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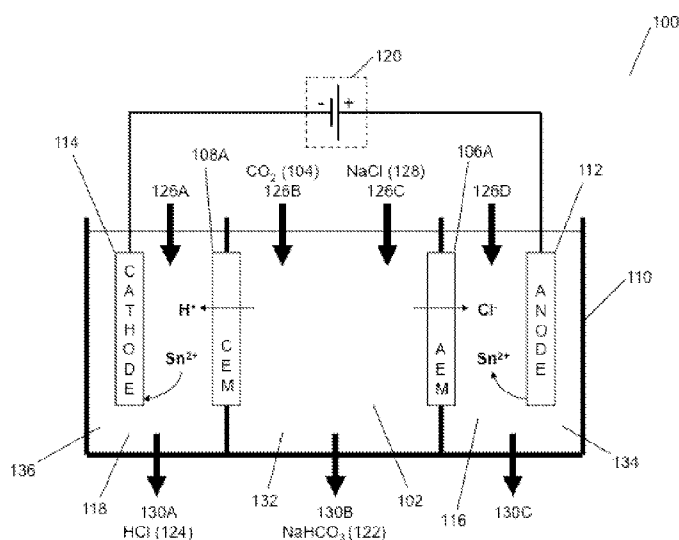


Fig. 1

(57) Abstract: A low-energy electrochemical method and system of forming bicarbonate ion solutions in an electrochemical cell utilizing carbon dioxide in contact with an electrolyte contained between two ion exchange membranes in an electrochemical cell. On applying a low voltage across an anode and cathode in electrical contact with the ion exchange membranes, bicarbonate ions form in the electrolyte without forming a gas, e.g., chlorine or oxygen at the electrodes.

LOW-ENERGY ELECTROCHEMICAL BICARBONATE ION SOLUTION

BACKGROUND

[0001] Bicarbonate ion solutions are used to regulate or achieve a chemical reaction or buffer the pH of a solution. Conventionally, bicarbonate ion solutions are obtained by dissolving bicarbonate salts, e.g., sodium bicarbonate, in water. However, producing bicarbonate salts conventionally is energy intensive and, consequently, bicarbonate ion solutions are expensive.

SUMMARY

[0002] This invention pertains to a low energy system and method of producing bicarbonate ions utilizing an electrolyte and carbon dioxide in an electrochemical cell. In one embodiment, the system comprises an anode, a cathode and an electrolyte contained between ion exchange membranes in an electrochemical cell. On applying a voltage across the anode and cathode while contacting the electrolyte with carbon dioxide, the system is capable of forming bicarbonate ions in the electrolyte without forming a gas at the electrodes, e.g., without forming hydrogen at the cathode or chlorine at the anode. The system is also capable of forming an acid, e.g., hydrochloric acid in another electrolyte in contact with an ion exchange membrane; and, in various embodiments, ions of the anode can be recovered at the cathode by reusing the anode electrolyte at the cathode.

[0003] In another embodiment, the system comprising an anode, a cathode and an electrolyte contained between ion exchange membranes, is capable of forming bicarbonate ions in the electrolyte on applying a voltage of, e.g., less than 0.05 V

across the anode and cathode while contacting the electrolyte with carbon dioxide. The system is also capable of forming an acid, e.g., hydrochloric acid in another electrolyte in contact with an ion exchange membrane; and, in various embodiments, ions of the anode can be recovered at the cathode by reusing the anode electrolyte at the cathode.

[0004] In one embodiment, the method comprises applying a voltage across an anode and a cathode in an electrochemical cell containing an electrolyte comprising carbon dioxide and contained between ion exchange membranes, to form bicarbonate ions in the electrolyte without forming a gas at the electrodes, e.g., without forming chlorine at the anode or hydrogen at the cathode. The method is also capable of forming an acid, e.g., hydrochloric acid in another electrolyte in contact with an ion exchange membrane; and, in various embodiments, ions of the anode can be recovered at the cathode by reusing the anode electrolyte at the cathode.

[0005] In another embodiment, the method comprises forming bicarbonate ions in an electrolyte contained between ion exchange membranes in an electrochemical cell by applying a voltage of less than 2.0 V, less than 1.5 V, less than 1.0 V, less than 0.5 V, less than 0.1 V or less than 0.05 V across the anode and cathode while contacting the electrolyte with carbon dioxide. The system is also capable of forming an acid, e.g., hydrochloric acid in another electrolyte in contact with an ion exchange membrane; and, in various embodiments, ions of the anode can be recovered at the cathode by reusing the anode electrolyte at the cathode.

[0006] With the present system and method, carbon dioxide from any convenient source can be used to contact the electrolyte between the ion exchange membranes. Such sources include carbon dioxide dissolved in a liquid, carbon dioxide in solid form, e.g., dry ice, or gaseous carbon dioxide. In particular embodiments, carbon dioxide in combustion gases of an industrial plant, e.g., the stack gases of fossil fuel power-generating plants or cement plants can be used.

[0007] In various embodiments, the present system and method are adaptable for batch, semi-batch or continuous flows of electrolytes, bicarbonate ions, carbon dioxide and acid in the electrochemical cell. In various embodiments, the solution comprising bicarbonates ions can be used to sequester carbon dioxide by contacting the bicarbonate ion solution with an alkaline earth metal ion solution in the presence of carbon dioxide to precipitate carbonates, e.g., to precipitate calcium and magnesium carbonates from saltwater as described in United States Patent Application Serial No. 12/126,776, filed on May 23, 2008, herein incorporated by reference. The precipitated carbonates, in various embodiments, can be used as building products, e.g., cements and other building products as described in the United States Patent Applications incorporated herein by reference.

[0008] In another embodiment, the system and method can be used to precipitate carbonates from saltwater to produce desalinated water as described in United States Patent Application Serial No. 12/163,205, filed on June 27, 2008, herein incorporated by reference. In various embodiments, the acids produced by the present method can be used to dissolve alkaline earth metal minerals to obtain

alkaline earth metal cations for use in sequestering carbon dioxide as described in the United States patent applications incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

The following figures illustrate by way of examples and not by limitation various embodiments of the present system and method:

- [0009] Fig. 1 illustrates an embodiment of the present system.
- [0010] Fig. 2 illustrates an embodiment of the present system.
- [0011] Fig. 3 illustrates an embodiment of the present system.
- [0012] Fig. 4 illustrates an embodiment of the present system.
- [0013] Fig. 5 is a flow chart of an embodiment of the present method.
- [0014] Fig. 6 is a flow chart of an embodiment of the present method.

DETAILED DESCRIPTION

[0015] In the following detailed description of exemplary embodiments of the system and method where a range of values is specified, each intervening value in the range is encompassed by the invention. Thus, values between the upper and lower limit of the range and any other stated and intervening value in the range are included unless the context clearly dictates otherwise. Also, upper and lower limits of smaller ranges are included in smaller ranges and are encompassed within the scope of the invention, subject to any specifically excluded limit in the stated range.

[0016] Herein, numerical values may be preceded by the term "about." The term "about" is used to provide literal support for the exact number that it precedes, and /or as a number that is near to or approximately the number that it precedes. In

determining whether a number is near to or approximately a specifically recited number, the near and/or approximating unrecited number may be a number that, in the context in which it is presented, provides the substantial equivalent of a specifically recited number.

[0017] Herein, unless otherwise specified, all technical and scientific terms have the same meaning as understood by one of ordinary skill in the art to which this invention pertains. Publications and patents incorporated by reference herein are fully incorporated to disclose their contents as disclosed. A publication, when cited, is cited for its disclosure on its publication date and is not an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. The date of a cited publication may differ from the actual publication date and may need independent confirmation.

[0018] Herein, the singular forms “a,” “an,” and “the” encompass plural forms unless the context clearly dictates otherwise. As will be apparent to one ordinarily skilled in the art, each of the embodiments described and illustrated herein comprises discrete elements that may be separated from, or combined with, other elements without departing from the scope of the claims, e.g., a recited method may be performed in the order of events recited or in another logical order without departing from the scope of the claims.

[0019] Herein, the invention in various embodiments is described for convenience in terms of producing sodium bicarbonate ions, and optionally, hydrochloric acid. However, it will be appreciated by one ordinarily skilled in the art that the present system and method may produce other bicarbonate ions such as,

e.g., potassium and calcium bicarbonate ions and other acids such as sulfuric acid, depending on the electrolytes used.

[0020] In various embodiments, the present invention is directed to a low voltage system and method of forming bicarbonate ions by contacting carbon dioxide with an electrolyte salt solution positioned between ion exchange membranes in an electrochemical cell. In one embodiment, on applying a low voltage across a cathode and anode in the cell, bicarbonate ions form in the solution without forming a gas at the electrodes, e.g., without forming chlorine at the anode or hydrogen at the cathode. By the present system and method, bicarbonate ions are formed in the solution on applying a voltage across the anode and cathode of less than 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V, and other low voltages as disclosed herein. In various embodiments, an acid solution is also formed in another electrolyte in contact with an ion exchange membrane, e.g., hydrochloric acid, in the electrochemical cell. Optionally, in some embodiments, the electrolyte in contact with the anode is reused as the electrolyte at the cathode to recover anode material at the cathode.

[0021] Referring to Fig.1, in one embodiment system 100 comprises first electrolyte 102 and carbon dioxide 104 contained between anion exchange membrane 106A and cation exchange membrane 108A in an electrochemical cell 110. Electrochemical cell 100 includes anode 112 and cathode 114; second electrolyte 116 contacting anion exchange membrane 106A and anode 112; and third electrolyte 118 contacting cation exchange 108A membrane and cathode 114.

On applying a voltage across the anode and cathode, the system is capable of forming bicarbonate ions 122 in first electrolyte 102 without forming a gas, e.g., hydrogen at cathode 114 or chlorine at anode 112. In various embodiments the system is capable of forming bicarbonate ions in first electrolyte 102 when a voltage of 0.2 V or less, 0.3 V or less, 0.4 V or less, 0.5 V or less, 0.6 V or less, 0.7 V or less, or 0.8 V or less is applied across the anode and cathode.

[0022] In various embodiments and with reference to Figs. 1 - 4, the system also capable of forming an acid 124 in third electrolyte solution 118 contacting cation exchange membrane 108A as a result of transfer of protons across cation exchange membrane 108A from first electrolyte 102. For example, as is illustrated in Fig.1, protons transferred from first electrolyte 102 to third electrolyte 118 will result in formation of an acid solution 124 in third electrolyte 118; thus, where third electrolyte contains chloride ions, hydrochloric acid 124 will form in third electrolyte 118.

[0023] Depending on whether a sacrificial anode is used, e.g., tin, copper, iron, zinc, the system in various embodiments is capable of oxidizing the anode to form cations in the electrolyte in contact with the anode e.g., tin ions, in second electrolyte 116. Hence, as is illustrated in Fig. 1, in various embodiments the system is capable of forming a chloride solution in second electrolyte 116 contacting the anode, e.g., where a tin anode is used and tin ions are present in the second electrolyte 116, stannous chloride will form in second electrolyte 116 as a result of transfer of chloride ions across anion exchange membrane 106A from first electrolyte 102. Similarly, as illustrated in Figs. 2 - 4, where a tin anode is used,

stannous chloride solution will form in electrolyte 116 a result of ions migrating to or from second electrolyte 116 across the ion exchange membrane in contact with second electrolyte 116 as discussed below. In various embodiments, optionally, the electrolyte solution 116 in contact with anode 112 comprising anode ions can be reused as electrolyte 118 in contact with cathode 114 to recover anode material at the cathode. As will be appreciated by one ordinarily skilled in the art, tin and other sacrificial metal can thus be recovered at the cathode, depending on the material used as the sacrificial anode.

[0024] With reference to Figs. 1 - 4, in various embodiments, system 100, system 200, system 300 and system 400 comprise inlet ports 126 A-E (where needed) for introducing substances in to the cell, e.g., for introducing fluids, gases, salts and the like into cells 110, 202, 302, 402; and outlet ports 130A-E (where needed) for removing fluids from the cells. For example, with reference to Fig. 1, system 100 comprises inlet port 126B for introducing carbon dioxide 104 into first electrolyte 102, and inlet port 126C for introducing sodium chloride solution 128 into first electrolyte 102. Similarly, system 100 of Fig.1 comprises outlet ports 130A for removing acid 124 from third compartment 136, and outlet port 130B for removing bicarbonate ion solution from first compartment 132. As will be appreciated by one ordinarily skilled in the art, the inlet and outlet ports are adaptable for various flow protocols including batch flow, semi-batch flow, or continuous flow. In various embodiments, the system includes voltage regulator 120 for regulating voltages across the electrodes and currents through the electrolytes.

[0025] In an embodiment illustrated in Fig. 1, electrochemical cell 110 comprises first compartment 132, second compartment 134 and third compartment 136 formed by positioning anion exchange membrane 106A and cation exchange membrane 108A in cell 110 such that first electrolyte 102 is separated from second electrolyte 116 and third electrolyte 118. As will be appreciated in the art, the ion exchange membranes are positioned to contact the electrolytes on opposite surfaces such that ions from one electrolyte will migrate to another electrolyte through the ion exchange membrane without mixing of the electrolytes.

[0026] In various embodiments as illustrated in Figs.1 - 4, the system, depending on its configuration, is initially charged (where appropriate) with first electrolyte 102, second electrolyte 116, third electrolyte 118, fourth electrolyte 206 and fifth electrolyte 404 comprising an aqueous salt solution such as a saltwater, e.g., seawater, brine, brackish water, sodium chloride, conductive fresh water and the like. In an embodiment that produced the results as set forth in Table 1, the system was initially charged with first electrolyte 102 and fifth electrolyte 404 comprising 2 M sodium chloride solution; in another embodiment the system was initially charged with first electrolyte 102 and fifth electrolyte 404 comprising 0.5 M sodium chloride solution. In other specific embodiments the system can be charged initially with a salt solution, e.g., sodium chloride, at a concentration from 0.1 to 4 M, e.g., 0.1 to 2.5 M, or 0.2 to 2.0 M, or 0.1 to 1.0 M, or 0.2 to 1.0 M, or 0.2 to 0.8 M, or 0.3 to 0.7 M, or 0.4 to 0.6 M, or 0.5 to 2.5 M, or 1.0 to 2.5 M, or 1.5 to 2.5 M, or 1.7 to 2.3 M.

[0027] With reference to Figs.1 - 4, anion exchange membranes 106A, 106B and cation exchange membranes 108A, 108B comprise ionic membranes

selectively permeable to one ion or one class of ions, e.g., cation membranes selectively permeable to sodium ions only or hydrogen ions only, or to cations generally; or anion membranes selectively permeable to chloride ions only or to anions generally, can be used. In various embodiments, anion exchange membranes 106A, 106B and cation exchange membranes 108A, 108B may comprise membranes that will function in an acid and/or basic electrolytic at pH from 1 to 14; also, the membranes may be selected to function with electrolytes wherein the temperatures ranges from about 0 °C to 100 °C or higher. Such ion exchange membranes are commercially available, e.g., PCA GmbH of Germany supplies a suitable anion exchange membrane permeable to chloride ions and identified as PCSA-250-250; and a cation exchange membrane permeable to sodium ions and identified as PCSK 250-250.

[0028] With reference to Figs. 1 - 4, in various embodiments anode 112 comprises a sacrificial anode, e.g., tin, copper, iron, zinc. Where a sacrificial anode such as tin is used, cations such as Sn^{2+} will form in second electrolyte 116 in contact with anode 112. Optionally, as will be appreciated by one ordinarily skilled in the art, cations in electrolyte 116 in contact with anode 112 can be recovered by plating out the cations at the cathode 114, e.g., using electrolyte 116 from the anode as the electrolyte at the cathode. Thus, the anode material can be recovered at the cathode by switching electrolyte 116 in contact anode 112 with the electrolyte in contact with the cathode 114 when a sufficient concentration of Sn^{2+} has accumulated in the electrolyte 116, and allowing the cations to plate out at the cathode. It will also be appreciated that when sacrificial anode 112 is diminished

and cathode 114 is augmented sufficiently, these electrodes may be switched so that anode 112 is transferred to replace cathode 114 and vice versa.

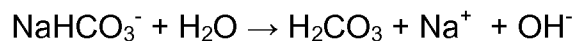
[0029] As is illustrated in Figs. 1 - 4, the voltage across anode 112 and cathode 114 can be regulated to form bicarbonate ions 122 in first electrolyte 102 without forming a gas, e.g., chlorine at anode 112 or hydrogen at cathode 114. In various embodiments, bicarbonate ions 122 are formed when the voltage applied across anode 112 and cathode 114 is less than 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.8 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when

the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0030] In various embodiments as illustrated in Figs. 1 - 4, a protonated solution, e.g., hydrochloric acid 124 is formed in third electrolyte 118. For example, with reference to Fig. 1, on transfer of protons from first electrolyte 102 to third electrolyte 118 through cation exchange membrane 108A, the pH of the third electrolyte 118 will adjust, e.g., become more acid if protons accumulate in the electrolyte. The acid formed will depend on the electrolytes used, e.g., as illustrated in Fig. 1, where third electrolyte 118 comprises chloride ions, hydrochloric acid will form in third electrolyte 118. With the accumulation of protons in third electrolyte 118, the pH of this electrolyte will decrease; it will be appreciated, however, that the pH of third electrolyte may increase, decrease or remain constant depending on the rate of removal of third electrolyte from the system.

[0031] Also as will be appreciated by one skilled in the art and as is illustrated, e.g., in Fig. 1, where first electrolyte 102 initially comprises sodium chloride solution 128, sodium bicarbonate 122 will form in first electrolyte 102 as a consequence of the migration of protons and chloride ions from first electrolyte 102. Further, as sodium bicarbonate is an amphoteric salt that forms a mildly alkaline solution in water, with the formation of sodium bicarbonate in first electrolyte 102 the pH of the first electrolyte will increase (assuming that first electrolyte 102 is not removed from the system) due to formation of hydroxyl ions (OH^-) in accordance with the following

reaction:

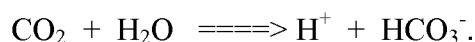


[0032] In various embodiments of the invention as illustrated in Figs. 1 - 6, carbon dioxide 104 from any convenient source can be used. Such sources include carbon dioxide dissolved in a liquid, solid carbon dioxide, e.g., dry ice, or gaseous carbon dioxide. In various embodiments, carbon dioxide in post-combustion effluent stacks of industrial plants such as power plants, cement plants and coal processing plants can be used. In various embodiments carbon dioxide 104 may comprise substantially pure carbon dioxide or a multi-component gaseous stream comprising carbon dioxide and one or more additional gases. Additional gases and other components may include CO, SO_x (e.g., SO₂), NO_x, mercury and other heavy metals and dust particles e.g., from calcining and combustion processes. In various embodiments, one or more of these additional components can be precipitated by contacting first electrolyte 102 with a solution of alkaline earth metal ions, e.g., where SO₂ is contained in the gas stream, sulfates and sulfides of calcium and magnesium can be precipitated.

[0033] Multi-component gaseous streams include reducing condition streams, e.g., syngas, shifted syngas, natural gas, and hydrogen and the like, and oxidizing condition streams, e.g., flue gases from combustion. Such gaseous streams include oxygen-containing flue gas, e.g., from a coal fired power plant, a cement plant, or a natural gas power plant; turbo charged boiler product gas; coal gasification product gas; shifted coal gasification product gas; anaerobic digester product gas; wellhead natural gas; reformed natural gas or methane hydrates; and the like. In various

embodiments, gases that are not absorbed in first electrolyte 102, e.g., nitrogen, in one embodiment are vented from the system; in other embodiments, the gases are collected for other uses.

[0034] As will be appreciated by one skilled in the art and with reference to Figs. 1 - 6, without being bound by any theory it is believed that bicarbonate ions (HCO_3^-) form in first electrolyte 102 as a result of carbon dioxide contacting water in the first electrolyte 102, as follows:



Thus, in accordance with the present invention and with reference to Fig. 1, where first electrolyte 102 comprise Na^+ and Cl^- ions from added sodium chloride 128, by placing first electrolyte 102 between cation exchange membrane 108A selective to transferring H^+ ions, and an anion exchange membrane 106A selective to transferring of Cl^- ions, and applying a voltage across the electrodes, H^+ will migrate through the cation exchange membrane 108A to adjacent third electrolyte 118. Similarly, Cl^- will migrate from first electrolyte 102 through the anion exchange membrane 106A to adjacent second electrolyte 116. Consequently, in first electrolyte 102, a solution comprising sodium bicarbonate will form. Depending on the rate of introduction and/or removal of first electrolyte from the system and the voltage applied across electrodes 112, 114, the concentration of bicarbonate ions in first electrolyte 102 will adjust, e.g., increase, decrease or will not change.

[0035] Also, with reference to Fig. 1, as H^+ migrate from first electrolyte 102 through cation exchange membrane 108A to adjacent electrolyte 118, the pH of adjacent third electrolyte 118 will adjust depending on rate of introduction and/or

removal of first electrolyte 102 from the system. Similarly, as chloride ions migrate from the first electrolyte to adjacent second electrolyte 114 across the anion exchange membrane 106A, the chloride in second electrolyte 114 will adjust, e.g., increase, decrease or does not change. Hence, as illustrated in Figs. 1 - 6, in various embodiments of the system and method, a solution of bicarbonate ions 122, e.g., sodium bicarbonate, is obtained in first electrolyte 102, an acid solution 124, e.g., hydrochloric acid, is obtained in third electrolyte 118, and a chloride solution is obtained in second electrolyte 116.

[0036] In an embodiment of system 200 as illustrated in Fig. 2, first electrolyte 102 and carbon dioxide 104 are contained between first anion exchange membrane 106A and first cation exchange membrane 108A in an electrochemical cell 202 comprising anode 112 and cathode 114. In the system, second electrolyte 116 contacts first anion exchange membrane 106A and anode 112; third electrolyte 118 is contained between first cation exchange membrane 108A and second anion exchange membrane 106B; and fourth electrolyte 206 contacts second anion exchange membrane 106B and cathode 114, wherein on applying a voltage 130 across cathode 114 and anode 112, the system forms bicarbonate ions 122 in first electrolyte 102 without forming a gas at the cathode or anode. In various embodiments, the system forms bicarbonate ions in first electrolyte 102 when a voltage of 0.4 V or less, or 0.6 V or less, or 0.8 V or less is applied across the anode and cathode. In various embodiments, bicarbonate ions 122 are formed when the voltage applied across anode 112 and cathode 114 is less than 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8,

0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.8 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0037] System 200 in various embodiments will form an acid, e.g., hydrochloric acid 124, depending on the electrolytes used. As is illustrated in Fig. 2, the system will form a protonated solution (acid solution) in third electrolyte 118, e.g.,

hydrochloric acid as a result of transfer of protons across cation exchange membrane 108A from first electrolyte 102; and an ionic solution, e.g., stannous chloride will form in second electrolyte 116 as a result of chloride ions transferring across anion exchange membrane 106 from first electrolyte 102, assuming tin ions are present in the second electrolyte 116 from oxidation of anode 112 comprising tin. In various embodiments, optionally, electrolyte 116 in contact with anode 112 is reused as electrolyte 118 in contact with cathode 114 to recover anodic metal that may have oxidized into second electrolyte 116 at anode 112. Likewise, electrolyte 206 in contact with cathode 114 may be reused as electrolyte 116 in contact with anode 112. It will be appreciated that when sacrificial anode 112 is diminished and cathode 114 is augmented sufficiently, these electrodes may be switched so that anode 112 is transferred to replace cathode 114 and vice versa.

[0038] As is illustrated in Fig. 2, system 200 includes inlet ports 126 A-E adapted for introducing materials into cell 202, e.g., for introducing carbon dioxide 104, sodium chloride solution 126 and other electrolytes into cell 202; and outlet ports 130 A-D for removing materials from the cell, e.g., removing bicarbonate solution 122 and acid 124 from the cell. As will be appreciated by one ordinarily skilled in the art, the inlet and outlet ports are adaptable for various flow protocols including batch flow, semi-batch flow, or continuous flow. In various embodiments, the system includes voltage/current regulator 120 for regulating currents and voltages across the anode, cathode and the electrolytes.

[0039] In the system illustrated in Fig. 2, electrochemical cell 202 comprises first compartment 132, second compartment 134, third compartment 136 and fourth

compartment 138 formed by positioning first anion exchange membrane 106A and first cation exchange membrane 108A to separate first electrolyte 102 from second electrolyte 116 and third electrolyte 118, and by positioning second anion exchange membrane 106B to separate third electrolyte 118 from fourth electrolyte 206. As will be appreciated in the art, the ion exchange membranes in various embodiments are positioned to contact the electrolytes at opposite surfaces to allow movement of ions from one electrolyte to another electrolyte through the ion exchange membranes without mixing of the electrolytes.

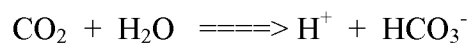
[0040] As with the system of Fig. 1, in the system of Fig. 2, first 102, second 116 third 118 and fourth 206 electrolytes initially may comprise an aqueous salt solution such as a saltwater, e.g., seawater, brine, brackish water, conductive fresh water and the like. In results obtained from one embodiment as set forth in Table 1, first electrolyte 102 initially comprised 2 M sodium chloride solution; in another embodiment first electrolyte 102 comprised 0.5 M sodium chloride solution. In specific embodiments the system may be charged initially with a salt solution, e.g., sodium chloride, at a concentration from 0.1 to 4 M, e.g., 0.1 to 2.5 M, or 0.2 to 2.0 M, or 0.1 to 1.0 M, or 0.2 to 1.0 M, or 0.2 to 0.8 M, or 0.3 to 0.7 M, or 0.4 to 0.6 M, or 0.5 to 2.5 M, or 1.0 to 2.5 M, or 1.5 to 2.5 M, or 1.7 to 2.3 M.

[0041] With reference to Fig. 2, the voltage across anode 112 and cathode 114 can be regulated to form bicarbonate ions 122 in first electrolyte 102 without forming a gas, e.g., chlorine at anode 112 or hydrogen at cathode 114. Similarly, by regulating a voltage across cathode 114 and anode 112 as with the system of Fig. 1, a protonated (acid) solution 124 is formed in third electrolyte 118 in contact with

cation exchange membrane 108A by protons transferred from first electrolyte 102. The acid solution formed will depend on the electrolytes used, e.g., as illustrated in Fig. 2, where the first electrolyte 102 comprises sodium chloride, the acid solution formed will comprise hydrochloric acid. An acid solution is formed, in various embodiments, when the voltage applied across anode 112 and cathode 114 is less than 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.8 V without forming a gas at the electrodes. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a gas at the electrodes. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, an acid solution is formed when the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, an acid

solution is formed when the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0042] In the system of Fig. 2 as with the system of Fig. 1, without being bound by any theory, it is believed that bicarbonate ions are formed in first electrolyte 102 by carbon dioxide contacting water in the first electrolyte, as follows:



Thus, in accordance with the present invention and with reference to Fig. 2, where first electrolyte 102 comprise Na^+ and Cl^- ions from added sodium chloride 128, by placing first electrolyte 102 between cation exchange membrane 108A selective to transferring H^+ ions, and anion exchange membrane 106A selective to transferring of Cl^- ions, and applying a voltage across the electrodes, H^+ will migrate through cation exchange membrane 108A to adjacent third electrolyte 118. Similarly, Cl^- will migrate from the first electrolyte through the anion exchange membrane 106A to adjacent second electrolyte 116. Consequently, in first electrolyte 102, a solution comprising sodium bicarbonate 122 will form. Depending on the rate of introduction and/or removal of first electrolyte from the cell and the voltage applied across electrodes 112, 114, the concentration of sodium bicarbonate 122 in first electrolyte 102 will be adjusted, e.g., increase, decrease or does not change.

[0043] Also with reference to Fig. 2, as H^+ migrate from first electrolyte 102 through cation exchange membrane 108A to adjacent third electrolyte 118, the acidity of adjacent third electrolyte 118 will adjust depending on rate of introduction and/or removal of third electrolyte 118 from the system. Similarly, as chloride ions migrate from fourth electrolyte 206 to adjacent third electrolyte 118 across second

anion exchange membrane 106B the chloride ions concentration in adjacent third electrolytes 118 and fourth electrolyte 206 will adjust.

[0044] Hence, as illustrated in Fig. 2, in various embodiments a solution of bicarbonate ions 122, e.g., sodium bicarbonate is obtained in first electrolyte 102; an acid solution 124, e.g., hydrochloric acid is obtained in third electrolyte 118; a chloride solution, e.g., tin chloride is obtained in second electrolyte 116 where a tin anode is used; and the fourth electrolyte 206 is depleted of chloride ions and cations, e.g., the electrolyte is depleted of Sn^{2+} where the fourth electrolyte was initially charged with a tin salt, e.g., stannous chloride.

[0045] Referring to Fig. 3, system 300 comprises first electrolyte 102 contained between first cation exchange membrane 108A and second cation exchange membrane 108B and to which carbon dioxide 104 is added in an electrochemical cell 302 comprising anode 112 and cathode 114; second electrolyte 116 contacting second cation exchange membrane 108B and anode 112; third electrolyte 118 contained between first cation exchange membrane 108A and anion exchange membrane 106B in electrochemical cell 302; and fourth electrolyte 206 contacting anion exchange membrane 106B and cathode 114, wherein on applying a voltage 120 across the cathode and anode the system is capable of forming bicarbonate ions 122 in first electrolyte 102 without forming a gas at cathode 114 or anode 112.

[0046] In system 300 illustrated in Fig. 3, electrochemical cell 302 comprises first compartment 132, second compartment 134, third compartment 136 and fourth compartment 138 formed by positioning first cation exchange membrane 108A and second cation exchange membrane 108B to separate first electrolyte 102 from

second electrolyte 116 and from third electrolyte 118; and by positioning second anion exchange membrane 106B to separate third electrolyte 118 from fourth electrolyte 206. As will be appreciated, the ion exchange membranes in various embodiments are positioned to contact the electrolytes at opposite surfaces to allow for movement of ions from one electrolyte to another electrolyte through the ion exchange membranes without mixing of the electrolytes.

[0047] As with the system of Figs. 1 and 2, in the system of Fig. 3, first 102, second 116 third 118 and fourth 206 electrolytes may initially comprise an aqueous salt solution, e.g., seawater, brine, brackish water, conductive fresh water and the like. With results achieved in one embodiment as set forth in Table 1, first electrolyte 102 initially comprised 2 M solution of sodium chloride; in another embodiment the first electrolyte 102 initially comprised 0.5 M solution of sodium chloride. In specific embodiments, electrolytes in the system may be charged initially with a salt solution, e.g., sodium chloride, at a concentration from 0.1 to 4 M, e.g., 0.1 to 2.5 M, or 0.2 to 2.0 M, or 0.1 to 1.0 M, or 0.2 to 1.0 M, or 0.2 to 0.8 M, or 0.3 to 0.7 M, or 0.4 to 0.6 M, or 0.5 to 2.5 M, or 1.0 to 2.5 M, or 1.5 to 2.5 M, or 1.7 to 2.3 M.

[0048] With reference to Fig. 3, the voltage across the anode 112 and cathode 114 can be regulated to form bicarbonate ions 122 in the first electrolyte 102 without forming a gas, e.g., chlorine at anode 112 or hydrogen at cathode 114. In various embodiments, bicarbonate ions 122 are formed in first electrolyte 102 when the voltage applied across anode 112 and cathode 114 is less than 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7,

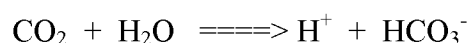
0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V. Similarly, on applying a voltage across the cathode and anode acid solution 124 is formed in third electrolyte 118 in contact with cation exchange membrane 108A as a result of protons transferring from first electrolyte 102. The acid formed depends on the electrolytes used, e.g., as illustrated in Fig. 3, where the first electrolyte 102 comprises sodium chloride, the acid formed comprises hydrochloric acid 124.

[0049] In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.8 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions

and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0050] As is illustrated in Fig. 3, system 300 includes inlet ports 126 A-D adapted for introducing materials into cell 302, e.g., for introducing carbon dioxide 104, sodium chloride solution 126 and other electrolytes into cell 302; and outlet ports 130 A-D for removing materials from the cell, e.g., removing bicarbonate solution 122 and acid 124 from the cell. As will be appreciated by one ordinarily skilled in the art, the inlet and outlet ports are adaptable for various flow protocols including batch flow, semi-batch flow, or continuous flow. In various embodiments, the system includes voltage/current regulator 120 for regulating voltages across the anode and cathode and currents through the electrolytes.

[0051] In the system of Fig. 3, as with the systems of Fig. 1 and 2, without being bound by any theory, it is believed that bicarbonate ions (HCO_3^-) are formed in first electrolyte 102 by carbon dioxide contacting water in the first electrolyte, as follows:



Thus, in accordance with the present invention and with reference to Fig. 3, where second electrolyte 116 comprise Na^+ and Cl^- ions from added sodium chloride 128, by placing first electrolyte 102 between cation exchange membrane 108A selective to transferring H^+ ions, and second cation exchange membrane 108B selective to transferring of cations, e.g., Na^+ ions, and on applying a voltage across the

electrodes, H^+ will migrate through first cation exchange membrane 108A to adjacent third electrolyte 118. Similarly, Na^+ will migrate from second electrolyte 116 through second cation exchange membrane 108B to adjacent first electrolyte 102. Consequently, in first electrolyte 102, a solution comprising sodium bicarbonate 122 will form. Depending on the rate of introduction and/or removal of first electrolyte 102 from the cell and the voltage applied across the electrodes 112, 114, the concentration of sodium bicarbonate in first electrolyte 102 will adjust, e.g., increase, decrease or will not change.

[0052] Also with reference to Fig. 3, as H^+ migrate from first electrolyte 102 through first cation exchange membrane 108A to adjacent third electrolyte 118, the acidity of adjacent third electrolyte 118 will adjust depending on the rate of introduction and/or removal of first electrolyte 102 from the system. Similarly, as chloride ions migrate from fourth electrolyte 206 to adjacent third electrolyte 118 across second anion exchange membrane 106B the chloride ion concentration in adjacent electrolytes 118 and 206 will adjust.

[0053] Hence, as illustrated in Fig. 3, in various embodiments a solution of bicarbonate ions 122, e.g., sodium bicarbonate is obtained in first electrolyte 102; an acid solution 124, e.g., hydrochloric acid is obtained in third electrolyte 118; a chloride solution, e.g., tin chloride is obtained in second electrolyte 116 where a tin anode is used; fourth electrolyte 206 is depleted of chloride ions due to chloride transfer across anion exchange membrane 106B; and fourth electrolyte 204 is also depleted of cations by a reduction reaction at the cathode, e.g., fourth electrolyte

206 is depleted of Sn^{2+} where the fourth electrolyte was initially charged with, e.g., stannous chloride.

[0054] Optionally, as will be appreciated by one ordinarily skilled in the art, cations in electrolyte 116 in contact with anode 112 can be recovered by plating out the cations at the cathode 114, e.g., using electrolyte 116 from the anode as the electrolyte at the cathode. Thus, the anode material can be recovered at the cathode by switching electrolyte 116 in contact anode 112 with the electrolyte in contact with the cathode 114 when a sufficient concentration of Sn^{2+} has accumulated in the electrolyte 116, and allowing the cations to plate out at the cathode. Similarly, it will be appreciated that when sacrificial anode 112 is diminished and cathode 114 is augmented sufficiently, these electrodes may be switched so that anode 112 is transferred to replace cathode 114 and vice versa.

[0055] In an embodiment as illustrated in Fig. 4, system 400 comprises first electrolyte 102 contained between first cation exchange membrane 108A and second cation exchange membrane 108B; second electrolyte 116 contacting anode 112 and separated from fifth electrolyte 404 by first anion exchange membrane 106A; third electrolyte 118 contained between first cation exchange membrane 108A and second anion exchange membrane 106B; fourth electrolyte 206 contacting second anion exchange membrane 106B and cathode 114; and fifth electrolyte 404 comprising an electrolyte containing, e.g., sodium chloride solution 128, and contained between first anion exchange membrane 106A and second cation exchange membrane 108B, wherein on applying a voltage across the cathode 114 and anode 112 and adding carbon dioxide 104 to first electrolyte 102,

the system is capable of forming bicarbonate ions 122 in first electrolyte 102 without forming a gas at cathode 114 and anode 112.

[0056] Referring to system 400 of Fig. 4, electrochemical cell 402 comprises first compartment 132, second compartment 134, third compartment 136, fourth compartment 138, and fifth compartment 140 formed by positioning first cation exchange membrane 108A and second cation exchange membrane 108B to separate first electrolyte 102 from fifth electrolyte 404 and from third electrolyte 118. In the system, second anion exchange membrane 106B is positioned to separate third electrolyte 118 from fourth electrolyte 206; and first anion exchange membrane 106A is positioned to separate second electrolyte 116 in contact with anode 112 from fifth electrolyte 404 comprising sodium chloride solution 128.

[0057] As is illustrated in Fig. 4, in various embodiments initially sodium chloride 128 is added to fifth compartment 140 and carbon dioxide is added to first electrolyte 102 in compartment 132. As will be appreciated in the art, the ion exchange membranes in various embodiments are positioned to contact the electrolytes at opposite surfaces to allow for transfer of ions from one electrolyte to another electrolyte through the ion exchange membranes without mixing of the electrolytes. In various embodiments system 400 is capable of forming bicarbonate ions in first electrolyte 102 when a voltage of 0.4 V or less, or 0.6 V or less, or 0.8 V or less is applied across the anode 112 and cathode 114.

[0058] In the system of Fig. 4, first electrolyte 102, second electrolyte 116 third electrolyte 118, and fourth electrolyte 206 initially may comprise an aqueous salt solution such as a saltwater, e.g., sodium chloride, stannous chloride, seawater,

brine, brackish water, conductive fresh water and the like. As indicated by the results achieved with one embodiment as set forth in Table 1, initially a 2 M solution of sodium chloride sodium chloride solution 128 was added to fourth compartment 140 to form fifth electrolyte 404; in another embodiment, initially fifth electrolyte 404 comprised 0.5 M solution of sodium chloride. In specific embodiments, the fifth electrolyte 404 may be charged initially with a salt solution, e.g., sodium chloride, at a concentration from 0.1 to 4 M, e.g., 0.1 to 2.5 M, or 0.2 to 2.0 M, or 0.1 to 1.0 M, or 0.2 to 1.0 M, or 0.2 to 0.8 M, or 0.3 to 0.7 M, or 0.4 to 0.6 M, or 0.5 to 2.5 M, or 1.0 to 2.5 M, or 1.5 to 2.5 M, or 1.7 to 2.3 M.

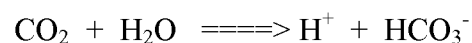
[0059] Referring to Fig. 4, the voltage across anode 112 and cathode 114 can be regulated to form bicarbonate ions 122 in first electrolyte 102 without forming a gas, e.g., chlorine at anode 112 or hydrogen at cathode 114. In various embodiments, bicarbonate ions 122 are formed in first electrolyte 102 where the voltage applied across anode 112 and cathode 114 is less than 2.8, 2.7, 2.6, 2.5, 2.4, 2.3, 2.2, 2.1, 2.0, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 V. Similarly, on applying a voltage across the cathode 114 and anode 112 an acid solution 124 is formed in third electrolyte 118 in contact with first cation exchange membrane 108A as a result of protons transfer through first cation exchange membrane 108A from first electrolyte 102. The acid formed depends on the electrolytes used, e.g., as illustrated in Fig. 4, where first electrolyte 102 comprises sodium chloride, the acid formed in third electrolyte 118 comprises hydrochloric acid. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.8

V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions and the acid solution are formed when the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0060] As is illustrated in Fig. 4, system 400 includes inlet ports 126 A-E adapted for introducing substances into cell 402, e.g., for introducing carbon dioxide 104, sodium chloride solution 128 and other electrolytes into cell 402; and outlet ports

130 A-E for removing substances from the cell, e.g., removing bicarbonate solution 122 and acid 124 from the cell. As will be appreciated by one ordinarily skilled in the art, the inlet and outlet ports are adaptable for various flow protocols including batch flow, semi-batch flow, or continuous flow. In various embodiments, the system includes voltage regulator 120 for regulating voltages across the anode and cathode and current through the electrolytes.

[0061] In system 400 of Fig. 4, as with the systems of Fig. 1, 2 and 3, without being bound by any theory, it is believed that bicarbonate ions (HCO_3^-) are formed in first electrolyte 102 by carbon dioxide contacting water in the first electrolyte 102, as follows:



Thus, in accordance with the present invention and with reference to Fig. 4, where fifth electrolyte 404 comprise Na^+ and Cl^- ions from added sodium chloride 128, by placing first electrolyte 102 between cation exchange membrane 108A selective to transferring H^+ ions, and second cation exchange membrane 108B selective to transferring of cations, e.g., Na^+ ions, and on applying a voltage across the electrodes, H^+ will migrate through first cation exchange membrane 108A to adjacent third electrolyte 118. Similarly, Na^+ will migrate from fifth electrolyte 404 through second cation exchange membrane 108B to first electrolyte 102.

Consequently, in first electrolyte 102, a solution comprising sodium bicarbonate 122 will form. Depending on the rate of introduction and/or removal of first electrolyte from the cell and the voltage applied across the electrodes 112, 114,

the concentration of sodium bicarbonate 122 in first electrolyte 102 will adjust, e.g., increase, decrease or will not change.

[0062] Also with reference to Fig. 4, as H^+ migrate from first electrolyte 102 through first cation exchange membrane 108A to adjacent third electrolyte 118, the acidity of adjacent third electrolyte 118 will adjust depending on the rate of introduction and/or removal of hydrochloric acid 124 from the system. Similarly, as chloride ions migrate from fourth electrolyte 206 to adjacent third electrolyte 118 across second anion exchange membrane 108B, the chloride ion concentration in adjacent electrolytes 118 and 206 will adjust. Additionally, as chloride ions migrate from sodium chloride solution 128 in fifth electrolyte 404 to the second electrolyte 116 across first anion exchange membrane 106A, fifth electrolyte 404 will be depleted of chloride ions; consequently, fifth electrolyte will be depleted of sodium chloride, and correspondingly, the chloride ion content of the second electrolyte 116 will adjust, e.g., increase, decrease or remain constant depending on the flow of second electrolyte 116 from the system.

[0063] Hence, as illustrated in Fig. 4, in various embodiments a solution of bicarbonate ions 122, e.g., sodium bicarbonate is obtained in first electrolyte 102; an acid solution 124, e.g., hydrochloric acid is obtained in third electrolyte 118; a chloride solution, e.g., stannous chloride, is obtained in second electrolyte 116; fourth electrolyte 206 will be depleted of chloride ions; and fifth electrolyte 404 initially comprising sodium chloride solution 128 will be depleted of sodium and chloride ions.

[0064] Optionally, as will be appreciated by one ordinarily skilled in the art, cations in electrolyte 116 in contact with anode 112 can be recovered by plating out the cations at the cathode 114, e.g., using electrolyte 116 from the anode as the electrolyte at the cathode. Thus, the anode material can be recovered at the cathode by switching electrolyte 116 in contact anode 112 with the electrolyte in contact with the cathode 114 when a sufficient concentration of Sn^{2+} has accumulated in the electrolyte 116, and allowing the cations to plate out at the cathode. Similarly, it will be appreciated that when sacrificial anode 112 is diminished and cathode 114 is augmented sufficiently, these electrodes may be switched so that anode 112 is transferred to replace cathode 114 and vice versa.

[0065] In an embodiment as illustrated in Fig. 5 and with reference to Figs. 1 - 4, present method 500 comprises step 502 of applying a voltage 120 across an anode 112 and a cathode 114 through a first electrolyte 102 comprising carbon dioxide 104 to form bicarbonate ions 122 in the first electrolyte without forming a gas at the cathode or the anode. In accordance with the method and with reference to Fig. 1, first electrolyte 102 is contained between first anion exchange membrane 106A and first cation exchange membrane 108A in electrochemical cell 100; the anion exchange membrane contacts the anode 112 through second electrolyte 116; and the cation exchange membrane contacts cathode 112 through third electrolyte 118. In various embodiments, the method forms bicarbonate ions 122 in first electrolyte 102 when a voltage, e.g., 0.4 V or less, or 0.6 V or less, or 0.8 V or less is applied across the anode and cathode. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.8 V

without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0066] As described with reference to the systems of Figs. 1 - 4 above, method 500 forms a protonated solution in third electrolyte 118, e.g., hydrochloric acid 124 as a result of transfer of protons across first cation exchange membrane 108A from first electrolyte 102; and an ionic solution, e.g., stannous chloride in second electrolyte 116, as a result of chloride ions transferring across first anion exchange

membrane 106A from first electrolyte 102, and tin ions forming in second electrolyte 116 by oxidation of anode 112 comprising tin.

[0067] In various embodiments of method 500, optionally, where anode 112 comprises a sacrificial anode, e.g., tin, copper, iron, zinc, cations such as Sn^{2+} will form in second electrolyte 116 in contact with anode 112. Optionally, as described above with reference to Figs. 1 - 4, cations in electrolyte 116 in contact with anode 112 can be recovered by plating out the cations at the cathode 114, e.g., using electrolyte 116 from the anode as the electrolyte at the cathode. Thus, anode material can be recovered at the cathode 114 by switching electrolyte 116 in contact anode 112 with the electrolyte in contact with the cathode 114 when a sufficient concentration of Sn^{2+} has accumulated in the electrolyte 116, and allowing the cations to plate out at the cathode.

[0068] In another embodiment and with reference to Figs. 1 - 4, method 600 comprises step 602 of applying a voltage 120 of less than 2.0 V, less than 1.5 V, less than 1.0 V, less than 0.5 V, less than 0.1 V or less than 0.05 V across an anode 112 and a cathode 114 through first electrolyte 102 comprising carbon dioxide 104 to form bicarbonate ions 122 in the first electrolyte. In various embodiments the method forms bicarbonate ions in first electrolyte when a voltage, e.g., 0.4 V or less, or 0.6 V or less, or 0.8 V or less is applied across the anode and cathode. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.8 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a

gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0069] In accordance with method 600, and with reference to Fig. 1, first electrolyte 102 is contained between first anion exchange membrane 106A and first cation exchange membrane 108A in electrochemical cell 302; first anion exchange membrane 106A contacts anode 112 through second electrolyte 116; and first cation exchange membrane 108A contacts the cathode through third electrolyte 118. In another embodiment of method 600, and with reference to Fig. 3, first electrolyte 102 is contained between first cation exchange membrane 108A and second cation exchange membrane 108B in electrochemical cell 303; second

cation exchange membrane 108B contacts anode 112 through second electrolyte 116; first cation exchange membrane 108A separates first electrolyte 102 from third electrolyte 118; second anion exchange membrane 106B separates third electrolyte 118 from fourth electrolyte 206; and fourth electrolyte 206 is in contact with cathode 114. In various embodiments, method 600 forms bicarbonate ions 122 in first electrolyte when a voltage, e.g., 0.4 V or less, or 0.6 V or less, or 0.8 V or less is applied across the anode and cathode.

[0070] As disclosed with reference to the system of Figs. 1 - 4 above, method 600 forms an acid, e.g., hydrochloric acid 124, depending on the electrolytes used. As is illustrated in Fig.1, the method forms a protonated solution in third electrolyte 118, e.g., hydrochloric acid as a result of transfer of protons across first cation exchange membrane 108A from first electrolyte 102; and an ionic solution, e.g., stannous chloride in second electrolyte 116, as a result of chlorine ions transferring across first anion exchange membrane 106A from first electrolyte 102, and tin ions forming by oxidation of the anode 112.

[0071] In various embodiments of method 600, optionally, where anode 112 comprises a sacrificial anode, e.g., tin, copper, iron, zinc, cations such as Sn^{2+} will form in second electrolyte 116 in contact with anode 112. Optionally, as described above with reference to Figs. 1 - 4, cations in electrolyte 116 in contact with anode 112 can be recovered by plating out the cations at the cathode 114, e.g., using electrolyte 116 from the anode as the electrolyte at the cathode. Thus, anode material can be recovered at the cathode 114 by switching electrolyte 116 in contact anode 112 with the electrolyte in contact with the cathode 114 when a

sufficient concentration of Sn^{2+} has accumulated in the electrolyte 116, and allowing the cations to plate out at the cathode. Similarly, it will be appreciated that when sacrificial anode 112 is diminished and cathode 114 is augmented sufficiently, these electrodes may be switched so that anode 112 is transferred to replace cathode 114 and vice versa.

[0072] Exemplary results achieved in one embodiment of the present system and method are set forth in Table 1.

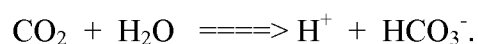
TABLE 1. LOW ENERGY ELECTROCHEMICAL BICARBONATE ION SOLUTIONS

Voltage across Anode and Cathode (V)		pH of electrolyte solution in Compartment 136	pH of Bicarbonate ion solution in Compartment 132
0.4	Initial pH	6.163	4.229
	Final pH	4.367	5.950
0.6	Initial pH	5.846	4.447
	Final pH	4.408	5.824
0.8	Initial pH	8.502	4.306
	Final pH	4.353	6.642

[0073] In this example, based on system 100 of Fig. 1 and method 500 of Fig. 5 and method 600 of Fig. 6, first electrolyte 102, contained in compartment 132, was charged with a 2 M sodium chloride solution 128 to which carbon dioxide gas 104 was added. Third electrolyte 118 comprising saltwater, e.g., stannous chloride was contained in compartment 136. First anion exchange membrane 106A separated

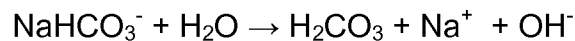
first electrolyte 102 from second electrolyte 116; first cation exchange membrane 108A separated first electrolyte 102 from third electrolyte 118; anode 112 formed of tin foil were placed in contact with second electrolyte 116, and cathode 114 formed of tin foil was placed in contact with third electrolyte 118. Voltages of 0.4 V, 0.6 V and 0.8 V were applied across anode 112 and cathode 114 in a batch mode operation for one hour. As set forth in Table 1, the pH of first electrolyte 102 in compartment 132 increased (correlating to an increase of hydroxide ion concentration in first electrolyte 102 as described above), while the pH of third electrolyte 118 in compartment 136 decreased (correlating to an increase in protons in third electrolyte 118 as described above), without the formation of a gas, e.g., chlorine at anode 112 or hydrogen at cathode 114.

[0074] As discussed above with reference to Figs. 1 - 4, without being bound by any theory it is believed that in first electrolyte 102 bicarbonate ions formed as a result of carbon dioxide contacting water in first electrolyte 102, as follows:



In first electrolyte 102, Na^+ and Cl^- ions are present from the sodium chloride 128. Thus, in accordance with the present invention, by placing first electrolyte 102 between first cation exchange membrane 108A selective to transferring H^+ ions, and first anion exchange membrane 106A selective to transferring of Cl^- ions, and on applying a voltage across the electrodes, H^+ migrated through cation exchange membrane 108A to adjacent third electrolyte 118. Similarly, Cl^- migrated from first electrolyte 102 through anion 106A exchange membrane to adjacent second electrolyte 116. Consequently, a solution comprising sodium bicarbonate 122

formed in first electrolyte 102. With the formation of sodium bicarbonate in first electrolyte 102 the pH of the first electrolyte increased in accordance with the following reaction:



As discussed with reference to Figs. 1 - 4, as H^+ migrated from the first electrolyte 102 through first cation exchange membrane 108A to adjacent third electrolyte 118 in third compartment 136, the acidity of adjacent third electrolyte 118 increased as indicated by the decrease in pH in third compartment 136 as set forth in Table 1.

[0075] As will be appreciated by one ordinary skilled in the art, the voltages may be adjusted up or down from these exemplary voltages; a minimum theoretical voltages 0 V or very close to 0 V, but to achieve a useful rate of production of bicarbonate ions, a practical lower limit may be in some embodiments 0.001 V or 0.01 V, or 0.1 V, depending on the desired time for bicarbonate ion production and/or pH adjustment, volume of first electrolyte solution 102, and other factors apparent to those of ordinary skill; e.g., in some embodiments system 100, system 200, system 300 and system 400 and method 500 and method 600 are capable of producing bicarbonate ions at voltages as low as 0.001 V, or 0.01 V, or 0.1V, and can also produce bicarbonate ions at higher voltages if more rapid production is desired, e.g., at 0.2 - 2.0 V; in various embodiments the bicarbonate ions are produced with no gas formation at the anode or cathode, e.g., no formation of hydrogen or chlorine at the electrodes.

[0076] In these examples, and in various embodiments of the invention, a pH difference of more than 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6, 6.5, 7.0,

7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, or 12.0 pH units may be produced in a first electrolyte solution 102 and in third electrolyte solution 118 when a voltage of 1.0 V or less, or 0.9 V or less, or 0.8 V or less, or 0.7 V or less, or 0.6V or less, or 0.5 V or less, or 0.4 V or less, or 0.3 V or less, or 0.2 V or less, or 0.1 V or less, or 0.05 V or less is applied across the anode and cathode. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.8 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.7 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.6 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.5 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.4 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.3 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.2 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when the voltage applied across the anode and cathode is less than 0.1 V without forming a gas at the electrodes. In certain embodiments, bicarbonate ions are formed when

the voltage applied across the anode and cathode is less than 0.05 V without forming a gas at the electrodes.

[0077] As will be appreciated, in particular embodiments, the present invention provides a system and method capable of producing a pH difference of more than 0.5 pH units in first electrolyte 102 and third electrolyte 118 when a voltage of 0.05 V or less is applied across the anode and cathode. In some embodiments, the invention provides a system and method capable of producing a pH difference of more than 1.0 pH units between first electrolyte 102 and third electrolyte 118 when a voltage of 0.1V or less is applied across the anode and cathode. In some embodiments, the invention provides a system and method capable of producing a pH difference of more than 2.0 pH units between a first electrolyte and third electrolyte when a voltage of 0.2 V or less is applied across the anode and cathode.

[0078] In some embodiments, the invention provides a system and method capable of producing bicarbonate ions in first electrolyte 102 when a voltage of 0.4V or less is applied across the anode and cathode. In some embodiments, the invention provides a system and method capable of producing bicarbonates ions 122 when a voltage of 0.6V or less is applied across the anode and cathode. In some embodiments, the invention provides a system and method capable of producing bicarbonate ions 122 when a voltage of 0.8V or less is applied across the anode and cathode. In particular embodiments, the invention provides a system capable of producing bicarbonate ions 122 when a voltage of 1.0 V or less is applied across the anode and cathode. In some embodiments the invention

provides a system capable of producing bicarbonate ions 122 in first electrolyte 102 when a voltage of 1.2 V or less is applied across the anode and cathode.

[0079] It will be appreciated that the voltage need not be kept constant and that the voltage applied across the anode and the cathode may be very low, e.g., 0.05V or less and that the voltage may be increased as needed as the concentration of bicarbonate ions in the solution 102 increases. In this manner, a desired bicarbonate ion concentration may be achieved with the minimum average voltage, without generating a gas at the electrodes. Thus, in some embodiments as described in the previous paragraph, the average voltage may be less than 80%, 70%, 60%, or less than 50% of the voltages noted in the previous paragraph for particular embodiments.

[0080] In some embodiments, one or more of the initial electrolytes charged into the system may be depleted of divalent cations, e.g., the electrolytes are depleted of magnesium or calcium ion as for example where the electrolytes are taken from an ion exchange process. Thus, in some embodiments the total concentration of divalent cations in the electrolyte solutions in contact with the ion exchange membrane or membranes is less than 0.06 mol/kg solution, or less than 0.05 mol/kg solution, or less than 0.04 mol/kg solution, or less than 0.02 mol/kg solution, or less than 0.01 mol/kg solution, or less than 0.005 mol/kg solution, or less than 0.001 mol/kg solution, or less than 0.0005 mol/kg solution, or less than 0.0001 mol/kg solution, or less than 0.00005 mol/kg solution.

[0081] As discussed in various embodiments herein, the carbon dioxide that contacts first electrolyte 102 may initially form bicarbonate ions 122 in the first

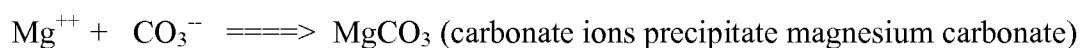
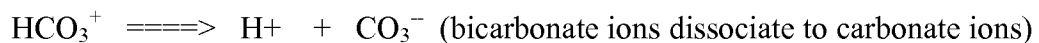
electrolyte. As bicarbonate ions are removed from first electrolyte 102 more carbon dioxide may dissolve in the electrolyte to form bicarbonate and/or carbonate ions. Depending on the pH of the first electrolyte, the balance is shifted toward bicarbonate or toward carbonate formation, as is well understood in the art. In these embodiments the pH of the first electrolyte may decrease, remain the same, or increase, depending on the rate of removal of bicarbonate and/or carbonate ions compared to rate of introduction of carbon dioxide. It will be appreciated that no bicarbonate ions need form in these embodiments, or that bicarbonate ions may not form during one period but form during another period.

[0082] Optionally, the present system is used to produce bicarbonate ions 122, which, when included in a solution comprising alkaline earth cations and hydroxide ions causes precipitation of carbonate and/or bicarbonate compounds such as calcium carbonate or magnesium carbonate and/or their bicarbonates. In various embodiments, divalent cations such as magnesium and/or calcium are present in the solutions used in the process, and/or are added. The precipitated carbonate compound can be used as cements and other building and construction material such as aggregates and the like as described in United States Patent Application Serial No. 12/126,776, filed on May 23, 2008, incorporated herein by reference.

[0083] In an optional step, the acidified electrolyte solution 118 illustrated in Figs. 1 - 4 is utilized to dissolve a calcium and/or magnesium rich mineral, such as mafic mineral including serpentine or olivine, to form a solution for precipitating carbonates and bicarbonates as described in the United States patent applications incorporated herein by reference. For example, acidified stream 118 can be used to

dissolve calcium and/or magnesium rich minerals such as serpentine and olivine to from an electrolyte solution that can be charged with bicarbonate ions 122 and then made sufficiently basic to precipitate carbonate compounds. Such precipitation reactions and the use of the precipitates, e.g., as in cements are described in the United States Patent Applications Serial No. 12/126,776, filed on May 23, 2008 and incorporated herein by reference.

[0084] In an other optional embodiment, the bicarbonate ion solutions of the present invention can be utilized to desalinate saltwater by removing divalent cations as insoluble carbonates, e.g., removing calcium and magnesium ions from a saltwater e.g., seawater based on the following reactions and as described in United States Patent Application Serial No. 12/163,205, filed on June 27, 2008, herein incorporated by reference:



[0085] Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

[0086] Accordingly, the preceding merely illustrates the principles of the invention. It will be appreciated that those skilled in the art will be able to devise various arrangements, which, although not explicitly described or shown herein,

embody the principles of the invention, and are included within its spirit and scope. Also, examples and conditional language recited herein are principally intended to aid the reader in understanding the principles of the invention and the concepts contributed by the inventors to furthering the art, and are to be construed as being without limitation to such specifically recited examples and conditions. Moreover, all statements herein reciting principles, aspects, and embodiments of the invention as well as specific examples thereof, are intended to encompass both structural and functional equivalents thereof. Additionally, it is intended that such equivalents include both currently known equivalents and equivalents developed in the future, i.e., any elements developed that perform the same function, regardless of structure. The scope of the present invention, therefore, is not intended to be limited to the exemplary embodiments shown and described herein. Rather, the scope and spirit of present invention is embodied by the appended claims.

CLAIMS:

1. An electrochemical system comprising:

an anode, a cathode and a first electrolyte, wherein the system is capable of forming bicarbonate ions in the first electrolyte without forming a gas at the cathode or anode on applying a voltage across the anode and cathode and contacting the first electrolyte with carbon dioxide.

2. An electrochemical system comprising:

an anode, a cathode and a first electrolyte, wherein the system is capable of forming bicarbonate ions in the first electrolyte on applying a voltage of less than 2.0 V, less than 1.5 V, less than 1.0 V, less than 0.5 V, less than 0.1 V or less than 0.05 V across the anode and cathode and contacting the first electrolyte with carbon dioxide.

3. The system of claim 1 or 2 comprising:

a first anion exchange membrane and a cation exchange membrane between which is contained the first electrolyte.

4. The system of claim 3, further comprising:

a second electrolyte contacting the anion exchange membrane and the anode; and

a third electrolyte contacting the cation exchange membrane and the cathode.

5. The system of claim 3, further comprising:

a second electrolyte contacting the first anion exchange membrane and the anode;

a third electrolyte contained between the cation exchange membrane and a second anion exchange membrane in the electrochemical cell; and

a fourth electrolyte contacting the second anion exchange membrane and the cathode.

6. The system of claim 1 or 2, further comprising:

a first cation exchange membrane and a second cation exchange membrane between which is contained the first electrolyte.

7. The system of claim 6, further comprising:

a second electrolyte contacting the first cation anion exchange membrane and the anode;

a third electrolyte contained between the second cation exchange membrane and an anion exchange membrane; and

a fourth electrolyte contacting the anion exchange membrane and the cathode.

8. The system of claim 5, further comprising:

a fifth electrolyte contained between the second cation exchange membrane and a second anion exchange membrane, and wherein the second electrolyte contacts the second anion exchange membrane and the anode.

9. The system of any of claims 1 - 8, wherein the first electrolyte comprises saltwater.

10. The system of claim 4, wherein the first, second and third electrolytes comprise saltwater.

11. The system of any of claim 5, wherein the first, second, third and fourth electrolytes comprise saltwater.

12. The system of claim 8, wherein the first, second third, fourth and fifth electrolytes comprise saltwater.

13. The system of claim 9, wherein the first electrolyte comprises sodium chloride and carbon dioxide.

14. The system of claim 12, wherein the fifth electrolyte comprises sodium chloride.

15. The system of claim 13, capable of transferring anions ions across the anion exchange membrane from the first electrolyte to the second electrolyte.
16. The system of claim 13, capable of transferring chloride ions across the anion exchange membrane from the first electrolyte to the second electrolyte.
17. The system of claim 13, capable of transferring cations across the cation exchange membrane from the first electrolyte to the third electrolyte.
18. The system of claim 13, capable of transferring protons across the cation exchange membrane from the first electrolyte to the third electrolyte.
19. The system of claim 4, wherein chlorine gas does not form at the anode.
20. The system of claim 4, wherein hydrogen gas does not form at the cathode.
21. The system of claim 4, wherein the voltage applied across the electrodes comprises 0.4 V or less, 0.6 V or less, or 0.8 V or less.
22. The system of claim 4, wherein the voltage applied across the electrodes comprises 0.1 to 0.8 V or 0.1 to 1 V.

23. The system of claim 13, capable of forming sodium bicarbonate in the first electrolyte.

24. The system of claim 13, capable of forming hydrochloric acid in the third electrolyte.

25. The system of claim 4, wherein the anode and cathode are selected from tin, nickel, cobalt or copper.

26. The system of claim 25, capable of oxidizing the anode to tin ions in the second electrolyte and reducing tin ions to tin at the cathode.

27. The system of claim 7, wherein the second cation exchange membrane is capable of selectively transferring sodium ions from the second electrolyte to the first electrolyte; the first cation exchange membrane is capable of selectively transferring protons from the first electrolyte to the third electrolyte; and the anion exchange membrane is capable of selectively transferring chloride ions from the fourth electrolyte to the third electrolyte.

28. The system of claim 27, capable of forming sodium bicarbonate in the first electrolyte.

29. The system of claim 27, capable of forming hydrochloric acid in the third electrolyte.

30. The system of claim 27, wherein the anode and cathode are selected from tin, nickel, cobalt or copper.

31. The system of claim 27, capable of forming tin ions in the electrolyte at the anode and reducing tin ions to tin from the electrolyte at the cathode.

32. The system of claim 8, capable of transferring sodium ions across the second cation exchange membrane from the fifth electrolyte to the first electrolyte; transferring protons across the first cation exchange membrane from the first electrolyte to the third electrolyte; transferring chloride ions across the first anion exchange membrane from the fourth electrolyte to the third electrolyte; and transferring chloride ions across the second anion exchange membrane from the fifth electrolyte to the second electrolyte.

33. The system of claim 32, capable of forming hydrochloric acid in the third electrolyte.

34. The system of claim 32, capable of forming sodium bicarbonate in the first electrolyte.

35. The system of claim 32, wherein chlorine gas does not form at the anode.
36. The system of claim 32, wherein hydrogen gas does not form at the cathode.
37. The system of claim 32, wherein the voltage applied across the electrodes comprises 0.4 V or less, 0.6 V or less, 0.8 V or less.
38. The system of claim 32, wherein the voltage applied across the electrodes comprises 0.1 to 0.8 V or 0.1 to 1 V.
39. The system of claim 32, wherein the anode and cathode are selected from tin, nickel, cobalt or copper.
40. The system of claim 39, capable of forming tin ions into the electrolyte at the anode and reducing tin ions to tin from the electrolyte at the cathode.
41. An electrochemical method comprising:
applying a voltage across an anode and a cathode through a first electrolyte comprising carbon dioxide to form bicarbonate ions in the first electrolyte without forming a gas at the cathode or the anode.
42. An electrochemical method comprising:

applying a voltage of less than 2.0 V, less than 1.5 V, less than 1.0 V, less than 0.5 V, less than 0.1 V or less than 0.05 V across an anode and a cathode through a first electrolyte comprising carbon dioxide to form bicarbonate ions in the first electrolyte.

43. The method of claim 41 or 42, wherein the first electrolyte is contained between an anion exchange membrane and a cation exchange membrane.

44. The method of claim 43, wherein the anion exchange membrane contacts the anode through the second electrolyte; and

the cation exchange membrane contacts the cathode through a third electrolyte.

45. The method of claim 41 or 42, wherein the first electrolyte is contained between a first cation exchange membrane and a second cation exchange membrane.

46. The method of claim 45, wherein

the first cation exchange membrane separates the first electrolyte from a third electrolyte;

the second cation exchange membrane contacts the anode through a second electrolyte;

a first anion exchange membrane separates the third electrolyte from the fourth electrolyte; and

the fourth electrolyte contacts the cathode.

47. The method of claim 45, wherein

the first cation exchange membrane separates the first electrolyte from a third electrolyte;

the first anion exchange membrane separates the third electrolyte from a fourth electrolyte;

the fourth electrolyte contacts the cathode;

a fifth electrolyte is contained between the second cation exchange membrane and a second anion exchange membrane; and

the second anion exchange membrane contacts the anode through the second electrolyte.

48. The method of claim 43, wherein the first electrolyte comprises sodium chloride and carbon dioxide.

49. The method of claim 43, further comprising transferring anions across the anion exchange membrane from the first electrolyte to the second electrolyte.

50. The method of claim 43, further comprising transferring chloride ions across the anion exchange membrane from the first electrolyte to the second electrolyte.

51. The method of claim 43, further comprising transferring cations across the cation exchange membrane from the first electrolyte to the third electrolyte.

52. The method of claim 43, further comprising transferring protons across the ion exchange membrane from the first electrolyte to the third electrolyte.

53. The method of claim 43, whereby chlorine gas does not form at the anode.

54. The method of claim 43, whereby hydrogen gas does not form at the cathode.

55. The method of claim 43, comprising precipitating alkaline metal carbonates utilizing the first electrolyte.

56. The method of claim 43, comprising forming bicarbonate ions in the first electrolyte.

57. The method of claim 43, comprising forming sodium bicarbonate in the first electrolyte.

58. The method of claim 43, further comprising separating the cathode from the third electrolyte utilizing second anion exchange membrane whereby the cathode is

electrically connected to second anion exchange membrane through fourth electrolyte.

59. The method of claim 58, further comprising transferring chloride ions across the second anion exchange membrane from the fourth electrolyte to the third electrolyte.

60. The method of claim 59, comprising forming bicarbonate ions in the first electrolyte.

61. The method of claim 59, comprising forming hydrochloric acid in the third electrolyte.

62. The method of claim 46, further comprising transferring sodium ions across the second cation exchange membrane from the second electrolyte to the first electrolyte.

63. The method of claim 43, whereby chlorine gas does not form at the anode.

64. The method of claim 43, whereby hydrogen gas does not form at the cathode.

65. The system of claim 43, comprising applying a voltage of 0.4 V or less, 0.6 V or less, 0.1 to 0.6 V, or 0.1 to 1 V across the electrodes.

66. The method of claim 43, comprising forming hydrochloric acid in the third electrolyte.

67. The method of claim 43, further comprising precipitating alkaline metal carbonates utilizing the first electrolyte.

68. The method of claim 47, further comprising transferring chloride ions across the second anion exchange membrane from the fifth electrolyte to the second electrolyte.

69. The method of claim 47, further comprising forming bicarbonate ions in the first electrolyte.

70. The method of claim 47, further comprising forming sodium bicarbonate in the first electrolyte.

71. The method of claim 47, further comprising forming hydrogen chloride in the third electrolyte.

72. The method of claim 47, wherein chlorine gas does not form at the anode.

73. The method of claim 47, wherein hydrogen gas does not form at the cathode.

74. The method of claim 47, comprising applying 0.4 V or less, 0.6 V or less, 0.8 V or less, 0.1 to 0.8 V or 0.1 to 1 V across the electrodes.

75. The method of claim 47, further comprising precipitating alkaline metal carbonates utilizing the first electrolyte.

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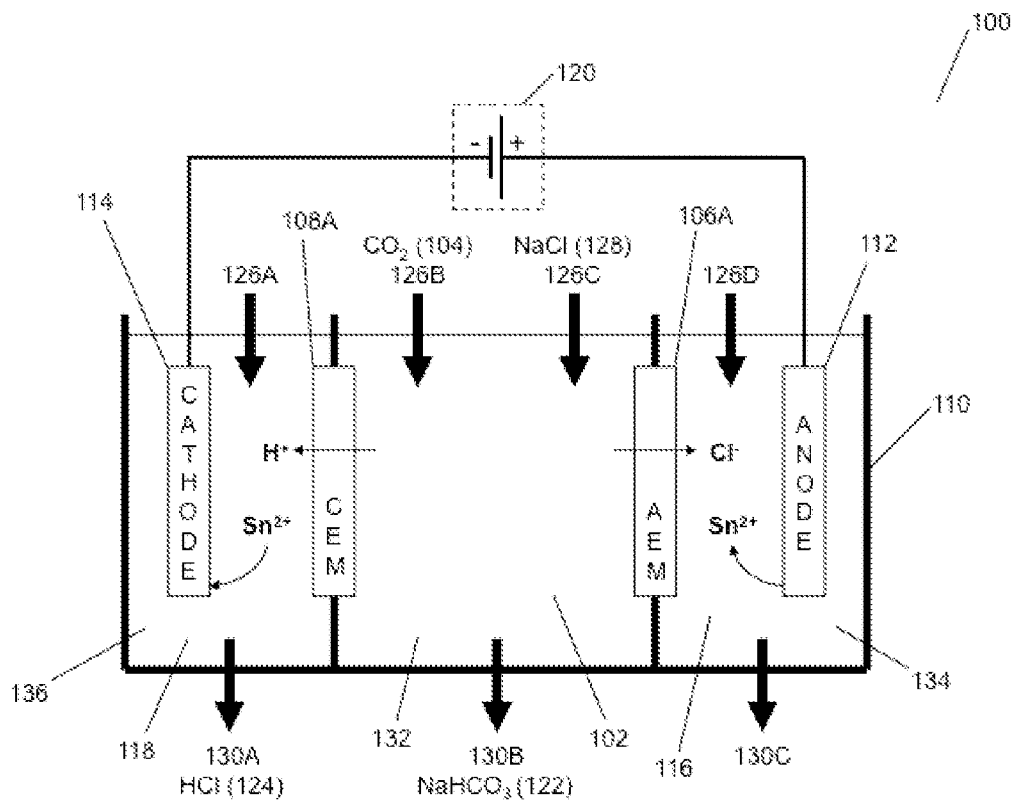


Fig. 1

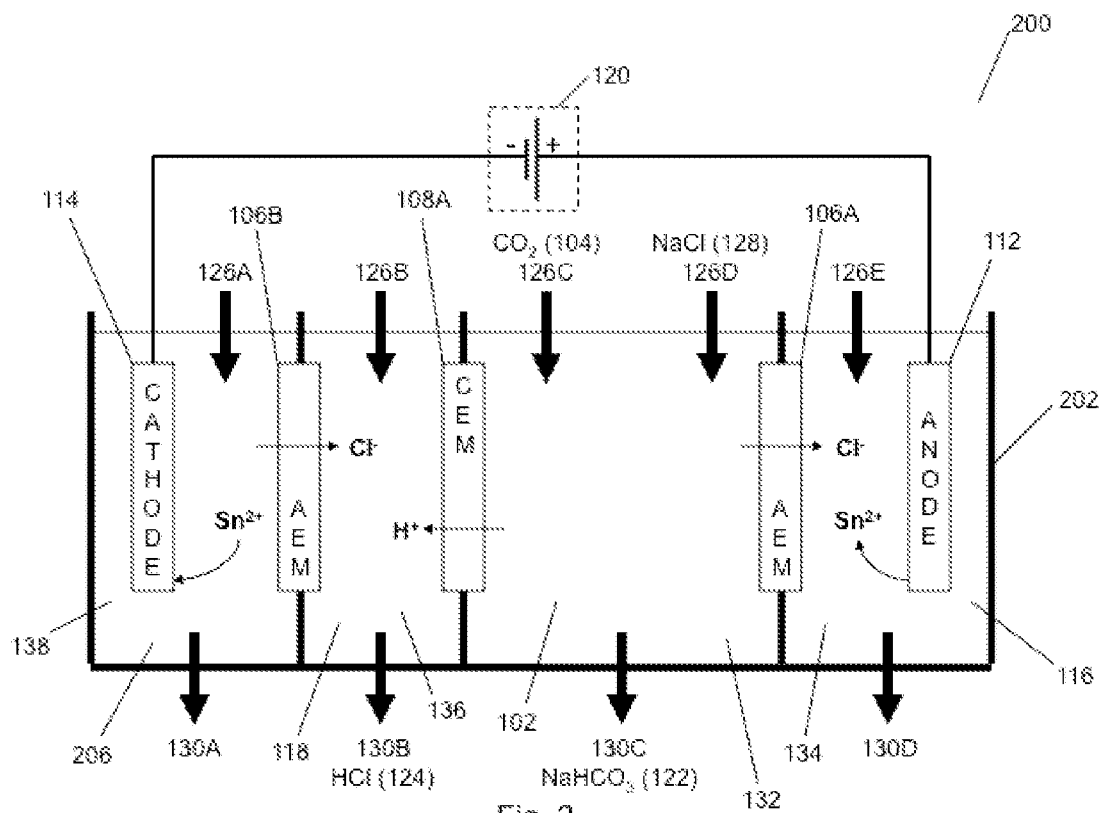


Fig. 2

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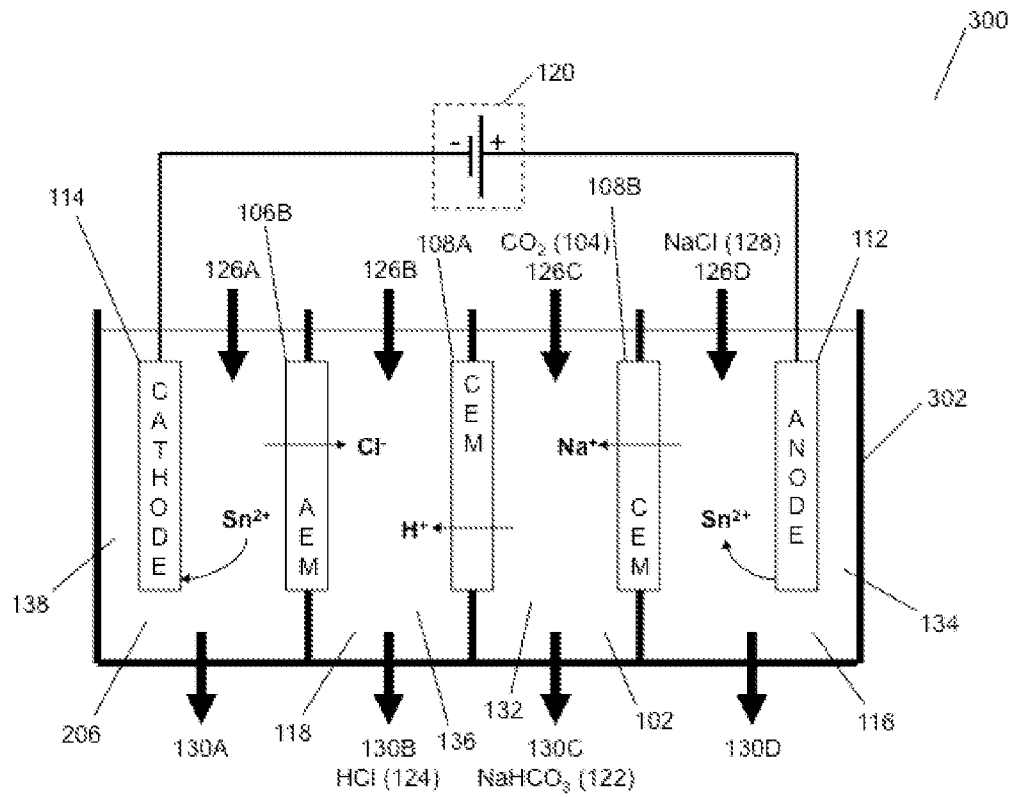


Fig. 3

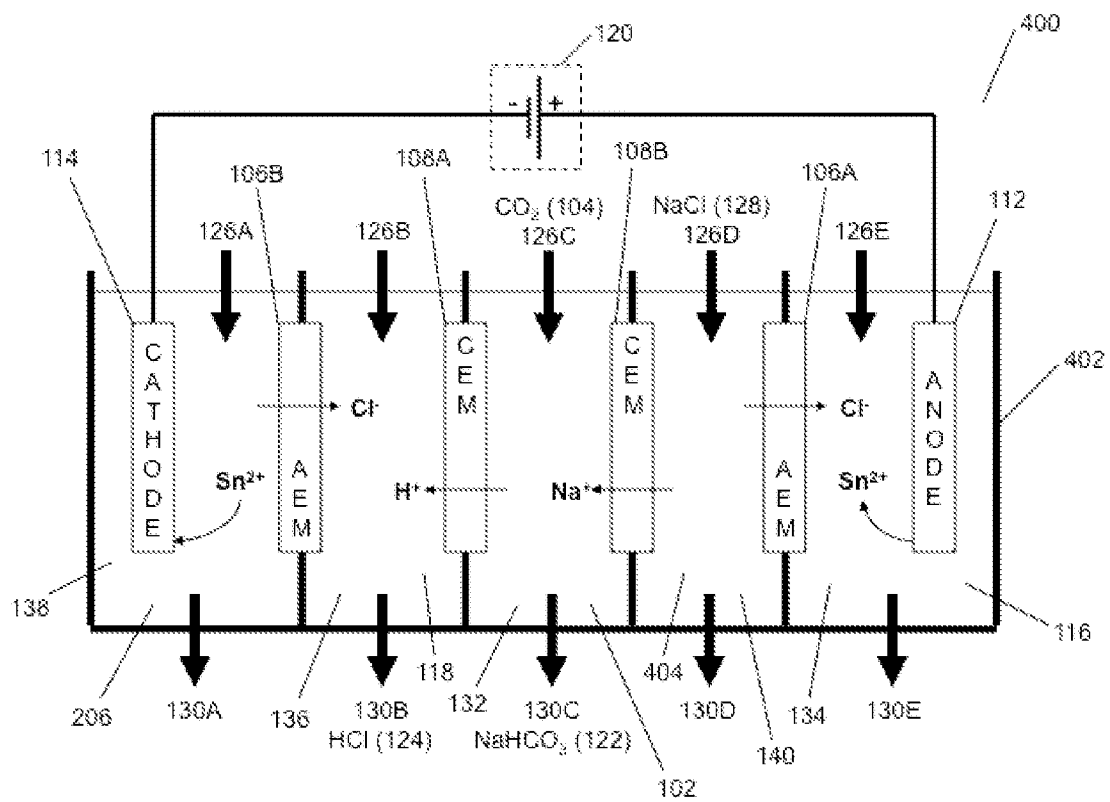


Fig. 4

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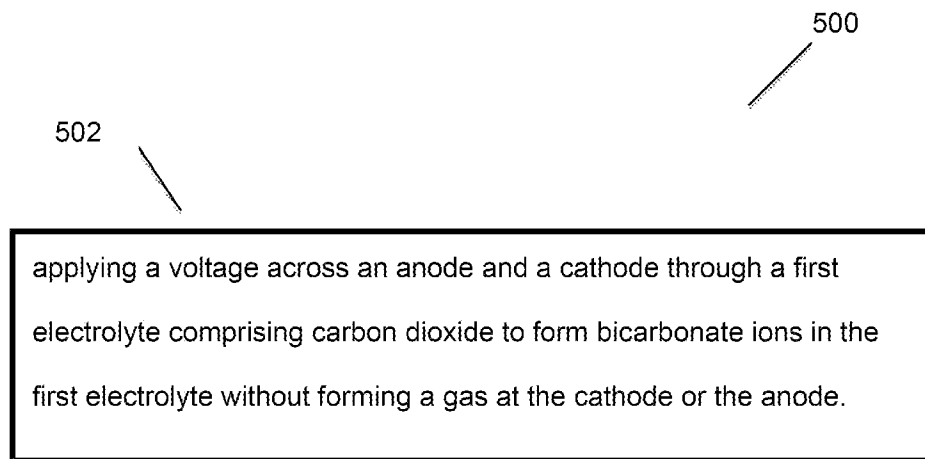


Fig. 5

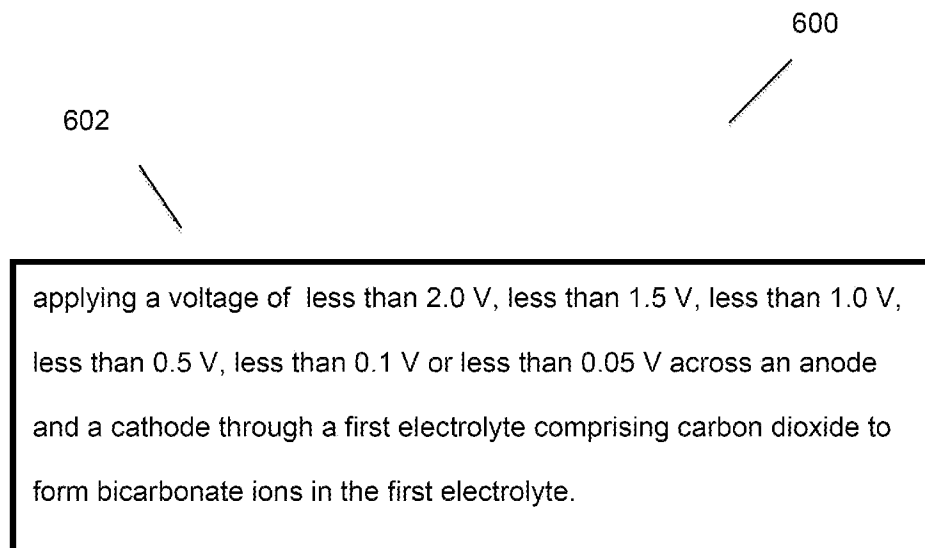


Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/32301

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C25B 1/00 (2009.01)

USPC - 205/555,343

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C25B 1/00 (2009.01)

USPC - 205/555,343

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

IPC(8) - C25B 1/00 (2009.01) - see keyword below

USPC - 205/555,343,480 - see keyword below

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPTO; PubWEST(USPT,PGPB,EPAB,JPAB); DialogClassic; Google Scholar

Search Terms Used: electrochemical system, anode, cathode, electrolyte/first, second, form/produce bicarbonate ions, without gas, apply voltage, contact carbon dioxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 2008/0245672 A1 (Little et al.) 9 October 2008 (09.10.2008), entire document especially abstract, Fig. 2-Fig. 4, para [0005], para [0031], para [0034]-para [0041], para [0051]-para [0057], para [0262]	1-8, 10-12, 14, 19, 21-22, 25, 27-30, 32-35, 37-39, 41-53, 55-63, 65-72, 74-75 ----- 20, 26, 31, 36, 40, 54, 64, 73
Y	US 4,440,611 A (Dhar et al.) 3 April 1984 (03.04.1984), col 4, ln 33-37	20, 36, 54, 64, 73
Y	US 4,900,406 A (Janssen et al.) 13 February 1990 (13.02.1990), col 1, ln 13-45	26, 31, 40

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

02 March 2009 (02.03.2009)

Date of mailing of the international search report

23 MAR 2009

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/32301

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 9,13,15-18,23-24
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.