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(54) **ALKALINE PRODUCTION USING A GAS DIFFUSION ANODE WITH A HYDROSTATIC PRESSURE**

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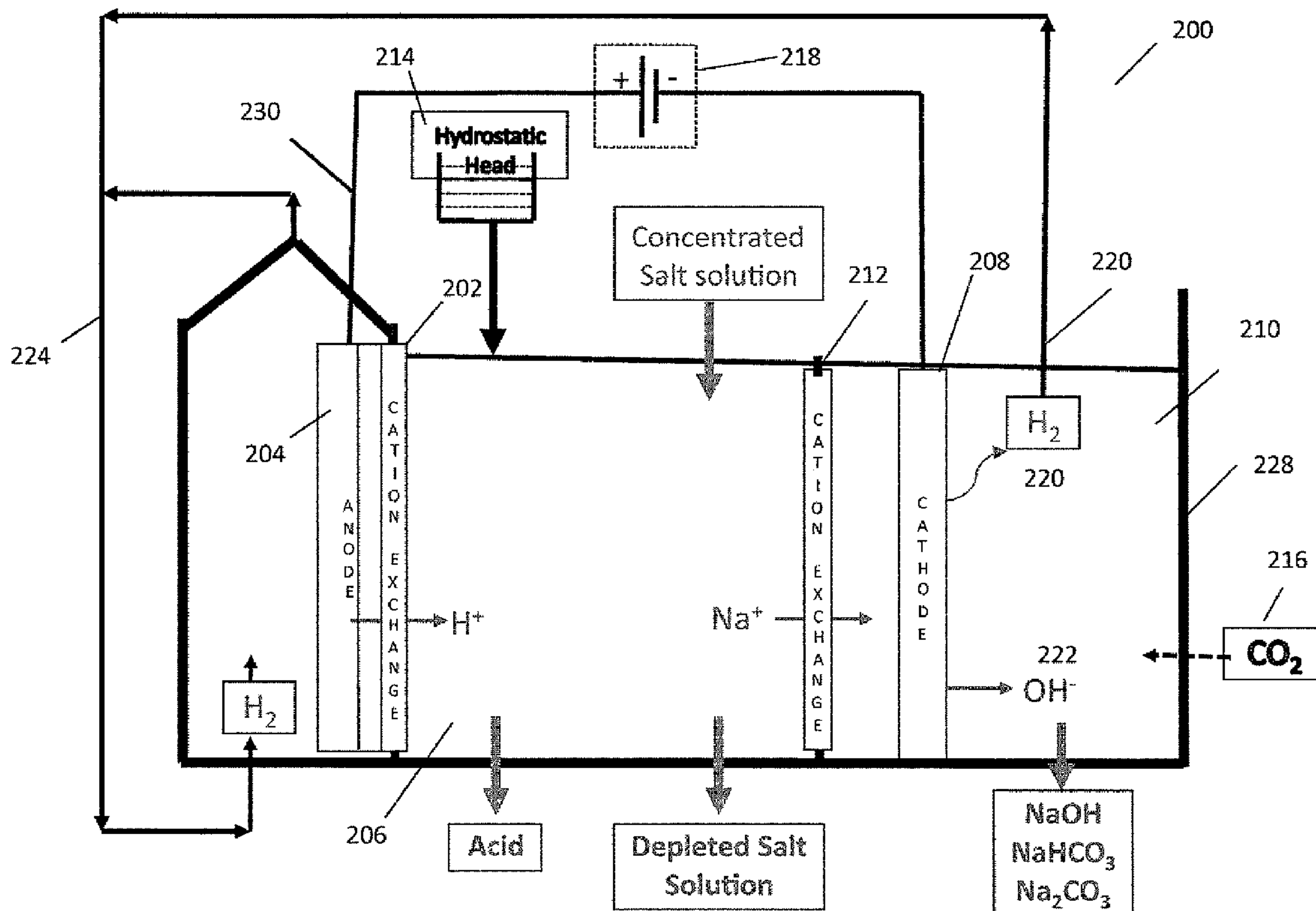
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(57) **ABSTRACT**

An electrochemical system comprising a first cation exchange membrane in contact with a gas diffusion anode and configured to separate the gas diffusion anode from an anode electrolyte; a cathode in contact with a cathode electrolyte; and a second cation ion exchange membrane configured to separate the cathode electrolyte from the anode electrolyte. In the system, an external pressure system is configured to apply a pressure against the first cation exchange membrane through the anode electrolyte, and an alkaline solution is produced in the cathode electrolyte by applying a voltage across the anode and cathode; in some embodiments, carbon dioxide is requested by reaction with the cathode electrolyte.

Related U.S. Application Data

(63) 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.



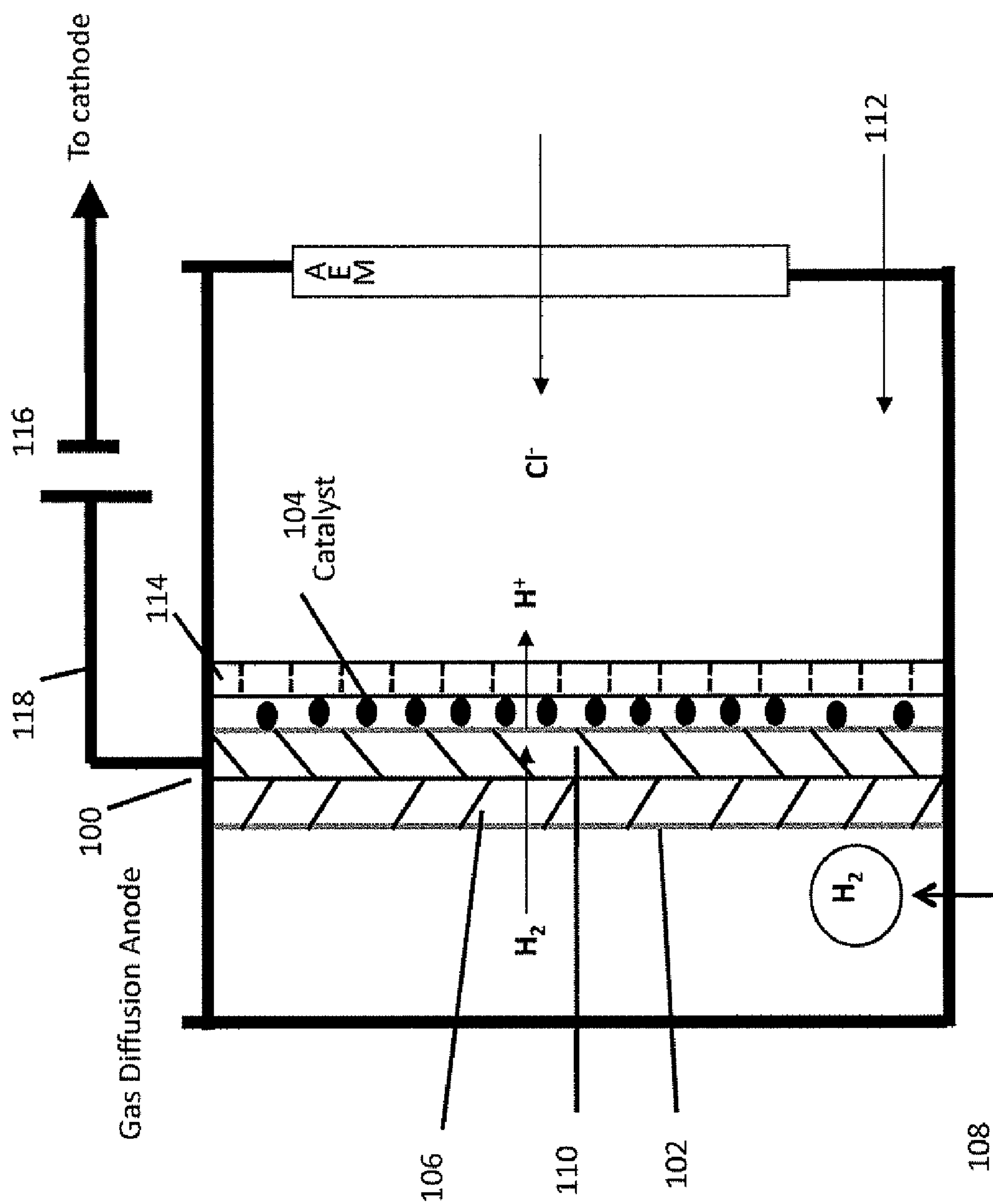


Fig. 1

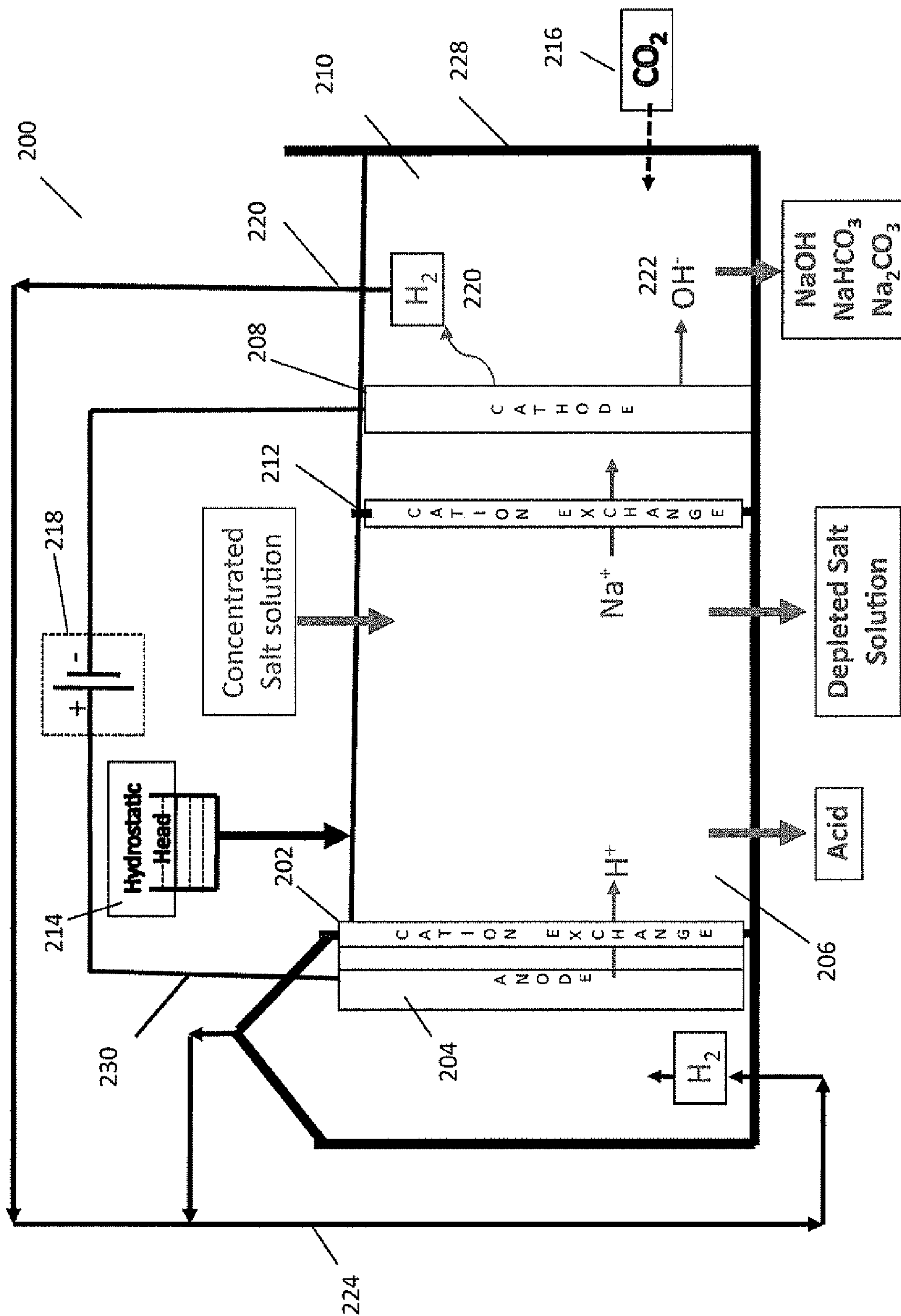


Fig. 2

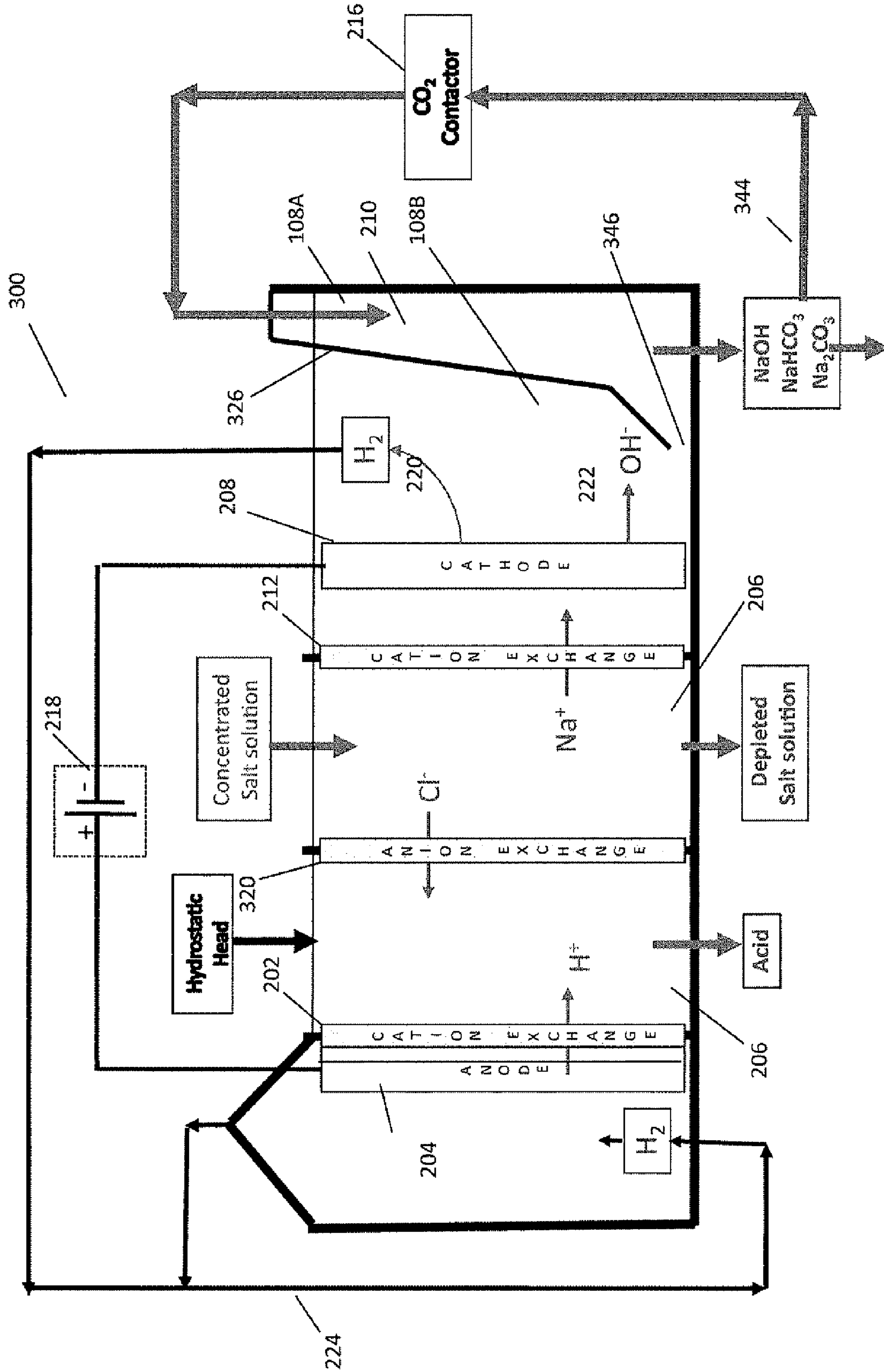


Fig. 3

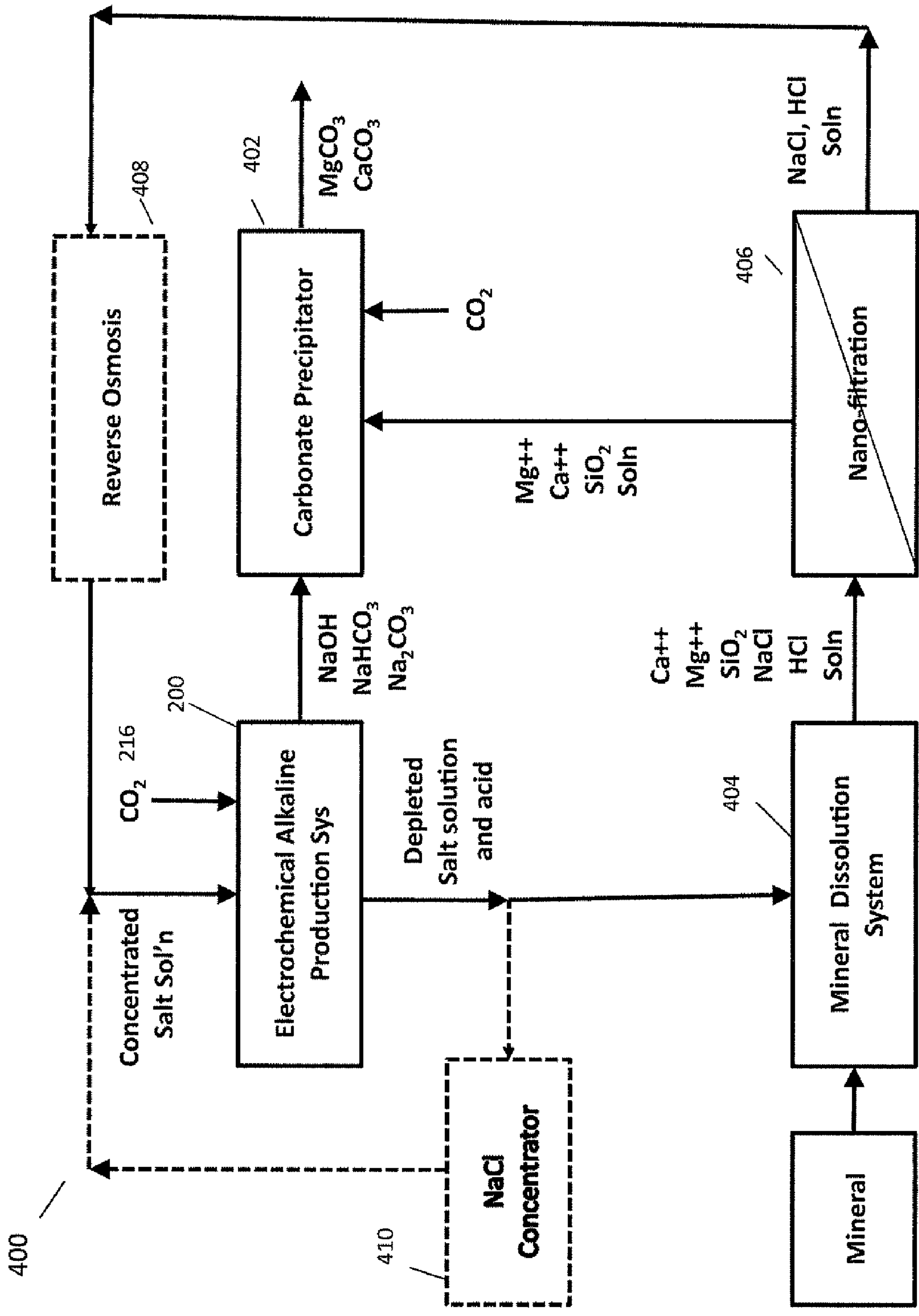


Fig. 4

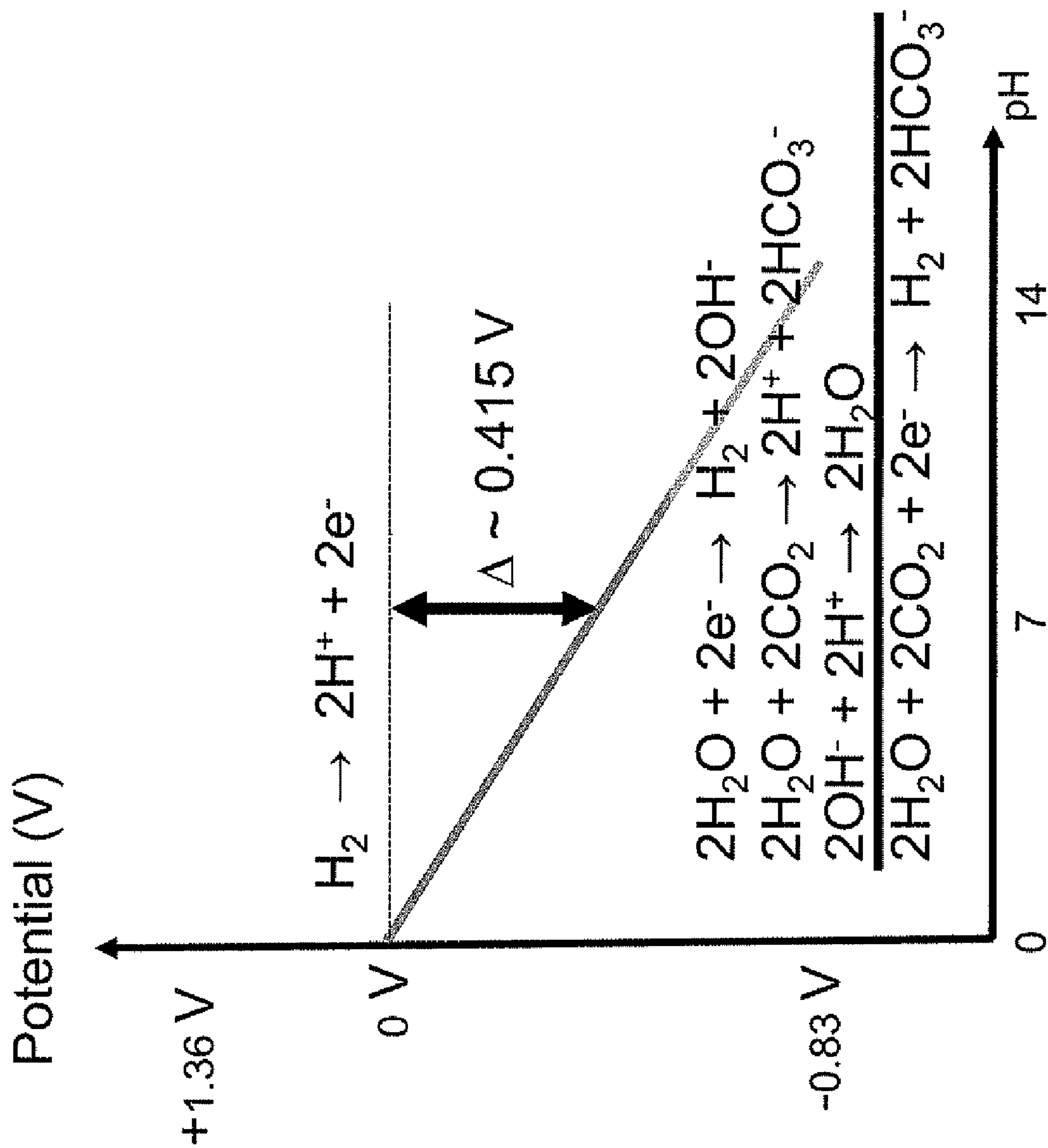


Fig. 5

**ALKALINE PRODUCTION USING A GAS
DIFFUSION ANODE WITH A HYDROSTATIC
PRESSURE**

CROSS-REFERENCE

[0001] This application claims priority to and the benefits of commonly assigned U.S. Provisional Patent Application No. 61/265,313 filed Nov. 30, 2009, and commonly assigned U.S. Provisional Patent Application No. 61/266,080 filed Dec. 2, 2009, both of which are herein incorporated by reference in their entirety.

[0002] This application is also a continuation-in-part of and claims priority to commonly assigned U.S. patent application Ser. No. 12/617,005 filed on Nov. 11, 2009, titled "Electrochemical Production of an Alkaline Solution Using CO₂", now US Patent publication no. US 2010-0084280 A1, which is a continuation-in-part of U.S. patent application Ser. No. 12/541,055 filed on Aug. 13, 2009, titled "Gas Diffusion Anode and CO₂ Cathode Electrolyte System", now US Patent publication no. US 2010-0140103 A1, which is a continuation-in-part of U.S. patent application Ser. No. 12/503,557 filed on Jul. 16, 2009, titled: "CO₂ Utilization In Electrochemical Systems", now US Patent publication no. US 2010-0230293 A1, all of which are herein incorporated by reference in their entirety.

BACKGROUND

[0003] As disclosed in commonly assigned US patent publication no. 2010-0084280 A1 herein incorporated by reference in its entirety, an alkaline solution e.g., an aqueous NaOH solution can be produced in an electrochemical system by reducing water to hydroxyl ions (OH⁻) and hydrogen gas (H₂) at the cathode, and migrating the OH⁻ into the cathode electrolyte where they combine with cations e.g., Na⁺ from an aqueous salt solution e.g., an NaCl solution to form the alkaline solution. In the system, at the anode, H₂ is oxidized to protons (H⁺) and electrons (e⁻), and the H⁺ are migrated into the anode electrolyte where they combine with anions e.g., Cl⁻ from the salt solution to form an acid, e.g., hydrochloric acid.

[0004] In some embodiments, the cathode electrolyte comprising the alkaline solution is mixed with carbon dioxide and a divalent cation solution e.g., CaCl₂ and/or MgSO₄ to sequester the gas as a carbonate and/or bicarbonate, e.g., CaCO₃, and/or MgCO₃ and/or Na₂CO₃ and/or NaHCO₃. In some embodiments, the anode electrolyte comprising the acid is used to dissolve a mineral e.g., olivine to produce the divalent cation solution.

[0005] As the production of an alkaline solution by an electrochemical system is very energy intensive due to the voltage required across the anode and cathode, it is desired to reduce the energy used.

SUMMARY

[0006] This invention pertains to an energy efficient system and method of producing an alkaline solution in the cathode electrolyte of an electrochemical system using a gas diffusion anode with an external hydrostatic pressure applied onto the gas diffusion anode.

[0007] In the system, the pressure applied on the anode squeezes the components of the anode for good physical and electrical contact and thereby eliminates ohmic voltage spikes at the anode that would otherwise occur due to inad-

equate contacts. Since a voltage spike at the anode will cause a voltage spike across the anode and cathode, the elimination of voltage spikes at the anode will reduce the energy used in the system.

[0008] As used herein, the cell voltage is the voltage across the anode and cathode required to produce the alkaline solution, and includes the half-cell voltages for the electrochemical reactions at the anode and cathode, and the voltage required to overcome ohmic resistance in the system e.g., at the electrodes, across the electrolytes, and across ion exchange membranes in the system.

[0009] In the system, the external hydrostatic pressure is applied to the anode via a pressure applied to the anode electrolyte. In some embodiments, a cation exchange membrane is in contact the anode and separates the anode from the anode electrolyte, hence in some embodiments, the hydrostatic pressure on the anode is transmitted to the anode from the anode electrolyte through the cation exchange membrane.

[0010] In the system, the alkaline solution is produced in the cathode electrolyte by oxidizing water to OH⁻ and H₂ at the cathode, and migrating the OH⁻ into the cathode electrolyte to combine with cations e.g., Na⁺ from a salt solution to produce the alkaline solution, e.g., a NaOH solution in the cathode electrolyte.

[0011] In the system at the anode, H₂ is oxidized to H⁺ and e⁻, and the H⁺ are migrated into the anode electrolyte where they combine with anions e.g., Cl⁻ from the salt solution to produce an acid e.g., hydrochloric acid in the anode electrolyte.

[0012] As used herein, the cathode electrolyte is the electrolyte that is configured to remove anions formed at the cathode and is usually in direct contact with the cathode; in some embodiments the cathode electrolyte may be separated from cathode by an anion exchange membrane that is configured to transmit the anions from the cathode to the cathode electrolyte. In some embodiments the cathode electrolyte may be referred to herein as the catholyte.

[0013] Similarly, the anode electrolyte is the electrolyte that is configured to remove cations formed at the cathode and is usually in direct contact with the anode; in some embodiments the anode electrolyte may be separated from anode by a cation exchange membrane that is configured to transmit the cations from the anode to the anode electrolyte. In some embodiments the anode electrolyte may be referred to herein as the anolyte.

[0014] In some embodiments, the system comprises a first cation exchange membrane in contact with the gas diffusion anode and configured to separate the gas diffusion anode from the anode electrolyte; a cathode in contact with a cathode electrolyte; and a second cation ion exchange membrane configured to separate the cathode electrolyte from the anode electrolyte.

[0015] In some embodiments of the system, an external pressure system is configured to apply a pressure on the anode electrolyte. In some embodiments, an external pressure system of at least 4 psi is transmitted to the anode via the first cation exchange membrane in contact with the anode.

[0016] In some embodiments, the system is configured with a gap of 5 mm or less between the first cation exchange membrane and the second cation exchange membrane.

[0017] In some embodiments of the system, the cathode electrolyte comprises added carbon dioxide and in some embodiments, the anode electrolyte comprises a salt solution comprising sodium chloride or potassium sulfate.

[0018] In some embodiments of the system, the gas diffusion anode comprises a substrate comprising a catalyst configured to catalyze oxidization of hydrogen gas to protons. In some embodiments, the substrate comprises a first side in contact with hydrogen and an opposed second side in contact with the first cation exchange membrane. In some embodiments, the substrate first side in contact with hydrogen is hydrophobic, and the substrate second side in contact with anode electrolyte is hydrophilic.

[0019] In some embodiments of the system, the substrate is porous and is configured to diffuse hydrogen from the first side in contact with hydrogen to the second side in contact with the first cation exchange membrane.

[0020] In some embodiments of the system, the catalyst comprises platinum, ruthenium, iridium, rhodium, manganese, silver or alloys thereof.

[0021] In some embodiments of the system, the first cation exchange membrane comprises a hydrocarbon-based cation exchange membrane; in some embodiments, the first cation exchange membrane comprises a monolayer hydrocarbon-based cation exchange membrane; in some embodiments, the first cation exchange membrane comprises polytetrafluoroethylene; and in some embodiments, the first cation exchange membrane comprises sulfonated polytetrafluoroethylene.

[0022] In some embodiments of the system, the first cation exchange membrane is configured to migrate protons from the substrate into the anode electrolyte on application of a voltage across the anode and the cathode. In some embodiments, the anode electrolyte comprises hydrochloric acid; in some embodiments, the anode electrolyte comprises sulfuric acid.

[0023] In some embodiments, the system is configured to produce hydrogen and hydroxyl ions at the cathode on applying the voltage across the anode and cathode. In some embodiments, the system is configured to migrate hydroxide ions from the cathode into the cathode electrolyte.

[0024] In some embodiments, the system is configured to migrate cations from the anode electrolyte into the cathode electrolyte through the second cation exchange membrane. In some embodiments, the cations comprise sodium or potassium ions.

[0025] In some embodiments, the system comprises a hydrogen delivery system configured to direct hydrogen to the anode. In some embodiments, the hydrogen delivery system is configured to direct hydrogen from the cathode to the anode.

[0026] In some embodiments, the system is configured to maintain a temperature of 70° C. to 75° C. in the anode electrolyte. In some embodiments, the system is configured to maintain a current density of 150-200 mA/cm² at the cathode.

[0027] In some embodiments, the system is configured to maintain a pH of 0 or less in the anode electrolyte, and 14 or more in the cathode electrolyte.

[0028] In some embodiments, the system comprises a current collector in contact with the gas diffusion layer of the gas diffusion anode; in some embodiments, the current collector comprises titanium or platinum.

[0029] In some embodiments, the system is comprised of a cell wall comprising a non-corrosive material. In some embodiments, the cell wall comprises a polymer e.g., polyvinyl chloride.

[0030] In some embodiments, the system is operatively connected to a waste gas system and configured to dissolve carbon dioxide from the waste gas into the cathode electrolyte.

[0031] In some embodiments, the system is configured to produce a carbonate and/or bicarbonate product by mixing the cathode electrolyte with a divalent cation solution. In some embodiments, the divalent cation solution comprises calcium and/or magnesium ions, and the carbonate/bicarbonate product comprises calcium carbonate and/or magnesium carbonate and/or sodium bicarbonate and/or sodium carbonate. In some embodiments, the system is configured to dissolve a mineral with the anode electrolyte to produce the divalent cation solution.

[0032] In some embodiments, the method comprises separating a gas diffusion anode from an anode electrolyte using a first cation exchange membrane in contact with the gas diffusion anode; separating the anode electrolyte from a cathode electrolyte contacting a cathode using a second cation exchange membrane; applying an external hydrostatic pressure on the anode electrolyte; producing an alkaline solution in the cathode electrolyte without producing a gas at the anode by applying a voltage across the gas diffusion anode and cathode.

[0033] In some embodiments, the method comprises applying at least 4 psi of hydrostatic pressure to the anode electrolyte and transmitting this pressure to the anode via the first cation exchange membrane.

[0034] In some embodiments, the method comprises oxidizing hydrogen to protons at the gas diffusion anode and migrating protons from the gas diffusion anode through the first cation exchange membrane and into the anode electrolyte. In some embodiments of the method, the anode electrolyte comprises sodium chloride or potassium sulfate.

[0035] In some embodiments, the method comprises migrating sodium or potassium ions from the anode electrolyte into the cathode electrolyte through the second cation exchange membrane. In some embodiments, the method comprises producing hydrochloric acid or sulfuric acid in the anode electrolyte.

[0036] In some embodiments, the method comprises producing hydroxyl ions and hydrogen at the cathode. In some embodiments, the method comprises migrating hydroxyl ions from the cathode into the cathode electrolyte. In some embodiments, the method comprises directing hydrogen generated at the cathode to the gas diffusion anode and oxidizing the hydrogen to protons and electrons at the anode.

[0037] In some embodiments of the method, the gas diffusion anode comprises a substrate comprising a catalyst configured to catalyze oxidation of hydrogen to protons and electrons. In some embodiments, the method comprising contacting the substrate at a first side with hydrogen and contacting the substrate at an opposed second side with the first cation exchange membrane. In some embodiments, the substrate first side is hydrophobic and the substrate second side is hydrophilic; in some embodiments, the substrate is porous and is configured to diffuse hydrogen from the first side in contact with hydrogen to the second side in contact with the first cation exchange membrane.

[0038] In some embodiments of the method, the catalyst comprises platinum, ruthenium, iridium, rhodium, manganese, silver or alloys thereof.

[0039] In some embodiments of the method, the first cation exchange membrane comprises a hydrocarbon-based cation

exchange membrane. In some embodiments, the first cation exchange membrane comprises a monolayer hydrocarbon-based cation exchange membrane. In some embodiments, the first cation exchange membrane comprises polytetrafluoroethylene; in some embodiments, the first cation exchange membrane comprises sulfonated polytetrafluoroethylene.

[0040] In some embodiments of the method, cations are migrated from the anode electrolyte into the cathode electrolyte through the second cation exchange membrane. In some embodiments, hydrogen gas is diffused through the substrate to the catalyst.

[0041] In some embodiments, the method comprises adding carbon dioxide to the cathode electrolyte and producing carbonates ions and/or bicarbonate ions in the cathode electrolyte. In some embodiments, the carbon dioxide is obtained from a waste gas; in some embodiments, the waste gas is obtained from an industrial plant. In some embodiments, the industrial plant is a fossil fuelled electrical power generating plant, a cement production plant or an ore processing facility that generates carbon dioxide. In some embodiments, carbon dioxide in ambient air is excluded from the cathode electrolyte and thus the cathode electrolyte is devoid of ambient carbon dioxide.

[0042] In some embodiments of the method, the ion exchange membranes are configured such that a gap of 5 mm or less is maintained between the first and second cation exchange membrane.

[0043] In some embodiments, the method comprises contacting the cathode electrolyte with a divalent cation solution to produce a carbonate or bicarbonate product comprising calcium and/or magnesium. In some embodiments, the divalent cation comprises magnesium ions or calcium ions. In some embodiments, the method comprises dissolving a mineral with the anode electrolyte to produce the divalent cation solution.

[0044] In some embodiments, the method comprises maintaining a pH of 7 or greater in the cathode electrolyte; in some embodiments, the method comprises maintaining a pH of between 7 and 9 in the cathode electrolyte. In some embodiments, the method comprises maintaining a pH of between 8 and 11 in the cathode electrolyte. In some embodiments, the method comprises maintaining a pH of less than 7 in the anode electrolyte. In some embodiments, the method comprises maintaining a pH of less than 4 in the anode electrolyte.

[0045] In some embodiments, the method comprises oxidizing hydrogen gas to hydrogen ions at the anode and migrating the hydrogen ions through the first cation exchange membrane into the anode electrolyte. In some embodiments, the method comprises producing hydroxide ions and hydrogen gas at the cathode. In some embodiments, the method comprises directing hydrogen gas from the cathode to the anode and oxidizing the hydrogen at the anode.

[0046] In some embodiments, the method comprises migrating cations ions through the second cation exchange membrane into the cathode electrolyte. In some embodiments, the cations comprise sodium ions. In some embodiments, the method comprises producing an acid in the anode electrolyte.

[0047] In some embodiments, the method comprises establishing a temperature of 70° C. to 75° C. in the anode electrolyte. In some embodiments, the method comprises establishing a current density of 150-200 mA/cm² at the cathode.

[0048] In some embodiments, the method comprises maintaining a pH of 0 or less in the anode electrolyte, and 14 or more in the cathode electrolyte.

[0049] In some embodiments, the anode and cathode are disposed in an electrochemical cell comprising cell walls comprising a non-corrosive material. In some embodiments, the cell walls comprise a polymer; in some embodiments the cell walls comprise polyvinyl chloride. In some embodiments, the method comprises maintaining a gap of 5 mm or less between the first and second cation exchange membrane.

[0050] Thus, by applying an external pressure on the anode electrolyte and transmitting this pressure to the gas diffusion anode to squeeze together the components of the gas diffusion anode, in accordance with the present system and method, the electrical and physical contact at the anode is improved.

[0051] Consequently, in the system, the ohmic voltage spikes at the anode this is otherwise caused by poor contacts at the anode are eliminated and consequently the voltage spikes across the anode and cathode attributed to poor contacts at the anode are eliminated and hence by the system and method the cell voltage required to produce the alkaline solution is reduced, thereby reducing the energy required to produce the alkaline solution.

[0052] Further, since hydrogen gas is oxidized to H⁺ and e⁻ at the anode, therefore the half-cell voltage at the anode is 0 V, and thus by the system and method the cell voltage across the anode and cathode required to produce the alkaline solution is further reduced which further reduces the energy used to produce the alkaline solution.

[0053] Also, in the system, as the first cation exchange membrane is configured to separate the anode from the anode electrolyte, and as this membrane will migrate H⁺ from the anode into the anode electrolyte while blocking migration of anions e.g., Cl⁻ from the anode electrolyte into the anode, therefore by this configuration of the system and method the anode does not come in contact with an acid.

[0054] Consequently, by the system and method, the catalyst at the anode is protected from contact with an acid that may otherwise form at the anode by a combination of H⁺ from the anode and anions from the anode electrolyte. Consequently, in the system, the efficiency of the catalyst is sustained, which will lower the voltage required across the anode and cathode, and hence lower the energy used in producing the alkaline solution.

[0055] In some embodiments of the system and method, the alkaline solution produced in the cathode electrolyte is mixed with carbon dioxide and a divalent cation solution to sequester the carbon dioxide as cementitious carbonate and/or bicarbonate as disclosed in commonly assigned U.S. Pat. No. 7,735,274 herein incorporated by reference in its entirety. In some embodiments, the acid produce in the anode electrolyte is used to dissolve a mineral to produce a divalent cation solution used in producing the cementitious carbonate and/or bicarbonate.

BRIEF DESCRIPTION OF DRAWINGS

[0056] The following drawings, not to scale, illustrate by way of examples and not by limitation embodiments of the present system and method.

[0057] FIG. 1 is an illustration of an embodiment of the present gas diffusion anode.

[0058] FIG. 2 is an illustration of an embodiment of the present electrochemical system comprising a gas diffusion anode.

[0059] FIG. 3 is an illustration of an embodiment of the present electrochemical system comprising a gas diffusion anode.

[0060] FIG. 4 is an illustration an embodiment of the present electrochemical system integrated with a carbon dioxide sequestration system.

[0061] FIG. 5 is an illustration voltage potential across the anode and cathode vs. the pH of the cathode electrolyte.

DETAILED DESCRIPTION

[0062] In an electrochemical system the energy used to produce an alkaline solution is correlated to the cell voltage. In the system, the cell voltage is the voltage across the anode and cathode required to produce the alkaline solution and is the cumulative voltage drops in the system, including: i) the half-cell voltages for the electrochemical reactions at the anode and cathode; ii) ohmic voltage drops due to electrical resistance e.g., at the electrodes, across the ion exchange membranes, across the electrolytes and elsewhere, and iii) the current density at the cathode required to produce a desired rate of OH^- in the cathode electrolyte.

[0063] As disclosed in commonly assigned US patent publication no. 2010-0084280 A1, supra, herein incorporated by reference in its entirety, the cell voltage can be reduced by oxidizing H_2 gas to H^+ and e^- at the anode while suppressing production of a gas e.g., oxygen or chlorine at the anode, and while reducing water at the cathode to OH^- and H_2 gas. This reduction in cell voltage is achieved since in such systems H_2 gas is oxidized to H^+ and e^- at the anode, and therefore in such systems the half-cell voltage at the anode is 0 V and therefore in the system the half-cell voltage at the anode does not contribute to the cell voltage.

[0064] In the system, an anode that can be used to oxidize H_2 gas to H^+ and e^- to achieve a 0 V half-cell voltage at the anode is a gas diffusion anode as illustrated schematically in FIG. 1. In some embodiments, the gas diffusion anode 100 comprises a conductive substrate 102 comprising a first side 106 that interfaces with the hydrogen 108 and an opposed second side 110 that interfaces with the anode electrolyte 112. In some embodiments, the side of the substrate 106 that interfaces with the hydrogen is hydrophobic and porous and will allow a gas to diffuse therein. Similarly, the side of the substrate 106 that interfaces with the anode electrolyte is hydrophilic and porous and will allow the anode electrolyte to diffuse therein.

[0065] In some embodiments, the gas diffusion anode includes a current collector 114 through which electrons generated at the anode are removed from the anode via the power supply 116 and are conducted to the cathode to facilitate the reduction reaction at the cathode.

[0066] In some embodiments, the substrate is infused with a catalyst 104 to catalyze the oxidation of hydrogen to protons and electrons. In some embodiments, the catalyst may comprise platinum, ruthenium, iridium, rhodium, manganese, silver or alloys thereof that promote oxidation of hydrogen to protons and electrons.

[0067] In some embodiments, to achieve the reaction at the anode, H_2 gas is fed to the first side of the anode 106 from where it diffuses into the substrate and into the second side 110. At the second side, the H_2 is oxidized to H^+ and e^- while the gas is in contact with the catalyst and while the voltage is applied across the anode and a cathode. From the second side 110, under the applied voltage the H^+ will migrate into the

anode electrolyte and e^- are conducted through the current collector to the voltage supply 116.

[0068] Thus, a gas diffusion anode can advantageously be configured with a cathode in an electrochemical system to produce an alkaline solution in the cathode electrolyte based on oxidizing H_2 at the anode to H^+ and e^- while reducing water to OH^- and H_2 at the cathode and migrating the OH^- into the catholyte electrolyte.

[0069] Gas diffusion anodes are commercially available e.g., from E-TEK (USA), or can be assembled from components as described in the publication titled: "Electrochemical Study of Hydrogen Diffusion Anode-membrane assembly for Membrane Electrolysis", *Electronica Acta* 51 (2005) 386-394, Frederic Faverjon, et al (2005) available online from www.sciencedirect.com, herein incorporated by reference.

[0070] In using a gas diffusion anode as described above, a problem that may occur is an unexpectedly high cell voltage across the anode and cathode notwithstanding that H_2 gas is oxidized to H^+ and e^- at the anode and therefore the half-cell voltage for the reaction at the anode is 0V.

[0071] In some embodiments, the problem can be attributed to inadequate physical and electrical contact at the anode possibly caused e.g., by poor assembly of the anode layers and/or by expansion of the anode layers due to temperature changes in the anode from ohmic heating at the anode and/or heat released by the electrochemical reaction at the anode.

[0072] As can be appreciated, since poor electrical and physical contacts at the anode will cause ohmic voltage spikes at the anode and consequently cause the cell voltage to spike, therefore a gas diffusion anode with poor contacts can increase the energy used in producing the alkaline solution.

[0073] However, since a gas diffusion anode is otherwise useful in making contact at the anode between the H_2 and the catalyst while allowing for migration of the H^+ and e^- from the anode in producing the alkaline solution in the cathode electrolyte, it is desired to avoid poor electrical and physical contacts at the anode.

[0074] With reference to FIG. 2, in accordance with the present invention an electrochemical system 200 capable of producing an alkaline solution in the catholyte with improved physical and electrical contacts at the anode 204 is illustrated, and comprises a first cation exchange membrane 202 in contact with a gas diffusion anode 204 and configured to separate the gas diffusion anode from the anode electrolyte 206; a cathode 208 in contact with a cathode electrolyte 210; and a second cation ion exchange membrane 212 configured to separate the cathode electrolyte from the anode electrolyte.

[0075] In some embodiments, the system 200 comprises an external hydrostatic pressure system 214 configured to apply a pressure onto the anode 204 through the anode electrolyte 206 and the cation exchange membrane 202, to thereby squeeze the components of the anode and achieve improved physical and electrical contact between the components of the substrate i.e., the first surface 106, the second surface and a current collector 118 as illustrate in FIG. 1.

[0076] Thus, in the system 200, since the hydrostatic pressure can be dynamically adjusted during use, the pressure on the gas diffusion anode 204 from the anode electrolyte 206 can be adjusted to establish good physical and electrical contact at the anode regardless of temperature changes at the anode during use that may cause poor contact to develop.

[0077] Hence, in the system 200, since good contact is established at the anode, undesired voltage spikes attributable

to inadequate contacts at the anode is avoided, thereby reducing the energy used in producing the alkaline solution.

[0078] With reference to FIG. 2, in some embodiments, the system 200 comprise a first cation exchange membrane 202 that contacts the hydrophilic side 110 of the anode and also contacts the anode electrolyte 206. In some embodiments, since the first cation ion exchange membrane 202 will allow the passage of cations e.g., protons from the anode but bar the passage of anions e.g., chloride ions to the anode 204, the first cation exchange membrane will allow migration of protons from the anode 204 into the anode electrolyte 206 and/or block the migration of anions from the anolyte to the anode.

[0079] Thus, advantageously, with system 200, an acid is prevented from forming on the substrate of the anode and thus the catalyst on the substrate is protected from the acid.

[0080] In some embodiments of the system 200, the external pressure system 214 is configured to apply a hydrostatic pressure of at least 4 psi on the anode electrolyte 206. In some embodiments, the hydrostatic pressure can be varied to apply any desired pressure on the ion exchange membranes e.g., 0, 1, 3, 4, 4, 5, 6, 7, 8, 9, 10, psi or greater depending on the strength of the membranes.

[0081] In some embodiments of the system 200, the hydrostatic pressure 214 on the anode can be produced by a column of liquid in contact with the anode electrolyte and may comprise anode electrolyte. In other embodiments, the hydrostatic pressure on the anode can be produced by other pressurizing means not illustrated in e.g., a gas pressure applied onto the anode electrolyte, or a mechanical system such as a piston configured to pressurize the anode electrolyte.

[0082] In some embodiments, the system 200 is configured with a gap of 5 mm or less between the first cation exchange membrane 202 and the second cation exchange membrane 212. In some embodiments, the gap between the cation exchange membranes is adjustable to any size including a gap of 0, 1, 2, 3, 4, 5, 6, 7 mm or greater, depending on the configuration of the system and the need to avoid voltage spikes in the system.

[0083] With reference to FIGS. 1 and 2, in some embodiments of the system 200, the gas diffusion anode 204 comprises a substrate 102 comprising a catalyst 104 configured to catalyze oxidization of hydrogen gas 108 to protons. In some embodiments of the system 200, the substrate 102 of the gas diffusion anode comprises a first side 106 in contact with hydrogen gas and an opposed second side 110 in contact with the first cation exchange membrane 114, 202. In some embodiments, the substrate first side in contact with hydrogen gas is hydrophobic, and the substrate second side in contact with anode electrolyte is hydrophilic.

[0084] In some embodiments of the system 200, the substrate 102 is porous and is configured to diffuse hydrogen therethrough from the first side 106 in contact with hydrogen 108 to the second side 110 in contact with the first cation exchange membrane 114, 202.

[0085] In some embodiments of the system 200, the catalyst 104 used may comprise platinum, ruthenium, iridium, rhodium, manganese, silver or alloys thereof.

[0086] In some embodiments of the system 200, the first cation exchange membrane 114, 202 comprises a hydrocarbon-based cation exchange membrane. In some embodiments of the system 200, the first cation exchange membrane 114, 202 comprises a monolayer hydrocarbon-based cation exchange membrane. In some embodiments of the system 200, the first cation exchange membrane 114, 202 comprises

polytetrafluoroethylene. In some embodiments of the system 200, the first cation exchange membrane comprises sulfonated polytetrafluoroethylene.

[0087] 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. Consequently, currently available membranes can be selected to provide a relatively low ohmic and ionic resistance while providing for improved strength and resistance in the system for a range of operating temperatures. Suitable membranes are commercially available from Asahi Kasei of Tokyo, Japan; or from Membrane International of Glen Rock, N.J., and USA.

[0088] With reference to FIGS. 1, 2 and 3 in some embodiments, cation exchange membranes used in the system are commercially available as discussed above, 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.

[0089] In some embodiments of the system 200, the first cation exchange membrane 114, 202 is configured to migrate protons from the substrate 102 or anode 204 into the anode electrolyte 112, 206 on application of a voltage 218 across the substrate/anode 102 204 and the cathode 208. In some embodiments of the system 200, the anode electrolyte 112, 206 may comprise hydrochloric acid where a chloride salt is used and wherein chloride ions are present in the anode electrolyte. In some embodiments, the anode electrolyte comprises sulfuric acid where a sulfate salt is used and wherein sulfate ions are present in the anode electrolyte.

[0090] In some embodiments, the system 200 is configured to produce an alkaline solution in the cathode electrolyte by producing hydroxyl ions 222 and hydrogen at the cathode 208 on applying the voltage 218 across the substrate/anode 102, 204 and the cathode 208. In some embodiments, the hydroxyl ions 222 are migrated into the cathode electrolyte 210 where they combine with cations e.g., Na⁺ from a salt solution e.g., from the anode electrolyte 206 to produce the alkaline solution. In some embodiments of the system 200, carbon dioxide 216 is added to the cathode electrolyte 210 to form carbonate ions and or bicarbonate ions. Thus in some embodiments of the system 200, the cathode electrolyte 210 comprises carbonate ions and/or bicarbonate ions.

[0091] In some embodiments, the system 200 is configured to migrate cations from the anode electrolyte 206 into the

cathode electrolyte **210** through the second cation exchange membrane **212**. In some embodiments, the cations comprise sodium where a sodium salt e.g., sodium chloride is used, or potassium ions where a potassium salt e.g., potassium sulfate is used.

[0092] In some embodiments, the system **200** comprises a hydrogen delivery system **224** configured to direct hydrogen to the gas diffusion anode. In some embodiments, the hydrogen delivery system is configured to direct hydrogen generated at the cathode **208** to the gas diffusion anode **204**.

[0093] In some embodiments, the system **200** is configured to maintain a temperature of 70° C. to 75° C. in the anode electrolyte **206**. In some embodiments, the system **200** is configured to maintain a current density of 150-200 mA/cm² at the cathode **208**.

[0094] In some embodiments, the system **200** is configured to maintain a pH of 0 or less in the anode electrolyte **206**, and a pH of 14 or more in the cathode electrolyte **210**.

[0095] In some embodiments, the system **200** comprises a current collector **118**, **230** in contact with the gas diffusion anode **204**. In some embodiments, the current collector comprises titanium or platinum. In some embodiments, the current collector is used to remove electrons from the anode **204** to the power supply **218**.

[0096] In some embodiments, the system **200** is comprised of a cell wall **228** comprising a non-corrosive material and configured to contain the anode electrolyte containing the acid, and the cathode electrolyte containing the alkaline solution. In some embodiments, the cell wall comprises a polymer e.g., polyvinyl chloride selected to resist corrosion attributed to the anode electrolyte and the cathode electrolyte.

[0097] With reference to FIGS. **2**, **3** and **4**, in some embodiments, the system **200**, **300**, **400** is operatively connected to a waste gas system **216** and configured to dissolve carbon dioxide into the cathode electrolyte **210** from the waste gas. In some embodiments, the system **200**, **300**, **400** is configured to produce a carbonate and/or bicarbonate product comprising calcium carbonate and/or magnesium carbonate and or sodium carbonate and/or sodium bicarbonate by mixing the cathode electrolyte with a divalent cation solution comprising calcium and/or magnesium ions. In some embodiments, the system **200**, **300**, **400** is configured to dissolve a mineral in a mineral dissolution system **404** with the anode electrolyte **206** to produce the divalent cation solution.

[0098] With reference to FIGS. **2**, **3** and **4**, in some embodiments, the waste gas is obtained from an industrial plant, e.g., a power generating plant, a cement plant, or an ore smelting plant. In some embodiments, the carbon dioxide in the waste gas is greater than the concentration of carbon dioxide in the ambient atmosphere. This source of carbon dioxide may also contain other gaseous and non-gaseous components of a combustion process, e.g., nitrogen gas, 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.

[0099] In some embodiments, the carbon dioxide used in the system may be obtained from an industrial source 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.

[0100] In some embodiments, although carbon dioxide is present in ordinary ambient air, because of its very low concentration, ambient carbon dioxide is not a suitable source of carbon dioxide to achieve the results obtained herein. Also, in some embodiments herein, since the cathode electrolyte is contained in a closed system wherein the pressure of the added carbon dioxide is greater than the ambient atmospheric pressure, therefore ambient carbon dioxide is prevented from infiltrating into the cathode electrolyte.

[0101] In some embodiments, and with reference to FIGS. **2**, **3** and **4**, carbon dioxide is added to the cathode electrolyte to produce carbonic acid and/or carbonate ions and/or bicarbonate ions, depending on the pH of the cathode electrolyte. Concurrently, hydroxyl ions, produced from electrolyzing water in the cathode electrolyte, may react with the carbonic acid to produce water in the cathode electrolyte. 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.

[0102] With reference to FIGS. **2**, **3** and **4**, in some embodiments, a portion of, or the entire amount of, cathode electrolyte 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 **216** to increase the absorbed carbon dioxide content in the solution. In some embodiments, the solution enriched with carbon dioxide is returned to the cathode compartment; in other embodiments, the solution enriched with carbon dioxide is reacted with a solution comprising divalent cations to produce divalent cation hydroxides, carbonates and/or bicarbonates. In some embodiments, the pH of the cathode electrolyte 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, the pH of the cathode electrolyte is determined, at least in part, by the balance of these two processes.

[0103] 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, 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, in equivalent systems, 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 diox-

ide 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.

[0104] With reference to FIG. 2, in some embodiments, the anode electrolyte 206 comprises a salt solution that includes sodium ions and chloride ions and the system 200 is configured to produce the alkaline solution in the cathode electrolyte 210 while also producing hydrogen ions at the anode 202, with less than 1V across the anode 202 and cathode 208, without producing a gas at the anode; in some embodiments, the system 200 is configured to migrate the hydrogen ions from the anode 204 into the anode electrolyte 206; in some embodiments, the anode electrolyte comprises an acid; in some embodiments, the system 200 is configured to produce bicarbonate ions and/or carbonate ions in the cathode electrolyte 210; in some embodiments, the system is configured to migrate hydroxide ions from the cathode 208 into the cathode electrolyte 210; migrate cations, e.g., sodium ions, from the anode electrolyte 206 into the cathode electrolyte through the second cation exchange membrane 212; in some embodiments, hydrogen gas from the cathode is collected and provided to the anode through and a hydrogen gas delivery system 224.

[0105] In some embodiments as illustrated in FIG. 3, the system 200, 300 comprises a partition 326 that partitions the cathode electrolyte into a first cathode electrolyte portion 108A and a second cathode electrolyte portion 108B, wherein the second cathode electrolyte portion 108B, comprising added carbon dioxide, contacts the cathode 208; and wherein the first cathode electrolyte portion 108A comprising added carbon dioxide is in contact with the second cathode electrolyte portion 108B under the partition 326.

[0106] In the system as illustrated in FIG. 3, the partition 326 is positioned in the cathode electrolyte such that a gas, e.g., carbon dioxide in the first cathode electrolyte portion 108A is isolated from cathode electrolyte in the second cathode electrolyte portion 108B. Thus, for example, where a gas, e.g., hydrogen, is generated at the cathode and it is desired to separate this cathode gas from a gas or vapor that may evolve from the cathode electrolyte, the partition may serve as a means to prevent mixing of the gases from the cathode and the gases and or vapor from the cathode electrolyte. While this system is illustrated in FIG. 3, it is applicable generally to any of the electrochemical system described and illustrated herein.

[0107] With reference to FIGS. 1, 2 and 3, the system includes a hydrogen gas supply system 108, 224 configured to provide hydrogen gas to the anode 102, 204. The hydrogen may be obtained from the cathode 208 or may be obtained from external source, e.g., from a commercial hydrogen gas supplier, e.g., at start-up of the system when the hydrogen supply from the cathode is insufficient. In the system, the hydrogen gas is oxidized to protons and electrons; in some embodiments, un-reacted hydrogen gas is recovered and circulated at the anode.

[0108] With reference to FIG. 3, the system in some embodiments includes a cathode electrolyte circulating system 344 adapted for withdrawing and circulating cathode electrolyte in the system. In one embodiment, the cathode electrolyte circulating system 344 comprises a carbon dioxide gas/liquid contactor 216 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 216.

[0109] With reference to FIGS. 2, 3 and 4, in some embodiments the electrochemical system 200 may be operatively connected to a carbon dioxide sequestration system 400 for sequestering carbon dioxide to produce e.g., a carbonate and/or bicarbonate. In some embodiments, the sequestration system 400 may comprise carbonate precipitator 402 configured to precipitate carbonates and/or bicarbonates from a solution, wherein in some embodiments the carbonates and/or bicarbonates comprise calcium and/or magnesium carbonate and/or bicarbonate. Also as illustrated in FIG. 4, in some embodiments, the anode electrolyte of the electrochemical system 200 comprising an acid, e.g., hydrochloric acid and a depleted salt solution comprising low amount sodium ions is used in a mineral dissolution system 404 that is configured to dissolve minerals and produce a mineral solution comprising calcium ions and/or magnesium ions, e.g., mafic minerals such as olivine and serpentine. In some embodiments, not shown in FIG. 4, the acid may be used for other purposes in addition to or instead of mineral dissolution e.g., use as a reactant in production of cellulosic biofuels, use the production of polyvinyl chloride (PVC), and the like. System appropriate to such uses may be operatively connected to the electrochemical system 200, 300, or the acid may be transported to the appropriate site for use.

[0110] In the some embodiments as illustrated in FIG. 4, the mineral dissolution system 404 is operatively connected to nano-filtration system 406 that is configured to separate sodium ions and chloride ions from the mineral solution comprising, e.g., calcium ions, magnesium ions, silica, hydrochloric acid and/or sodium hydroxide. In some embodiments, the nano-filtration system 406 is configured with a reverse osmosis system 408 that is capable of concentrating sodium ions and chloride ions into a salt solution that is used as the anode electrolyte 206.

[0111] With reference to FIGS. 1-3, in some embodiments, the method comprises a step of oxidizing hydrogen gas 108, 220 to hydrogen ions at the anode 100, 204 and migrating the hydrogen ions through the first cation exchange membrane 202 into the anode electrolyte 206. In some embodiments, the method comprises producing hydroxide ions and hydrogen gas at the cathode. In some embodiments, the method comprises directing hydrogen gas from the cathode 208 to the anode 204 and oxidizing the hydrogen at the anode.

[0112] In some embodiments, the method comprises migrating cations ions through the second cation exchange membrane 212 into the cathode electrolyte 210. In some embodiments, the cations are obtained from a salt solution comprising sodium ions. In some embodiments, the method comprises producing an acid, hydrochloric acid or sulfuric acid in the anode electrolyte.

[0113] In some embodiments, the method comprises establishing a temperature of 70° C. to 75° C. in the anode electrolyte. In some embodiments, the method comprises establishing a current density of 150-200 mA/cm² at the cathode.

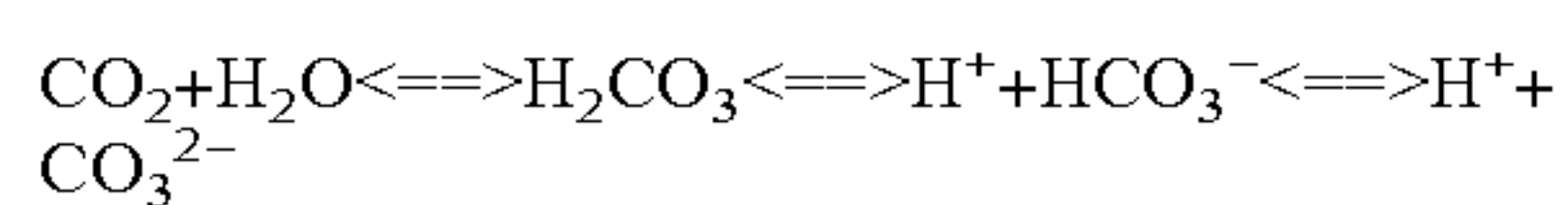
[0114] In some embodiments, the method comprises maintaining a pH of 0 or less in the anode electrolyte, and 14 or more in the cathode electrolyte.

[0115] In some embodiments, the anode and cathode are disposed in an electrochemical cell comprising cell walls comprising a non-corrosive material. In some embodiments, the cell walls comprise a polymer; in some embodiments the cell walls comprise polyvinyl chloride. In some embodiments, the method comprises maintaining a gap of 5 mm or less between the first and second cation exchange membrane.

[0116] With reference to FIGS. 1-3, in some embodiments of the method, carbon dioxide is absorbed into the cathode electrolyte 210 utilizing a gas mixer/gas absorber 216. In one embodiment, 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.

[0117] In some embodiments of the method, 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. In some embodiments, the system includes a gas treatment system that removes constituents in the carbon dioxide gas stream before the gas is utilized in the cathode electrolyte. In some embodiments, a portion of, or the entire amount of, cathode electrolyte 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 to increase the absorbed carbon dioxide content in the solution. In some embodiments, the solution enriched with carbon dioxide is returned to the cathode compartment; in other embodiments, the solution enriched with carbon dioxide is reacted with a solution comprising divalent cations to produce divalent cation hydroxides, carbonates and/or bicarbonates. In some embodiments, the pH of the cathode electrolyte 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, the pH of the cathode electrolyte is determined, at least in part, by the balance of these two processes.

[0118] With reference to FIG. 4 depending on the pH of the cathode electrolyte, carbon dioxide gas introduced into the cathode electrolyte 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:



Thus, in some embodiments, the cathode electrolyte may comprise dissolved and un-dissolved carbon dioxide gas, and/or carbonic acid, and/or bicarbonate ions and/or carbonate ions.

[0119] In embodiments wherein it is desired to produce bicarbonate and/or carbonate ions in the cathode electrolyte, the system as illustrated in FIGS. 2, 3 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 first cathode electrolyte by dissolving carbon dioxide in the first 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.

[0120] 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. 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.

[0121] 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.

[0122] 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.

[0123] In some embodiments, the cathode and anode are also operatively connected to an off-peak electrical power-supply system 114 that supplies off-peak voltage to the electrodes. 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.

[0124] In some embodiments, depending on the ionic species desired in cathode electrolyte and/or the anode electrolyte, 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, then a potassium salt such as potassium chloride can be utilized in the anode electrolyte. Similarly, if sulfuric acid is desired in the anode electrolyte, then a sulfate such as sodium sulfate can be utilized.

[0125] In an alternative embodiment, the present system and method are integrated with a carbonate and/or bicarbonate solution disposal system wherein, rather than producing precipitates by contacting a solution of divalent cations with the cathode electrolyte solution to form precipitates as illus-

trated in FIG. 4, the system produces a solution or a slurry or a suspension comprising carbonates and/or bicarbonates. In some embodiments, the solution, slurry or suspension is disposed of in a location where it is held stable for an extended periods of time, e.g., the solution/slurry/suspension is disposed in an ocean at a depth where the temperature and pressure are sufficient to keep the slurry stable indefinitely, or in a subterranean site as described in U.S. patent application Ser. No. 12/344,019 filed on Dec. 24, 2008, herein incorporated by reference in its entirety.

1. An electrochemical system comprising:
 - a first cation exchange membrane in contact with a gas diffusion anode and configured to separate the gas diffusion anode from an anode electrolyte;
 - a cathode in contact with a cathode electrolyte; and
 - a second cation ion exchange membrane configured to separate the cathode electrolyte from the anode electrolyte.
2. The electrochemical system of claim 1, comprising an external pressure system configured to apply a pressure on the anode electrolyte and the first cation exchange membrane.
3. (canceled)
4. (canceled)
5. The electrochemical system of claim 2, wherein the cathode electrolyte comprises added carbon dioxide.
6. (canceled)
7. The electrochemical system of claim 5, wherein the gas diffusion anode comprises a substrate comprising a catalyst configured to catalyze oxidization of hydrogen gas to protons.
8. The electrochemical system of claim 7, wherein the substrate comprises a first side in contact with the hydrogen and an opposed second side in contact with the first cation exchange membrane.
9. (canceled)
10. (canceled)
11. (canceled)
12. (canceled)
13. (canceled)
14. (canceled)
15. (canceled)
16. The electrochemical system of claim 8, wherein first cation exchange membrane is configured to migrate protons from the substrate into the anode electrolyte on application of a voltage across the substrate and the cathode.
17. The electrochemical system of claim 16, wherein the system is configured to produce hydrogen gas and hydroxyl ions at the cathode on applying a voltage across the substrate and cathode.
18. The electrochemical system of claim 17, wherein the system is configured to migrate cations from the anode electrolyte into the cathode electrolyte through the second cation exchange membrane.
19. (canceled)
20. The electrochemical system of claim 18, wherein the system is configured to migrate hydroxide ions from the cathode into the cathode electrolyte.
21. The electrochemical system of claim 20, wherein the cathode electrolyte comprises carbonate ions and/or bicarbonate ions.
22. (canceled)
23. (canceled)
24. The electrochemical system of claim 21, further comprising a hydrogen delivery system configured to direct hydrogen gas to the anode from the cathode.

25. (canceled)

26. The electrochemical system of claim 24, operatively connected to a waste gas system and configured to dissolve carbon dioxide from the waste gas and into the cathode electrolyte.

27. The electrochemical system of claim 26, configured to produce a carbonate or bicarbonate by mixing the cathode electrolyte with a divalent cation solution comprising calcium or magnesium ions.

28. (canceled)

29. The electrochemical system of claim 27, configured to dissolve a mineral with the anode electrolyte to produce the divalent cation solution.

30. An electrochemical method comprising:

separating a gas diffusion anode from an anode electrolyte using a first cation exchange membrane in contact with the gas diffusion anode;

separating the anode electrolyte from a cathode electrolyte contacting a cathode using a second cation exchange membrane;

applying an external hydrostatic pressure on the anode electrolyte;

producing an alkaline solution in the cathode electrolyte without producing a gas at the anode by applying a voltage across the gas diffusion anode and cathode.

31. (canceled)

32. The electrochemical method of claim 30, comprising adding carbon dioxide to the cathode electrolyte.

33. The electrochemical method of claim 32, comprising oxidizing hydrogen gas to protons at the gas diffusion anode and migrating protons from the gas diffusion anode through the first cation exchange membrane into the anode electrolyte.

34. (canceled)

35. (canceled)

36. The electrochemical method of claim 33, comprising migrating sodium or potassium ions from the anode electrolyte into the cathode electrolyte through the second cation exchange membrane.

37. (canceled)

38. The electrochemical method of claim 36, comprising producing hydroxyl ions and hydrogen gas at the cathode, migrating hydroxyl ions from the cathode into the cathode electrolyte and directing hydrogen gas from the cathode to the gas diffusion anode.

39. (canceled)

40. (canceled)

41. (canceled)

42. The electrochemical method of claim 38, comprising contacting the substrate at a first side with hydrogen and contacting the substrate at an opposed second side with the first cation exchange membrane.

43. (canceled)

44. (canceled)

45. (canceled)

46. (canceled)

47. (canceled)

48. (canceled)

49. (canceled)

50. The electrochemical method of claim 42, wherein the system is configured to migrate cations from the anode electrolyte into the cathode electrolyte through the second cation exchange membrane.

51. (canceled)

52. The electrochemical method of claim **50**, wherein the cathode electrolyte comprises carbonate ions and/or bicarbonate ions.

53. (canceled)

54. (canceled)

55. (canceled)

56. The electrochemical method of claim **52**, wherein carbon dioxide in ambient air is excluded from the cathode electrolyte.

57. (canceled)

58. The electrochemical method of claim **56**, comprising contacting the cathode electrolyte with a divalent cation solution comprising magnesium ions or calcium ions to produce a carbonate or bicarbonate.

59. (canceled)

60. The electrochemical method of claim **58**, comprising dissolving a mineral with the anode electrolyte to produce the divalent cation solution.

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