemical process, an acid and a dilute salt solution are produced in some processes. In some cases, the acid and dilute salt solutions are produced in the same compartment of the electrochemical system, i.e., in the anode electrolyte, and the acid and the salt are mixed. As the salt without the acid can be recycled to produce more hydroxide ions in the cathode electrolyte and as the acid without the salt can be used elsewhere, it is desirable to separate the salt and acid.

SUMMARY OF THE INVENTION

[0004] This invention pertains to a method and system of separating an acid from an acid-salt solution produced in an electrochemical system by processing the acid-salt solution through an ion exchange resin bed to retard the acid at the bottom of the bed, and accumulate the de-acidified salt solution at the top of the bed. In some embodiments, the de-acidified salt solution is extracted from the top of the bed, and the acid is recovered by back-flushing the resin bed from the top of the bed with water after the salt solution is extracted.

[0005] The methods, compositions, and apparatus of the invention may be used in any suitable electrochemical system in which an acid is produced. In some embodiments of the method, the acid-salt solution is produced in the anode electrolyte of the system by adding a concentrated salt solution e.g., a concentrated sodium chloride solution, or a sodium sulfate solution, to the anode electrolyte; reducing hydrogen gas to protons at the anode and migrating the protons into the salt solution/anode electrolyte by applying a voltage across the anode and a cathode in contact with a cathode electrolyte; and migrating cations e.g., Na⁺ ions from the salt solution/anode electrolyte into the cathode electrolyte. It will be appreciated that while this embodiment is described and is illustrative, any embodiment in which the methods, compositions, and apparatus of the invention may be used is encompassed by the invention.

[0006] In some embodiments of the method, the hydroxide is produced in the cathode electrolyte by reducing water to hydroxide ions and hydrogen gas at the cathode; migrating the hydroxide ions into the cathode electrolyte; and migrating cations e.g., Na⁺ ions from the salt solution to the cathode electrolyte across a cation exchange membrane separating the salt solution from the cathode electrolyte. It will be appreciated that other reactions might occur at the cathode, for

example the well-known reactions of the oxygen depolarized electrode, so long as an acid is produced in some part of the cell (e.g., at the anode).

[0007] In some embodiments of the method, the salt solution may comprise sodium chloride or sodium sulfate; the acid may comprise hydrochloric acid or sulfuric acid; and the hydroxide may comprise sodium hydroxide.

[0008] In some embodiments of the method, hydrogen gas produced at the cathode is directed to the anode for oxidation to protons that produce the acid in the anode electrolyte.

[0009] In some embodiments of the method, the hydroxide produced in the cathode electrolyte is used to sequester carbon dioxide as a bicarbonate and/or carbonate; in certain embodiments this is done by adding carbon dioxide to the cathode electrolyte to produce bicarbonate ions or carbonate ions in the cathode electrolyte, and, in some cases, mixing the cathode electrolyte with a divalent cation solution comprising Ca⁺⁺ ions or Mg⁺⁺ ions to produce the divalent cation carbonate or bicarbonate (e.g., calcium and/or magnesium carbonate).

[0010] In some embodiments, the sequestered carbon dioxide is taken from a waste gas emitted from an industrial facility. In certain embodiments the industrial facility is a fossil fuelled power generating plant, such as a coal-fired plant or natural gas-fired plant, a cement production plant, an ore smelter or a carbon fermentation plant.

[0011] In some embodiments of the method, the ion exchange resin comprises a strong base anion exchange resin comprising particle sizes in the range of 525-625 microns.

[0012] In some embodiments of the method, the recovered acid is used to dissolve a mineral comprising divalent cations e.g., Ca⁺⁺ ions or Mg⁺⁺ ions to produce a divalent cation solution for use in sequestering the carbon dioxide as a divalent carbonate and/or bicarbonate.

[0013] In some embodiments of the method, the recovered salt solution is cleaned in a nano-filtration system and concentrated in a reverse osmosis system and reused as the anode electrolyte.

[0014] In some embodiments, the system or method comprises an electrochemical system comprising an anode electrolyte in contact with an anode in an anode compartment, and is configured to produce an acid in the anode electrolyte; and an acid retardation system comprising an ion exchange resin bed operatively connected to the anode compartment and is configured to receive the anode electrolyte and retard the acid on an ion exchange resin and produce a de-acidified anode electrolyte.

[0015] In some embodiments, the system or method is configured to retard the acid in the lower portion of the ion resin bed and produce the de-acidified anode electrolyte in the upper portion of the bed. In some embodiments, the ion exchange resin bed comprises a strong base anion exchange resin comprising particles ranging in size from 525 to 625 microns and is specially designed to retard the acid without retarding the salt. In some embodiments, the acid retardation system is configured to return the de-acidified salt solution to the anode electrolyte compartment.

[0016] In some embodiments, the system or method comprises an evaporating system operatively linked to the acid retardation system and is configured to concentrate and return the recovered salt solution to the anode electrolyte.

[0017] In some embodiments, the system or method comprises a mineral dissolution system operatively connected to the acid retardation system and is configured to dissolve a

mineral with the recovered acid to produce a mineral solution comprising divalent cations; in some embodiments, the divalent cation solution is used to sequester carbon dioxide as a divalent carbonate and/or bicarbonate with the cathode electrolyte.

[0018] In some embodiments of the system or method the acid is produced in the anode electrolyte by reducing hydrogen gas at the anode to protons and migrating the protons into the anode electrolyte; and migrating cations from the anode electrolyte, with a voltage applied across the anode and cathode.

[0019] In some embodiments, the system or method is configured to produce a hydroxide in the cathode electrolyte by reducing water at the cathode to hydroxide ions and hydrogen gas; migrating cations from the anode electrolyte to the cathode electrolyte across a cation exchange membrane separating the anode electrolyte and the cathode electrolyte; and migrating the hydroxide ions into the cathode electrolyte. In some embodiments, the system or method includes a hydrogen supply system configured to direct hydrogen gas produced at the cathode to the anode.

[0020] In some embodiments, the system or method includes a nano-filtration system configured to clean the salt solution, and a reverse osmosis system configured to concentrate the recovered salt solution.

[0021] In some embodiments, the system or method includes a carbonate precipitation system operatively connected to the cathode compartment and the nano-filtration system and configured to mix the divalent cation solution with cathode electrolyte and carbon dioxide to sequester the carbon dioxide as a divalent cation carbonate and/or bicarbonate. In some embodiments, the carbon dioxide gas is mixed with the cathode electrolyte to produce bicarbonate ions or carbonate ions in the cathode electrolyte, and this cathode electrolyte is used to sequester the carbon dioxide as a divalent carbonate or biocarbonate.

[0022] Any suitable ion exchange medium may be used, such as commercially available resin e.g., from the Dow Chemical Company under the product name DOWEX*21K XLT™. For example, the resin may be used in an ion exchange column commercially available from the Colgon Carbon Corporation in the USA or from Eco-tech Limited in Canada.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] The following drawings illustrate by way of examples and not by limitation embodiments of the present system and method.

[0024] FIGS. 1 and 2 illustrate embodiments of an electrochemical system configured to produce an acid-salt solution in an electrolyte in the system and a hydroxide in the cathode electrolyte, in accordance with the present system.

[0025] FIGS. 3 and 4 illustrate embodiment of a system configured to separate the acid and salt from the acid-salt solution and re-use the salt and acid, in accordance with the present system.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The invention provides methods, compositions, and apparatus directed at separating an acid and a salt solution from an acid-salt solution produced in an electrochemical system. In certain embodiments, the acid-salt solution is produced in the anode electrolyte; for example, the anode reaction may produce protons from the oxidation of hydrogen. It will be understood by those of skill in the art that, while the

latter embodiment is used for illustrative purposes, many anodic reactions may produce an acid in a salt solution and the methods, compositions, and apparatus are directed to all such reactions for which they are suitable.

[0027] With reference to the illustrative embodiments as exemplified, but not limited, by FIGS. 1-4, in some embodiments the system and method pertains to separating an acid (e.g., 306) and a salt solution (e.g., 304) from an acid-salt solution (e.g., 102) produced in an electrolyte in an electrochemical system (e.g., 100, 300, 400). In some embodiments, the acid-salt solution (e.g., 102) is produced in the anode electrolyte (e.g., 104) by charging the anode electrolyte with a concentrated salt solution (e.g., 126); oxidizing hydrogen gas (e.g., 120) at the anode to form protons and migrating the protons into the anode electrolyte in contact with the anode (e.g., 106A, 106B) by applying a voltage (e.g., 118) across the anode and cathode; and migrating cations from the anode electrolyte (e.g., 104).

[0028] In some embodiments and with reference to FIG. 3 for illustrative purposes, as the acid is produced in the anode electrolyte (e.g., 104), it is continually withdrawn (e.g., 102) from the system by withdrawing some of the anode electrolyte. Since the anode electrolyte is continuously replenished with a concentrated salt solution (e.g., 126), and since in some embodiments not all the cations from the salt solution will migrate from the anode electrolyte to the cathode electrolyte (e.g., 110), the withdrawn anode electrolyte/salt solution may contain a solution of the acid and salt.

[0029] However, as the salt solution without the acid can be reused e.g., in the anode electrolyte and as the acid without the salt can be used elsewhere for any purpose for which it is suited, e.g., to dissolve a mineral in mineral dissolution system, such as the one illustrated in FIG. 4, it is desired to separate the acid and salt solution from the withdrawn acid-salt solution.

[0030] In some embodiments, as is shown in FIG. 3 for illustrative purposes, the salt/acid separation is achieved by withdrawing a portion of the anode electrolyte and passing the withdrawn anode electrolyte through in an acid retardation system (e.g., 302A, 302B) operatively connected to the anode compartment (e.g., 108). In the acid retardation system (e.g., 302A, 302B) the withdrawn anode electrolyte is flowed upwards through an ion exchange resin bed configured to retard the acid in the lower portion of the bed (e.g., 302B), and produce a de-acidified anode electrolyte/salt solution in the upper portion of the bed (e.g., 302A).

[0031] In some embodiments and with reference to FIG. 3 for illustrative purposes, the de-acidified anode electrolyte (e.g., 304) is extracted from the top of bed (e.g., 302A) and is reused as anode electrolyte (e.g., 104) in the electrochemical system (e.g., 300). In some embodiments, after the salt solution is removed from the upper portion of the ion exchange resin bed (e.g., 302A), the acid is recovered by back-flushing the lower portion of the ion exchange resin bed (e.g., 302B) with water (e.g., 310).

[0032] The systems and methods of the invention are suitable for electrochemical systems in which an acid/salt solution is produced in any compartment (e.g., the anode compartment) and where it is desired to separate the acid and the salt; thus, the half-reaction at the cathode, which generally does not produce an acid, may be any half-reaction that is coupled with a half-reaction at the anode that produces acid at the anode. In some embodiments of the system and method and with reference to FIG. 1 for illustrative purposes, as the acid is produced in the anode electrolyte (e.g., 104), a hydroxide solution is concurrently produced in the cathode electrolyte (e.g., 110) by reducing water at the cathode (e.g., 114) to

hydroxide ions and hydrogen gas (e.g., 124A); migrating the hydroxide ions into the cathode electrolyte (e.g., 110); and migrating cations from the salt solution (e.g., 104) into the cathode electrolyte (e.g., 110).

[0033] In some embodiments, the hydrogen gas produced at the cathode (e.g., 124A) is directed to the anode (e.g., 106A, 106B) for oxidation to protons, and the protons are migrated into the anode electrolyte to produce the acid in the anode electrolyte. In some embodiments, the voltage (e.g., 118) across the anode and cathode is regulated to prevent the formation a gas e.g., oxygen or chlorine at the anode.

[0034] In some embodiments and with reference to FIGS. 1 and 3 for illustrative purposes, carbon dioxide is added to the cathode electrolyte (e.g., 110A, 110B) to form carbonic acid and/or carbonate ions and/or bicarbonate ions in the cathode electrolyte (e.g., 110), depending on the pH of the cathode electrolyte. Thus in some embodiments wherein Na⁺ ions are migrated from the anode electrolyte (e.g., 104) into the cathode electrolyte (e.g., 110), the cathode electrolyte (e.g., 110) may comprise sodium hydroxide and/or sodium carbonate and/or sodium bicarbonate.

[0035] In some embodiments and with reference to FIGS. 1 and 4 for illustrative purposes, the cathode electrolyte (e.g., 110) comprising bicarbonate ions and/or carbonate ions is reacted with a divalent cation solution (e.g., 410) comprising e.g., Ca⁺⁺ ions and/or Mg⁺⁺ ions in a carbonate precipitating system (e.g., 412) to precipitate a divalent cation carbonate and/or bicarbonate and thereby sequester the carbon dioxide in the precipitate. In some embodiments the acid solution recovered from the anode electrolyte (e.g., 306, 418) is utilized to dissolve a mineral, which may be any suitable mineral, e.g. serpentine or olivine, that can be contacted with the acid of the system to release divalent cations and/or other useful species, e.g., in a mineral dissolution system (e.g., 402) to obtain a portion or all of the divalent cation solution used to produce the divalent carbonates and/ or bicarbonates.

[0036] As can be appreciated by those of ordinary skill in the art and with reference to FIGS. 1-4 for illustrative purposes, although the present system and method are described herein with reference to producing the acid-salt solution (e.g., 102) in the anode electrolyte (e.g., 104) in contact with the anode (e.g., 106), in some embodiments the system can be configured to produce the acid/salt in another electrolyte that is not in direct contact with the anode.

[0037] This can be accomplished, e.g., by separating the anode electrolyte from a salt solution located in other electrolyte by a cation exchange membrane (e.g., 127) such that protons from the anode electrolyte will migrate into the salt solution (e.g., 106) from the anode electrolyte through the cation exchange membrane (e.g., 127).

[0038] In some embodiments, the salt solution can be separated from the anode electrolyte by an anion exchange membrane such that anions from the salt solution will migrate into the anode electrolyte through the anion exchange membrane to produce the acid in the anode electrolyte. In some embodiments of the system as is illustrated in FIG. 1, since the cation exchange membrane (e.g., 127) will prevent the migration of anions (e.g., e.g., Cl⁻ ions), from the salt solution to the anode (e.g., 106), therefore the acid/salt solution will not form in direct contact with the anode (e.g., 106). However, as will be appreciated, while this feature may be present in some embodiments, it is optional, depending on the nature of the anode, the anions, and other factors that will be apparent to those of skill in the art.

[0039] To the extent that one of ordinary skill in the art can modify the present system based on the present disclosure, to produce the acid/salt solution in any compartment of the electrochemical system, such modifications are within the scope of the present system and method as defined by the appended claims.

[0040] Also, as can be appreciated by those of ordinary skill in the art, although the present system and method are described herein with reference to producing a salt/acid solution (e.g., 102) comprising hydrochloric acid and sodium chloride, since the system can be modified based on the present disclosure to use another salt e.g., sodium sulfate to produce an salt/acid solution comprising sulfuric acid and sodium sulfate, such modifications are also within the scope of the present system and method as defined by the appended claims. Other salt/acid combinations, such as but not limited to salts and the corresponding acids formed from alkali salts, such as where the alkali salt is a salt of the groups 1(IA) or 2(IIA) of the periodic table. Exemplary electrolytes suitable for use with the present invention include, but are not limited to, the following: sodium chloride, potassium chloride, sodium sulfate, potassium sulfate, calcium sulfate, magnesium sulfate, sodium nitrate, potassium nitrate, sodium bicarbonate, sodium carbonate, potassium bicarbonate, or potassium carbonate. Other suitable electrolyte solutions include sea water and aqueous sea salt solutions.

[0041] Further, as can be appreciated by those of ordinary skill in the art, although the present system and method are described herein with reference to producing a salt/acid solution (e.g., 102) by oxidizing hydrogen gas (e.g., 120) at the anode to protons and reducing water at the cathode to hydroxide ions and hydrogen gas, since the system can be modified based on the present disclosure to produce the acid/salt solution by another mechanism e.g., by producing a gas e.g., chlorine gas at the anode and dissolving the chlorine gas in the anode electrolyte, therefore such modifications are also within the scope of the present system and method as defined by the appended claims.

[0042] Also, as can be appreciated by those of ordinary skill in the art, although the present system and method are described herein with reference to producing a salt/acid solution (e.g., 102) in an electrolyte in the system by using one or more cation ion exchange membranes (e.g., 112, 127) to separate the electrolytes in the system, and migrating cations from the salt solution (e.g., 104) to the cathode electrolyte (e.g., 110) through cation exchange membrane (e.g., 112), the system can be modified based on the present disclosure to use other separation means such as a diaphragm. Therefore, to the extent that one of ordinary skill can modify the present system, based on the present disclosure, to produce the acid/salt solution in any compartment of an electrochemical system using any separation means, such modifications are within the scope of the present system and method as defined by the appended claims.

[0043] With reference to FIGS. 1-4 for illustrative purposes, in some embodiments the system (e.g., 100, 200, 300, 400) comprises an electrochemical system comprising an anode electrolyte (e.g., 104) in contact with an anode (e.g., 106A, 106B) in an anode compartment (e.g., 108) and configured to produce an acid-salt solution (e.g., 102) in the anode electrolyte; and an acid retardation system (e.g., 302A, 302B) comprising an ion exchange resin bed operatively connected to the anode compartment (e.g., 108) and configured to receive the acid-salt solution (e.g., 102) and retard the acid on an ion exchange resin and produce a de-acidified anode electrolyte (e.g., 304). In some embodiments as illustrated in FIGS. 3 and 4, the system is configured to retard the acid in a

lower portion of the ion resin bed (e.g., 302B) and produce the de-acidified anolyte in an upper portion of the ion exchange resin bed (e.g., 302A).

[0044] In some embodiments, the ion exchange resin bed (e.g., 302A, 302B) comprises a short bed comprising a fine mesh resin. In some embodiments, the ion exchange resin comprises a strong base anion exchange resin comprising particle sizes in the range of (e.g., 525-625) microns and is specially designed to retard the acid without retarding the salt. For all embodiments, the resin is commercially available from several suppliers including the Dow Chemical Company under the product name DOWEX*21K XLT™. In some embodiments the resin is used in an ion exchange column commercially available from the Colgon Carbon Corporation in the USA or from Eco-tech Limited in Canada and can be configured in an ion retardation system as described in U.S. Pat. No. 4,673,507 herein incorporated by reference.

[0045] In some embodiments of the system as illustrated in FIGS. 3 and 4, the acid retardation system (e.g., 302A, 302B) is configured to extract and return the de-acidified anode electrolyte (e.g., 304) to the anode electrolyte compartment (e.g., 108). In some embodiments also as are illustrated in FIGS. 3 and 4, the system comprises an evaporating system (e.g., 306) operatively linked to the acid retardation system (e.g., 302A, 302B) and the anode compartment (e.g., 108). In some embodiments, the evaporating system is configured to concentrate the de-acidified anode electrolyte and return the concentrated de-acidified anode electrolyte (e.g., 126) to the anode electrolyte compartment. In some embodiments, the acid retardation system (e.g., 302A, 302B) is configured to back-flush the acid from the ion resin after the salt solution is removed, by flushing the ion exchange resin with water (e.g., 310).

[0046] With reference to FIGS. 3 and 4 for illustrative purposes, in some embodiments, the system 300, 400 comprises a mineral dissolution system (e.g., 402) operatively connected to the acid retardation system (e.g., 302A, 302B) and is configured to dissolve a mineral with the recovered acid (e.g., 306) to produce a mineral solution (e.g., 404) comprising divalent cations. In some embodiments, the mineral dissolution system (e.g., 402) is operatively connected to the anode compartment (e.g., 108) and is configured to receive the recovered acid (e.g., 306) from the acid retardation system and mix this recovered acid with anode electrolyte comprising the acid/salt solution (e.g., 102) to dissolve the mineral.

[0047] With reference to FIG. 1 for illustrative purposes, in some embodiments, the system (e.g., 100) comprises a cathode (e.g., 114) in electrical contact with the anode (e.g., 106A) which is in contact with a cathode electrolyte (e.g., 108), and is configured to produce the acid-salt solution (e.g., 102) in the anode electrolyte (e.g., 104) by reducing hydrogen gas at the anode to protons and migrating the protons into the anode electrolyte, on application of a voltage (e.g., 118) across the anode and cathode.

[0048] In some embodiments and with reference to FIG. 1 for illustrative purposes, in the electrochemical system (e.g., 100), a concentrated salt solution (e.g., 126) is added to the anode electrolyte and the system is configured to: produce a hydroxide in the cathode electrolyte (e.g., 110) by reducing water at the cathode to hydroxide ions and hydrogen gas; migrate cations e.g., Na⁺ ions from the anode electrolyte (e.g., 104) to the cathode electrolyte (e.g., 110) across a first cation exchange membrane (e.g., 112) separating the anode electrolyte (e.g., 104) and the cathode electrolyte (e.g., 110);

and migrate the hydroxide ions into the cathode electrolyte. As can be appreciated by one of ordinary skill in the art, although a cation exchange membrane (e.g., 126), as is illustrated in FIG. 1, is configured to separate the anode from the anode electrolyte (e.g., 108), in some embodiments the system as illustrated in FIG. 3, will function without cation exchange membrane (e.g., 126) in which case the salt solution (e.g., 102) will be produced in the anode electrolyte (e.g., 104).

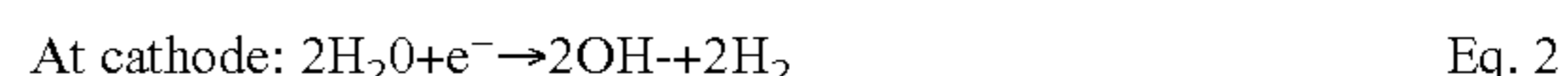
[0049] With reference to FIG. 4 for illustrative purposes, in some embodiments, the system comprises a nano-filtration system (e.g., 406), operatively connected to the mineral dissolution system (e.g., 402) and is configured to filter the mineral solution and produce an acid-salt solution comprising un-reacted acid and the salt solution in a first solution stream (e.g., 408) and a divalent cation solution comprising calcium and/or magnesium ions in a second solution stream (e.g., 410).

[0050] In some embodiments of the system and with reference to FIGS. 1 and 4 for illustrative purposes, the system includes a carbonate precipitation system (e.g., 412) operatively connected to the cathode compartment (e.g., 116) and the nano-filtration system (e.g., 406). In some embodiments, the carbonate precipitation system is configured to mix the divalent cation solution (e.g., 410) with cathode electrolyte (e.g., 110) and carbon dioxide, and sequester the carbon dioxide as a divalent cation carbonate and/or bicarbonate comprising calcium and/or magnesium.

[0051] In some embodiments as illustrated in FIG. 4, the system includes a reverse osmosis system (e.g., 414) operatively connected to the nano-filtration system (e.g., 406) and the electrochemical system 100, and is configured to separate a salt solution (e.g., 416) from the un-reacted acid (e.g., 418). In some embodiments as illustrated in FIG. 4, the anode compartment (e.g., 108) of the electrochemical system (e.g., 100) is configured to utilize the salt solution (e.g., 416) as the anode electrolyte, and the mineral dissolution system is configured to utilize the dilute acid (e.g., 418) to dissolve the mineral in the mineral dissolution system (e.g., 402).

[0052] With reference to FIGS. 1, 2 and 3 for illustrative purposes, in some embodiments of the system, the anode electrolyte (e.g., 104) is separated from the cathode electrolyte (e.g., 110) by a first cation exchange membrane (e.g., 112). In some embodiments, the cathode electrolyte (e.g., 110) is in contact with a cathode (e.g., 114) and both the cathode electrolyte and the cathode are contained in a cathode electrolyte compartment (e.g., 116).

[0053] In the system as illustrated in FIG. 1, a direct-current voltage supply system (e.g., 118) is configured to electrically connect the anode and the cathode, to oxidize hydrogen gas to protons at the anode and reduce water to hydrogen gas and hydrogen ions at the cathode, in accordance with Eq. 1 and 2:



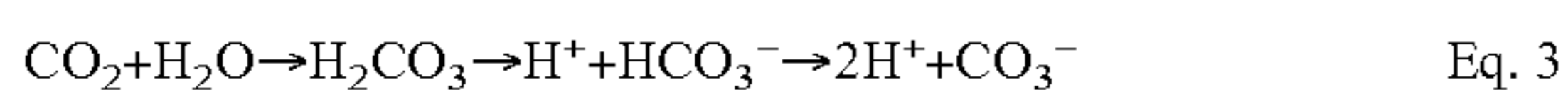
[0054] In some embodiments of the system, hydrogen gas (e.g., 120) is provided to the anode (e.g., 106A, 106B) through a hydrogen supply system (e.g., 122); in some embodiments, the system includes a hydrogen recirculation loop (e.g., 124A) configured to re-circulate un-reacted hydrogen to the anode (e.g., 106A, 106B). In some embodiments, the hydrogen gas (e.g., 124B) generated at the cathode is provided to the anode.

[0055] In some embodiments as illustrated in FIGS. 1 and 2, the anode may comprise a gas diffusion anode (e.g., 106A, 106B). In some embodiments as illustrated in FIG. 1, the anode may comprise a second cation exchange membrane (e.g., 127) that contacts the anode electrolyte (e.g., 104) and thus separates the anode (e.g., 106A) from the anode electrolyte (e.g., 104). In some embodiments as illustrated in FIG. 2, the system does not include the second cation exchange membrane of FIG. 1 and hence the anode is in direct contact with the anode electrolyte (e.g., 104).

[0056] In some embodiments as illustrated in FIG. 1, the system includes a hydrostatic pressure system (e.g., 128) configured to apply a hydrostatic pressure on to the anode electrolyte (e.g., 104) and thus transmit the pressure on to the second cation exchange membrane (e.g., 127) and against the anode (e.g., 106A). In some embodiments, a column of anode electrolyte above the anode compartment achieves the desired hydrostatic pressure on the cation exchange membrane (e.g., 126). In some embodiments, compressed air is used to apply the pressure on the anode electrolyte. In various embodiments, the pressure applied to the second cation ion exchange membrane assists in securing the cation exchange membrane (e.g., 127) against the anode (e.g., 106A).

[0057] With reference to FIG. 2 for illustrative purposes, in some embodiments the gas diffusion anode (e.g., 126B) may comprise a catalyst (e.g., 130) configured to catalyze the oxidation of hydrogen gas at the anode (e.g., 106A, 16B) to protons. In some embodiments, the catalyst is supported on a substrate (e.g., 132). In some embodiments the catalyst may comprise platinum or a platinum alloy.

[0058] In some embodiments as illustrated in FIG. 1, carbon dioxide is added to the cathode electrolyte (e.g., 110) to produce an alkaline solution comprising carbonate ions or bicarbonate ions in the cathode electrolyte in accordance with Eq. 3:



[0059] In some embodiments, the carbon dioxide in gaseous form is added directly to the cathode electrolyte (e.g., 110) by sparging the gas directly into the cathode electrolyte in the cathode compartment (e.g., 116); in some embodiments the carbon dioxide is added to the cathode electrolyte by withdrawing a portion of the cathode electrolyte (e.g., 134) from the cathode compartment and contacting the carbon dioxide and cathode electrolyte in a carbon dioxide contactor (e.g., 136) to absorb the gas in the cathode electrolyte, and returning the cathode electrolyte/carbon dioxide/carbonate ion/bicarbonate ion solution (e.g., 138) to the cathode compartment.

[0060] In some embodiments as illustrated in FIG. 1, the system comprises a partition (e.g., 134) that partitions the cathode electrolyte (e.g., 110) into a first cathode electrolyte portion (e.g., 110A) and a second cathode electrolyte portion (e.g., 110B). In this embodiment of the system, the second cathode electrolyte portion (e.g., 110B) comprising dissolved carbon dioxide is in contact with the cathode (e.g., 114) and the first cathode electrolyte portion (e.g., 110A) comprising dissolved carbon dioxide and gaseous carbon dioxide is under partition (e.g., 134) and is not in direct contact with the cathode. Thus in this embodiment of the system, the partition will prevent gaseous carbon dioxide in the first cathode electrolyte portion (e.g., 110A) from coming in contact with the cathode electrolyte in the second cathode electrolyte portion (e.g., 110B). Consequently in this embodiment of the system, where hydrogen is generated at the cathode and where it is desired to separate the hydrogen gas from carbon dioxide gas

or water vapor from the cathode electrolyte, the partition will prevent mixing of the hydrogen gas with carbon dioxide gas and the water vapor.

[0061] In some embodiments as illustrated in FIG. 1, the first cation exchange membrane (e.g., 112) is located between the cathode (e.g., 114) and anode (e.g., 106A) such the cation exchange membrane separates the cathode electrolyte (e.g., 110) from the anode electrolyte (e.g., 104). Thus as is illustrated in FIG. 1, on applying a relatively low voltage, e.g., less than 2V or less than 1V, across the anode (e.g., 106A) and cathode (e.g., 114), hydroxide ions (OH^-) and hydrogen gas (H_2) will be produced at the cathode (e.g., 114), and hydrogen gas will be oxidized at the anode (e.g., 106) to produce hydrogen ions at the anode (e.g., 106A), without producing a gas at the anode. In some embodiments, the hydrogen gas produced at the cathode (e.g., 114) is directed to the anode through a hydrogen gas delivery system (e.g., 122), and is oxidized to hydrogen ions at the anode. In some embodiments, the use of hydrogen gas at the anode from the cathode will reduce the need for externally produced hydrogen, which consequently will reduce the energy required by the system to produce the hydroxide in the cathode electrolyte.

[0062] Also, as illustrated in FIG. 1, under the applied voltage (e.g., 118) across the anode (e.g., 106A) and cathode (e.g., 114), hydrogen ions produced at the anode (e.g., 106A) will migrate from the anode (e.g., 106) into the anode electrolyte (e.g., 104) to produce an acid, e.g., hydrochloric acid, in the anode electrolyte.

[0063] In some embodiments, the first cation exchange membrane (e.g., 112) is selected to allow passage of cations therethrough but restrict passage of anions therethrough. Thus, as is illustrated in FIG. 1, on applying the low voltage across the anode (e.g., 106A) and cathode (e.g., 114), cations in the anode electrolyte (e.g., 104), e.g., sodium ions in the anode electrolyte comprising sodium chloride, will migrate into the cathode electrolyte through the first cation exchange membrane (e.g., 112), while anions in the cathode electrolyte (e.g., 110), e.g., hydroxide ions, and/or carbonate ions, and/or bicarbonate ions, will be blocked from migrating from the cathode electrolyte through the first cation exchange membrane (e.g., 112) and into the anode electrolyte 104.

[0064] Thus, as is illustrated in FIG. 1, where the anode electrolyte (e.g., 104) comprises an aqueous salt solution such as an aqueous sodium chloride solution, in the cathode electrolyte (e.g., 110) an alkaline solution will be produced comprising sodium ions that migrate from the anode electrolyte (e.g., 104), and hydroxide ions produced at the cathode and/or carbonate ions and or bicarbonate ions produced by dissolving carbon dioxide in the cathode electrolyte.

[0065] Concurrently, in the system of FIG. 1 for illustrative purposes, in the anode electrolyte (e.g., 104), an acid, e.g., hydrochloric acid, will be produced from hydrogen ions migrating from the anode (e.g., 106A) and chloride ions present from the anode electrolyte.

[0066] With reference to FIG. 1 for illustrative purposes, in some embodiments an anode (e.g., 106A) comprising a second cation exchange membrane (e.g., 127) is utilized to separate the anode (e.g., 106) from the anode electrolyte (e.g., 104) such that on a first surface, the cation exchange membrane (e.g., 126) is in contact with the anode (e.g., 106), and an opposed second surface it is in contact with the anode electrode electrolyte (e.g., 104). Thus, in this embodiment of the system, since the second cation exchange membrane (e.g., 126) will allow passage of cations, e.g., hydrogen ions, there-

fore the hydrogen ions produced in at the anode will migrate through the second cation exchange membrane (e.g., 126) and into the anode electrolyte (e.g., 104).

[0067] In some embodiments, suitable cation exchange membranes (e.g., 112 and 126) are conventional and are available from Asahi Kasei of Tokyo, Japan; or from Membrane International of Glen Rock, N.J., or DuPont or DOW Chemicals, in the USA. However, it will be appreciated that in some embodiments, depending on the need to restrict or allow migration of a specific cation or an anion species between the electrolytes, a cation exchange membrane that is more restrictive and thus allows migration of one species of cations while restricting the migration of another species of cations may be used as, e.g., a cation exchange membrane that allows migration of sodium ions into the cathode electrolyte from the anode electrolyte while restricting migration of hydrogen ions from the anode electrolyte into the cathode electrolyte, may be used. Such restrictive cation exchange membranes are commercially available and can be selected by one ordinarily skilled in the art.

[0068] With reference to FIG. 1 for illustrative purposes, in some embodiments of the system, the cathode electrolyte (e.g., 110A) is operatively connected to a supply of carbon dioxide gas contained in a waste gas from an industrial plant, e.g., a power generating plant, a cement plant, or an ore smelting plant. As can be appreciated, the concentration of carbon dioxide in the waste gases from these sources is greater than the concentration of carbon dioxide in the ambient atmosphere; this source of carbon dioxide may also contain other gases and non-gases such as nitrogen, SO_x , NO_x , as is described in co-pending and commonly assigned U.S. Provisional Patent application No. 61/223,657, titled "Gas, Liquids, Solids Contacting Methods and Apparatus", filed Jul. 7, 2009, herein fully incorporated by reference. In some embodiments, although carbon dioxide is present in the atmosphere, in view of the very low concentration of atmospheric carbon dioxide, this source of carbon dioxide may not provide sufficient carbon dioxide to achieve the results obtained with the present system. Also, in some embodiments, since the cathode electrolyte is contained in closed system wherein the pressure of the added carbon dioxide gas within the system is greater than the ambient atmospheric pressure, ambient air and hence ambient carbon dioxide is typically prevented from infiltrating into the cathode electrolyte.

[0069] In some embodiments of the system, and with reference to FIG. 1 for illustrative purposes, carbon dioxide is added to the cathode electrolyte (e.g., 110A) to produce carbonic acid that may dissociate to hydrogen ions and carbonate ions and/or bicarbonate ions, depending on the pH of the cathode electrolyte. Concurrently, as described above, hydroxide ions, produced in the cathode electrolyte from electrolyzing water in the cathode, may react with the hydrogen ions to produce water in the cathode electrolyte.

[0070] Thus, depending on the degree of alkalinity desired in the cathode electrolyte, the pH of the cathode electrolyte may be adjusted and in some embodiments is maintained between and 7 and 14 or greater; or between 7 and 9; or between 8 and 11 as is well understood in the art. In some embodiments, the pH of the cathode electrolyte may be adjusted to any value between 7 and 14 or greater, including a pH 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0, 13.5, 14.0 and greater.

[0071] In some embodiments of the system, the pH of the anode electrolyte is adjusted and is maintained between less than 0 and up to 7 and/or between less than 0 and up to 4, by regulating the concentration of hydrogen ions that migrate into the anode electrolyte from oxidation of hydrogen gas at

the anode, and/or the withdrawal and replenishment of anode electrolyte in the system. In this regard and with reference to FIG. 1 for illustrative purposes, since the voltage across the anode and cathode is dependent on several factors including the difference in pH between the anode electrolyte and the cathode electrolyte as can be determined by the Nernst equation, in some embodiments, the pH of the anode electrolyte is adjusted to a value between 0 and 7, including 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7, depending on the desired operating voltage across the anode and cathode. Thus, as can be appreciated, where it is desired to reduce the energy used and/ or the voltage across the anode and cathode, e.g., as in the Chloralkali process, carbon dioxide can be added to the electrolyte as disclosed herein to achieve a desired pH difference between the anode electrolyte and cathode electrolyte. Thus, to the extent that such systems utilize carbon dioxide, these equivalent systems are within the scope of the present invention.

[0072] With reference to FIGS. 1-4 for illustrative purposes, the method in some embodiments comprises a step of changing the anode electrolyte (e.g., 104) with a concentrated salt solution (e.g., 126); reducing hydrogen gas (e.g., 120) to protons at the anode (e.g., 106A, 106B) and migrating the protons into the anode electrolyte, by applying a voltage (e.g., 118) across the anode and a cathode in contact with a cathode electrolyte; and migrating cations from the anode electrolyte.

[0073] In some embodiments of the method, a hydroxide is produced in the cathode electrolyte (e.g., 110, 110B) by reducing water to hydroxide ions and hydrogen gas at the cathode (e.g., 114); migrating the hydroxide ions into the cathode electrolyte (e.g., 110, 110B); and migrating cations e.g., Na^+ ions from the salt solution (e.g., 104, 126) to the cathode electrolyte across a cation exchange membrane (e.g., 114) separating the salt solution from the cathode electrolyte.

[0074] In some embodiments of the method, the salt solution (e.g., 126) may comprise sodium chloride or sodium sulfate; the acid may comprise hydrochloric acid or sulfuric acid; and the hydroxide in the cathode electrolyte may comprise sodium hydroxide.

[0075] In some embodiments of the method, hydrogen gas produced at the cathode (e.g., 124A) is directed to the anode (e.g., 106A, 106B) to be oxidized to protons and form the acid in the anode electrolyte.

[0076] In some embodiments of the method and with reference to FIG. 4 for illustrative purposes, the cathode electrolyte is used to sequester carbon dioxide as a divalent bicarbonate and/or carbonate by mixing the cathode electrolyte with a divalent cation solution comprising Ca^{++} ions or Mg^{++} ions in carbonate precipitation system (e.g., 412). In some embodiments, the sequestered carbon dioxide is obtained from a waste gas emitted from an industrial facility comprising a fossil fuelled power generating plant, a cement production plant, an ore smelter or a carbon fermentation plant.

[0077] As described above with reference to embodiments of the system and with reference to FIG. 3 for illustrative purposes, in some embodiments of the method, the acid is separated from acid-salt solution by feeding the acid-salt solution into a lower portion of the ion exchange resin bed (e.g., 302B) comprising a resin selected to retard the acid on the resin without retarding the salt; removing the salt solution from the upper portion of the ion exchange resin bed (e.g., 302A); and eluting or back-flushing the acid (e.g., 306) from the ion exchange resin with water (e.g., 310).

[0078] In some embodiments of the method, the ion exchange resin comprises a strong base anion exchange resin comprising particle sizes in the range of 525-625 microns and the bed is short e.g., less than 1 ft.

[0079] In some embodiments of the method, the eluted acid (e.g., 306) is reacted in mineral dissolution system (e.g., 402) with a mineral comprising divalent cations to produce the divalent cation solution (e.g., 410) used in sequestering carbon dioxide as a carbonate or bicarbonate.

[0080] In some embodiments of the method, the divalent cation solution is subjected to nano-filtration in nano-filtration system (e.g., 406) to clean the solution and reverse osmosis system (e.g., 414) to concentrate the salt solution. In some embodiments, the concentrated salt solution (e.g., 416) is reused as concentrated salt solution (e.g., 126) added to the anode electrolyte (e.g., 104).

[0081] With reference to FIGS. 2 and 4 for illustrative purposes, in some embodiments, carbon dioxide is absorbed into the cathode electrolyte (e.g., 110) utilizing a gas mixer/gas absorber (e.g., 136). In some embodiments, the gas mixer/gas absorber comprises a series of spray nozzles that produces a flat sheet or curtain of liquid into which the gas is absorbed; in another embodiment, the gas mixer/gas absorber comprises a spray absorber that creates a mist and into which the gas is absorbed; in other embodiments, other commercially available gas/liquid absorber, e.g., an absorber available from Neumann Systems, Colorado, USA is used.

[0082] The carbon dioxide used in the system may be obtained from various industrial sources that releases carbon dioxide including carbon dioxide from combustion gases of fossil fuelled power plants, e.g., conventional coal, oil and gas power plants, or IGCC (Integrated Gasification Combined Cycle) power plants that generate power by burning sygas; cement manufacturing plants that convert limestone to lime; ore processing plants; fermentation plants; and the like. In some embodiments, the carbon dioxide may comprise other gases, e.g., nitrogen, oxides of nitrogen (nitrous oxide, nitric oxide), sulfur and sulfur gases (sulfur dioxide, hydrogen sulfide), and vaporized materials.

[0083] In some embodiments, the system includes a gas treatment system (not illustrated) that removes constituents in the carbon dioxide gas stream before the gas is utilized in the cathode electrolyte.

[0084] In some embodiments, as illustrated in FIG. 1 a portion of, or the entire amount of, cathode electrolyte (e.g., 110) comprising bicarbonate ions and/or carbonate ions/ and or hydroxide ions is withdrawn from the system and is contacted with carbon dioxide gas in an exogenous carbon dioxide gas/liquid contactor (e.g., 136) to increase the absorbed carbon dioxide content in the solution.

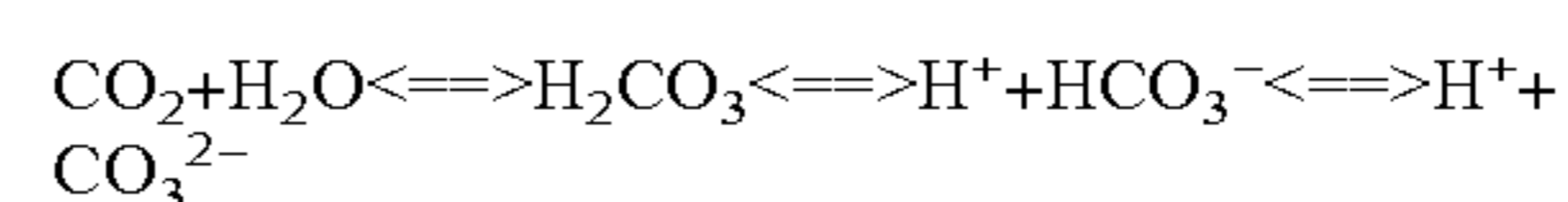
[0085] In some embodiments, the solution enriched with carbon dioxide (e.g., 138) is returned to the cathode compartment (e.g., 116); in other embodiments, the solution enriched with carbon dioxide is reacted with a solution comprising divalent cations in a carbonate precipitating system (e.g., 412) to produce divalent cation hydroxides, carbonates and/or bicarbonates.

[0086] In some embodiments, the pH of the cathode electrolyte (e.g., 110) is adjusted upwards by hydroxide ions that migrate from the cathode, and/or downwards by dissolving carbon dioxide gas in the cathode electrolyte to produce carbonic acid and carbonic ions that react with and remove hydroxide ions. Thus, as can be appreciated that the pH of the cathode electrolyte is determined, at least in part, by the balance of these two processes.

[0087] With reference to FIG. 1 for illustrative purposes, in some embodiments, the system includes a partition (e.g., 134) configured into J-shape structure and positioned in the cathode electrolyte (e.g., 110A, 110B) to define an upward-tapering channel (e.g., 144) in the upper portion of the cathode electrolyte compartment. The partition also defines a downward-tapering channel (e.g., 146) in lower portion of the cathode electrolyte. Thus, with the partition in the place, the cathode electrolyte (e.g., 110) is partitioned into the first cathode electrolyte portion (e.g., 110A) and a second cathode electrolyte portion (e.g., 110B). As is illustrated in FIG. 1, cathode electrolyte in the first cathode electrolyte portion (e.g., 110A) is in contact with cathode electrolyte in the second cathode electrolyte portion (e.g., 110B); however, a gas in the first electrolyte portion (e.g., 110A), e.g., carbon dioxide, is prevented from mixing with cathode electrolyte in the second cathode electrolyte (e.g., 110B).

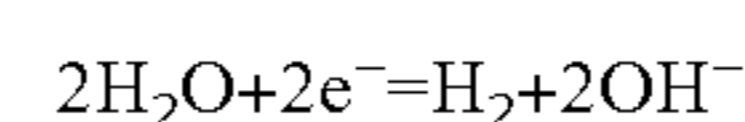
[0088] With reference to FIG. 1 for illustrative purposes, the system in some embodiments includes a cathode electrolyte circulating system (e.g., 134) adapted for withdrawing and circulating cathode electrolyte in the system. In one embodiment, the cathode electrolyte circulating system comprises a carbon dioxide gas/liquid contactor (e.g., 136) that is adapted for dissolving carbon dioxide in the circulating cathode electrolyte, and for circulating the electrolyte in the system. As can be appreciated, since the pH of the cathode electrolyte can be adjusted by withdrawing and/or circulating cathode electrolyte from the system, the pH of the cathode electrolyte compartment can be regulated by regulating an amount of cathode electrolyte removed from the system through the carbon dioxide gas/liquid contactor (e.g., 136).

[0089] With reference to FIG. 1 for illustrative purposes, depending on the pH of the cathode electrolyte, carbon dioxide gas introduced into the first cathode electrolyte portion (e.g., 108A) will dissolve in the cathode electrolyte and reversibly dissociate and equilibrate to produce carbonic acid, protons, carbonate and/or bicarbonate ions in the first cathode electrolyte compartment as follows:



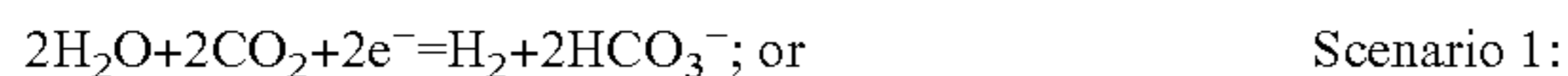
In the system, as cathode electrolyte in the first cathode electrolyte portion (e.g., 110A) may mix with second cathode electrolyte portion (e.g., 110B), the carbonic acid, bicarbonate and carbonate ions formed in the first cathode electrolyte portion (e.g., 110A) by absorption of carbon dioxide in the cathode electrolyte may migrate and equilibrate with cathode electrolyte in the second cathode electrolyte portion (e.g., 110B). Thus, in some embodiments, first cathode electrolyte portion (e.g., 110A) may comprise dissolved and un-dissolved carbon dioxide gas, and/or carbonic acid, and/or bicarbonate ions and/or carbonate ions; while second cathode electrolyte portion (e.g., 108B) may comprise dissolved carbon dioxide, and/or carbonic acid, and/or bicarbonate ions and/or carbonate ions.

[0090] With reference to FIG. 1 for illustrative purposes, on applying a voltage across anode (e.g., 106) and cathode (e.g., 114), the system (e.g., 100) may produce hydroxide ions and hydrogen gas at the cathode from water, as follows:



As cathode electrolyte in first cathode electrolyte portion (e.g., 110A) can intermix with cathode electrolyte in second cathode electrolyte portion (e.g., 110B), hydroxide ions formed in the second cathode electrolyte portion may migrate

and equilibrate with carbonate and bicarbonate ions in the first cathode electrolyte portion (e.g., **110A**). Thus, in some embodiments, the cathode electrolyte in the system may comprise hydroxide ions and dissolved and/or un-dissolved carbon dioxide gas, and/or carbonic acid, and/or bicarbonate ions and/or carbonate ions. In the system, as the solubility of carbon dioxide and the concentration of bicarbonate and carbonate ions in the cathode electrolyte are dependent on the pH of the electrolyte, the overall reaction in the cathode electrolyte (e.g., **104**) is either:



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

[0091] In embodiments wherein it is desired to produce bicarbonate and/or carbonate ions in the cathode electrolyte, the system as illustrated in FIG. 1, and as described above with reference to production of hydroxide ions in the cathode electrolyte, can be configured to produce bicarbonate ions and/or carbonate ions in the cathode electrolyte by dissolving carbon dioxide in cathode electrolyte and applying a voltage of less than 3V, or less than 2.5 V, or less than 2V, or less than 1.5V such as less than 1.0V, or even less than 0.8 V or 0.6V across the cathode and anode.

[0092] In some embodiments, hydroxide ions, carbonate ions and/or bicarbonate ions produced in the cathode electrolyte, and hydrochloric acid produced in the anode electrolyte are removed from the system, while sodium chloride in the salt solution electrolyte is replenished to maintain continuous operation of the system. As can be appreciated, in some 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 hydroxide solution produced in the cathode electrolyte, or withdraw all or a portions of the acid produced in the anode electrolyte, or direct the hydrogen gas produced at the cathode to the anode where it may be oxidized.

[0093] In some embodiments, 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 3V, 2.9V or less, 2.8V or less, 2.7V or less, 2.6V or less, 2.5V or less, 2.4V or less, 2.3V or less, 2.2V or less, 2.1V or less, 2.0V or less, 1.9V or less, 1.8V or less, 1.7V or less, 1.6V, or less 1.5V or less, 1.4V or less, 1.3V or less, 1.2V or less, 1.1V or less, 1.0V or less, 0.9V or less or less, 0.8V or less, 0.7V or less, 0.6V or less, 0.5V or less, 0.4V or less, 0.3V or less, 0.2V or less, or 0.1 V or less.

[0094] In another embodiment, the voltage across the anode and cathode can be adjusted such that gas will form 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. As can be appreciated by one ordinarily skilled in the art, in this embodiment, the voltage across the anode and cathode will be generally higher compared to the embodiment when a gas does not form at the anode.

[0095] With reference to FIG. 1 for illustrative purposes, in some embodiments, the invention provides for a system comprising one or more ion exchange membrane **112**, **126** located between the gas diffusion anode (e.g., **106A**, **106B**) and the cathode (e.g., **114**). In some embodiments, the membranes

should be selected such that they can function in an acidic and/or basic electrolytic solution as appropriate. Other desirable characteristics of the membranes include high ion selectivity, low ionic resistance, high burst strength, and high stability in an acidic electrolytic solution in a temperature range of 0° C. to 100° C. or higher, or a alkaline solution in similar temperature range may be used. In some embodiments, a membrane that is stable in the range of 0° C. to 80° C., or 0° C. to 90° C., but not stable above these ranges may be used.

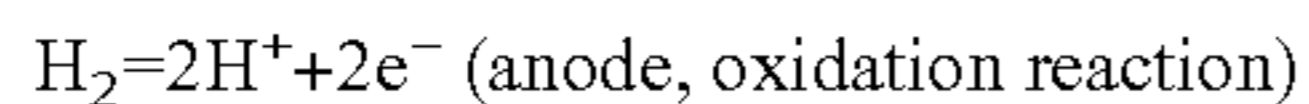
[0096] For other embodiments, it may be useful to utilize an ion-specific ion exchange membranes that allows migration of one type of cation but not another; or migration of one type of anion and not another, to achieve a desired product or products in an electrolyte. In some embodiments, the membrane should be stable and functional for a desirable length of time in the system, e.g., several days, weeks or months or years at temperatures in the range of 0° C. to 80° C., or 0° C. to 90° C. and higher and/or lower. In some embodiments, for example, the membranes should be stable and functional for at least 5 days, 10 days, 15 days, 20 days, 100 days, 1000 days or more in electrolyte temperatures at 80° C., 70° C., 60° C., 50° C., 40° C., 30° C., 20° C., 10° C., 5° C. and more or less.

[0097] As can be appreciated, the ohmic resistance of the membranes will affect the voltage drop across the anode and cathode, e.g., as the ohmic resistance of the membranes increase, the voltage drop across the anode and cathode will increase, and vice versa. Membranes currently available can be used and they include membranes with relatively low ohmic resistance and relatively high ionic mobility; similarly, membranes currently available with relatively high hydration characteristics that increase with temperatures, and thus decreasing the ohmic resistance can be used. Consequently, as can be appreciated, by selecting currently available membranes with lower ohmic resistance, the voltage drop across the anode and cathode at a specified temperature can be lowered.

[0098] In some embodiments, the cathode electrolyte, (e.g., **110A**, **110B**) is operatively connected to a waste gas treatment system where the alkaline solution produced in the cathode electrolyte is utilized, e.g., to sequester carbon dioxide contained in the waste gas by contacting the waste gas and the cathode electrolyte with a solution of divalent cations to precipitate hydroxides, carbonates and/or bicarbonates as described in commonly assigned U.S. patent application Ser. No. 12/344,019 filed on Dec. 24, 2008, herein incorporated by reference in its entirety. The precipitates, comprising, e.g., calcium and magnesium hydroxides, carbonates and bicarbonates in some embodiments may be utilized as building materials, e.g., as cements and aggregates, as described in commonly assigned U.S. patent application Ser. No. 12/126,776 filed on May 23, 2008, supra, herein incorporated by reference in its entirety. In some embodiments, some or all of the carbonates and/or bicarbonates are allowed to remain in an aqueous medium, e.g., a slurry or a suspension, and are disposed of in an aqueous medium, e.g., in the ocean depths or a subterranean site.

[0099] In some embodiments, the cathode and anode are also operatively connected to an off-peak electrical power-supply system that supplies off-peak voltage to the electrodes through the voltage supply (e.g., **118** of FIG. 1 or of FIG. 3). Since the cost of off-peak power is lower than the cost of power supplied during peak power-supply times, the system can utilize off-peak power to produce an alkaline solution in the cathode electrolyte at a relatively lower cost.

[0100] With reference to FIG. 1 for illustrative purposes, on applying a voltage (e.g., **118**) across the anode (e.g., **106**) and cathode (e.g., **114**), protons will form at the anode from oxidation of hydrogen gas supplied to the anode, while hydroxide ions and hydrogen gas will form at the cathode electrolyte from the reduction of water, as follows:



[0101] Since protons are formed at the anode from hydrogen gas provided to the anode; and since a gas such as oxygen does not form at the anode; and since water in the cathode electrolyte forms hydroxide ions and hydrogen gas at the cathode, the system will produce hydroxide ions in the cathode electrolyte and protons in the anode electrolyte when a voltage is applied across the anode and cathode. Further, as can be appreciated, 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 cathode and hydrogen ions at the anode when less than 2V is applied across the anode and cathode, in contrast to the higher voltage that is required when a gas is generated at the anode, e.g., chlorine or oxygen. For example, in some embodiments, hydroxide ions are produced when less than 2.0V, 1.5V, 1.4V, 1.3V, 1.2V, 1.1V, 1.0V, 0.9V, 0.8V, 0.7V, 0.6V, 0.5V, 0.4V, 0.3V, 0.2V, 0.1 V or less is applied across the anode and cathode.

[0102] As discussed above, in the system, on applying a voltage across the anode (e.g., **106**) and cathode (e.g., **114**) the positively charged protons formed at the anode will attempt to migrate to the cathode through the anode electrolyte (e.g., **104**), while the negatively charged hydroxide ions formed at the cathode will attempt to migrate to the anode through the cathode electrolyte (e.g., **110A**, **110B**). As is illustrated in FIG. 1 and with reference to hydroxide ions in the cathode electrolyte (e.g., **110A**, **110B**), since the first cation exchange membrane (e.g., **116**) will restrict the migration of anions from the cathode electrolyte (e.g., **110A**, **110B**), and since the anion exchange membrane (e.g., **120**) will prevent the migration of anions from the anode electrolyte (e.g., **104**) to the salt solution (e.g., **118**), the hydroxide ions generated in the cathode electrolyte will be prevented from migrating out of the cathode electrolyte through the cation exchange membrane. Consequently, on applying the voltage across the anode and cathode, the hydroxide ions produced at the cathode will be contained in the cathode electrolyte. Thus, depending on the flow rate of fluids into and out of the cathode electrolyte and the rate of carbon dioxide dissolution in the cathode electrolyte, the pH of the cathode electrolyte will adjust, e.g., the pH may increase, decrease or remain the same.

[0103] In some embodiments, depending on the ionic species desired in cathode electrolyte (e.g., **110A**, **110B**) and/or the anode electrolyte (e.g., **104**) and/or the salt solution (e.g., **126**), alternative reactants can be utilized. Thus, for example, if a potassium salt such as potassium hydroxide or potassium carbonate is desired in the cathode electrolyte (e.g., **108A**, **108B**), then a potassium salt such as potassium chloride can be utilized in the salt solution (e.g., **126**). Similarly, if sulfuric acid is desired in the anode electrolyte, then a sulfate such as sodium sulfate can be utilized in the salt solution (e.g., **126**). As described in some embodiments herein, carbon dioxide gas is absorbed in the cathode electrolyte; however, it will be appreciated that other gases, including volatile vapors, can be

absorbed in the electrolyte, e.g., sulfur dioxide, or organic vapors to produce a desired result. As can be appreciated, the gas can be added to the electrolyte in various ways, e.g., by bubbling it directly into the electrolyte, or dissolving the gas in a separate compartment connected to the cathode compartment and then directed to the cathode electrolyte as described herein.

[0104] In some embodiments, hydroxide ions are formed at the cathode (e.g., **114**) and in the cathode electrolyte (e.g., **110A**, **110B**) by applying a voltage of less than 2V across the anode and cathode without forming a gas at the anode, while providing hydrogen gas at the anode for oxidation at the anode. In some embodiments, method (e.g., **300**) does not form a gas at the anode when the voltage applied across the anode and cathode is less than 3V or less, 2.9V or less, 2.8V or less, 2.7V or less, 2.6V or less, 2.5V or less, 2.4V or less, 2.3V or less, 2.2V or less, 2.1V or less, 2.0V or less, 1.9V or less, 1.8V or less, 1.7V or less, 1.6V or less, 1.5V or less, 1.4V or less, 1.3V or less, 1.2V or less, 1.1V or less, 1.0V or less, 0.9V or less, 0.8V or less, 0.7V or less, 0.6V or less, 0.5V or less, 0.4V or less, 0.3V or less, 0.2V 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 the system for example by decreasing the electrolyte path lengths and by selecting ionic membranes with low resistance and any other method known in the art, hydroxide ions can be produced in the cathode electrolyte with the present lower voltages.

[0105] In the system as illustrated in FIG. 1, the solubility of carbon dioxide in the cathode electrolyte is dependent on the pH of the electrolyte. Also in the system, the voltage across the cathode and anode is dependent on several factors including the pH difference between the anode electrolyte and cathode electrolyte. Thus, in some embodiments the system can be configured to operate at a specified pH and voltage to absorb carbon dioxide and produce carbonic acid, carbonate ions and/or bicarbonate ions in the cathode electrolyte. In embodiments where carbon dioxide gas is dissolved in the cathode electrolyte, as protons are removed from the cathode electrolyte more carbon dioxide may be dissolved to form carbonic acid, bicarbonate ions and/or carbonate ions. Depending on the pH of the cathode electrolyte the balance is shifted toward bicarbonate ions or toward carbonate ions, as is well understood in the art and as is illustrated in the carbonate specification diagram, above. In these embodiments the pH of the 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 carbonic acid, hydroxide ions, carbonate ions or bicarbonate ions are formed in these embodiments, or that carbonic acid, hydroxide ions, carbonate ions, bicarbonate ions may not form during one period but form during another period.

[0106] For illustrative and descriptive purposes, the systems and methods are described wherein a salt solution comprising sodium chloride is used in the cathode electrolyte. Thus, in the systems and methods herein, the acid produced in the anode catholyte comprises hydrochloric acid and the alkaline solution produced in the cathode electrolyte comprises sodium hydroxide. However, as can be appreciated by those ordinarily skilled in the art, the present system and method are

not limited to using sodium chloride solution since an equivalent salt solution can be used in the anode electrolyte, e.g., a potassium sulfate solution, to produce an equivalent alkaline solution in the cathode electrolyte, e.g., potassium hydroxide and/or potassium carbonate and/or potassium bicarbonate, and since an equivalent acid, e.g., sulfuric acid, can be produced in the anode electrolyte. Thus, to the extent that such equivalents are based on the present system and method, these equivalents are within the scope of the present system and method as defined by the claims.

1. A method comprising:
 - producing an acid in an anode electrolyte in contact with an anode in an anode compartment of an electrochemical system; and
 - separating the acid from the anode electrolyte by retarding the acid on an ion exchange resin to produce a de-acidified anode electrolyte.
2. The method of claim 1, further comprising returning the de-acidified anode electrolyte to the anode compartment.
- 3-4. (canceled)
5. The method of claim 1, comprising producing the acid in the anode electrolyte by reducing hydrogen gas to protons at the anode and migrating the protons into the anode electrolyte by applying a voltage across the anode and a cathode in contact with a cathode electrolyte in the electrochemical system.
6. The method of claim 5, comprising preventing formation of a gas at the anode.
7. (canceled)
8. The method of claim 1, further comprising reducing water to hydroxide ions and hydrogen gas at the cathode and producing a hydroxide in the cathode electrolyte by migrating the hydroxide ions into the cathode electrolyte.
9. The method of claim 8, wherein the anode electrolyte, the cathode electrolyte, or both comprise salt solution and the salt solution comprises sodium chloride or sodium sulfate and wherein the anode electrolyte comprises hydrochloric acid or sulfuric acid and the cathode electrolyte comprises sodium hydroxide.
10. (canceled)
11. The method of claim 9, further comprising contacting the cathode electrolyte with carbon dioxide and producing carbonic acid and/or bicarbonate ions and/or carbonate ions in the cathode electrolyte.
- 12-13. (canceled)
14. The method of claim 1, comprising separating the acid from the anode electrolyte by: feeding the anode electrolyte comprising the acid into a lower portion of an ion exchange resin bed comprising a resin selected to retard the acid on the resin without retarding the salt; and removing the anode electrolyte comprising the salt from the upper portion of the ion exchange resin bed.
15. The method of claim 14, further comprising eluting the acid from the ion exchange resin bed by back-flushing the ion exchange resin to produce an eluted acid.
16. The method of claim 15, wherein the ion exchange resin comprises a strong base anion exchange resin comprising particle sizes in the range of 525-625 microns.
- 17-18. (canceled)
19. The method of claim 16, further comprising dissolving a mineral with the eluted acid in a mineral dissolution system to produce a mineral solution comprising divalent cations and un-reacted acid and processing the mineral solution through a nano-filtration system to produce an acid-salt solution com-

prising the un-reacted acid and the salt solution in a first solution stream, and a divalent cation solution comprising calcium and/or magnesium ions in a second solution stream.

20. (canceled)
21. The method of claim 19, further comprising processing the first solution stream through a reverse osmosis system to separate the salt solution from the un-reacted acid and produce a concentrated salt solution and a dilute acid.
22. (canceled)
23. A system comprising:
 - an electrochemical system comprising an anode electrolyte in contact with an anode in an anode compartment and configured to produce an acid in the anode electrolyte; and
 - an acid retardation system comprising an ion exchange resin bed operatively connected to the anode compartment and configured to receive the anode electrolyte and retard the acid on an ion exchange resin and produce a de-acidified anode electrolyte.
24. The system of claim 23, wherein the acid retardation system is configured to retard the acid in a lower portion of the ion resin bed and produce the de-acidified anolyte in an upper portion of the ion exchange resin bed.
25. The system of claim 24, wherein the ion exchange resin bed comprises a short bed comprising a fine mesh resin.
26. (canceled)
27. The system of claim 24, wherein the acid retardation system is configured to extract and return the de-acidified anode electrolyte to the anode electrolyte compartment.
- 28-29. (canceled)
30. The system of claim 23, further comprising a mineral dissolution system operatively connected to the acid retardation system, wherein the mineral dissolution system is configured to dissolve a mineral with the eluted acid to produce a mineral solution comprising divalent cations.
31. (canceled)
32. The system of claim 30, wherein the electrochemical system comprises a cathode in electrical communication with the anode and in contact with a cathode electrolyte, wherein the electrochemical system is configured to produce the acid in the anode electrolyte by reducing hydrogen gas at the anode to protons and migrating the protons into the anode electrolyte, on application of a voltage across the anode and cathode.
33. The system of claim 32, wherein the electrochemical system comprises a salt solution in the anode electrolyte and wherein the cathode is configured to produce a hydroxide in the cathode electrolyte by reducing water at the cathode to hydroxide ions and hydrogen gas, migrate cations from the anode electrolyte to the cathode electrolyte across a cation exchange membrane separating anode electrolyte and the cathode electrolyte, and migrate the hydroxide ions into the cathode electrolyte.
34. (canceled)
35. The system of claim 23, further comprising a carbonate precipitation system operatively connected to the cathode compartment, and wherein the carbonate precipitation system is configured to mix the divalent cation solution with cathode electrolyte and carbon dioxide, and sequester the carbon dioxide as a divalent cation carbonate and/or bicarbonate comprising calcium and/or magnesium.
- 36-37. (canceled)