

AN ELECTROCHEMICAL APPROACH FOR MINERALS RECOVERY FROM
BRINE WATER AND CO₂ CAPTURE

Cross-Reference to Related Application

- 5 [0001] This application claims the benefit of priority of Singapore Patent Application No. 10202302768X, filed 28 September 2023, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

- 10 [0002] The present disclosure relates to an electrochemical reactor and a method for recovering minerals with carbon dioxide capture. The present disclosure also relates to a system that includes the electrochemical reactor.

Background

- 15 [0003] Traditionally, the discharge and treatment methods for concentrated brine from seawater desalination include, for example, (1) use pipelines to transport concentrated brine to relatively open seas for discharge so as to minimize the impact on the ecological environment of the offshore area, (2) attempt to increase the concentration of salty water discharged by desalination equipment and use such concentrated brine as a raw material
20 for downstream salt industry, (3) use unit operations such as evaporation-crystallization-drying process, wherein the middle salt was recovered in the form of solid crystals. In addition, concentrated brine may also contain preservatives, defoamers, scale inhibitors, sterilants, biocides, pickling agents, etc., with complex components. These may make it difficult to recover valuable minerals and/or some/all
25 of these components from the brine, or recovery of valuable minerals and/or some/all of these components may require recovery technologies of high efficiency that may be uneconomical.

- [0004] The recovery of minerals may be useful but quite challenging. Several extraction methods may have been studied on a lab scale, including solar evaporation,
30 electrodialysis (ED), membrane distillation crystallization (MDC), and adsorption/desorption. Among these methods, the first three approaches tend to only recover high concentrations of mineral ions (e.g., Na⁺, Mg²⁺, and Ca²⁺), while the

adsorption/desorption method tends to concentrate minerals that exist at low concentrations by selectively adsorbing a mineral and quantitatively desorbing it for the evaporative crystallization. All these technologies, unfortunately, appear still in their infancy, hindered by economic considerations.

- 5 [0005] Recently, the combination of CO₂ abatement together with minerals production from wastewater may have become an emerging research area and received researchers' attention globally. For example, alkali industrial by-products were applied to produce CaCO₃ from CO₂ and seawater. Seawater pre-treatment by CO₂ mineral carbonation using brine pre-treatment waste from soda ash plant as alkali sources were reported. An
- 10 electrolysis method was recently proposed to process saline water through mineralization with CO₂ dissolved in seawater. However, aforesaid method, such as electrolysis, often tend to involve or may be a process with low energy efficiency. Moreover, the anodic oxygen evolution reaction increased the acidity, leading to the release of CO₂ again from carbonate. Electrochemical capture and storage of CO₂ as
- 15 calcium carbonate are also investigated. Compared with the selective electrodialysis method, which is used to separate monovalent and divalent ions from seawater reverse osmosis brine, the electrolysis method consumes more energy due to the higher cell voltage required for water electrolysis.
- 20 [0006] There is thus a need to provide for a solution that addresses one or more of the limitations mentioned above. The solution should at least provide for an effective and economical way to recover minerals from brine water with CO₂ capture.

Summary

[0007] In a first aspect, there is provided an electrochemical reactor comprising:

an anode;

a cathode; and

an enclosure configured to (i) house the anode and the cathode in an electrolyte, and (ii) have a gaseous mixture comprising oxygen and carbon dioxide directed into a region of the electrolyte proximal to the cathode,

wherein the cathode is configured to generate a metal carbonate from the electrolyte in the presence of the oxygen and carbon dioxide, and wherein the anode is configured to generate chlorine gas.

[0008] In another aspect, there is provided a method for recovering minerals with carbon dioxide capture, the method comprising:

directing the electrolyte into the electrochemical reactor described in various embodiments of the first aspect;

directing the gaseous mixture comprising oxygen and carbon dioxide into the region of the electrolyte proximal to the cathode in the electrochemical reactor described in various embodiments of the first aspect; and

operating the electrochemical reactor to generate the metal carbonate from the electrolyte at the cathode in the presence of the oxygen and carbon dioxide, and to generate chlorine gas at the anode.

[0009] In another aspect, there is provided a system comprising:

the electrochemical reactor described in various embodiments of the first aspect; and

a separation unit in fluid communication with the electrochemical reactor, wherein the separation unit is operable to receive precipitates generated by the cathode and separate the precipitates from the electrolyte.

Brief Description of the Drawings

[0010] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the present disclosure. In the following description, various embodiments of the present disclosure are described with reference to the following drawings, in which:

[0011] FIG. 1 is a process flow diagram of a system involving an electrochemical reactor of the present disclosure. The oxygen and carbon dioxide source may be, for example, separate gas cylinders wherein one contains oxygen and the other contains carbon dioxide. Where needed, the system and units may be denoted by reference numerals. The system may be denoted 100. The oxygen gas cylinder may be denoted 102 and the carbon dioxide cylinder may be denoted 104. The gas mixer may be denoted 106. The valve may be denoted 108. The brine water tank may be denoted 110. Each of the one or more pumps may be denoted 112. Each of the one or more pumps may be, for example, a peristaltic pump (any other pumps that can deliver the respective chemicals may be used). The electrochemical reactor may be denoted 114. The one or

more gas (chlorine, carbon dioxide, oxygen, etc.) collection units may be denoted 116. The treated brine may be denoted 118. The precipitate settling unit may be denoted 120, which may be a tank. The precipitate storage unit may be denoted 122. The supernatant from the precipitate settling unit may be denoted 124.

5 **[0012]** FIG. 2 shows the reaction processes for minerals production combined with carbon abatement from waste streams (e.g., desalination seawater brine). SW denotes seawater. The desalination seawater brine may contain metal ions, such as Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , Cl^- . The chlorine released from the anode may be recycled to a unit for water disinfection. Air and carbon dioxide are reacted at the cathode. Minerals (e.g., CaCO_3 , MgCO_3 , $\text{Al}(\text{OH})_x(\text{CO}_3)_y$, $\text{Fe}(\text{OH})_x(\text{CO}_3)_y$) are channeled to a unit operable for sedimentation separation. x and y in $\text{Al}(\text{OH})_x(\text{CO}_3)_y$ and $\text{Fe}(\text{OH})_x(\text{CO}_3)_y$ can be any
10 valuc which maintains charge neutrality in the compound.

[0013] FIG. 3 shows a non-limiting example of a prototype of the electrochemical reactor of the present disclosure. The electrochemical reactor shown in this instance is referred to as a “H-type” batch reactor, as it has a “H-shape” configuration. The cathode
15 may be a 20% platinum/carbon (Pt/C) on carbon paper as the composite cathode catalyst. The anode may be IrO_2 on carbon paper as the composite anode catalyst. At the anode, the reaction of $\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$ occurs. At the cathode, the reaction of $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ occurs.

20 **[0014]** FIG. 4 is a plot of the current versus potential curve of the H-Type batch reactor using 20% platinum/carbon (Pt/C) composite catalyst as the cathode and IrO_2 as the anode.

[0015] FIG. 5 is a plot of the current recorded for about 19 hours of continuous reaction at a voltage of 4 V using the catalysts mentioned for FIG. 4 and seawater brine.

25 **[0016]** FIG. 6 shows precipitates generated after 19 hours of continuous reaction at 4 V.

[0017] FIG. 7 shows the XRD analysis of the precipitates.

[0018] FIG. 8 shows setup of a continuous version of the flow reactor (i.e., electrochemical reactor) of the present disclosure. In this setup, the gas bubbler can be
30 optionally filled with an alkaline solution, such as NaOH or KOH, to absorb any chlorine gas and prevent it from being released into the air. In another setup, the alkaline solution and/or the gas bubbler may not be needed, as the chlorine gas generated at the

anode can be directly collected as a product. The setup in FIG. 8 is an example with no membrane separator between the anode and cathode. The bottom left image shows two pumps leading to the cathode and anode chamber, respectively.

[0019] FIG. 9 shows the voltage current curve (left image) and precipitates (right image) in an experimental test using the electrochemical reactor of FIG. 8.

Detailed Description

[0020] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the present disclosure may be practiced.

[0021] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0022] The present disclosure relates to an electrochemical reactor, and a system including the electrochemical reactor. Advantageously, the electrochemical reactor is operable to recover minerals from an electrolyte, and at the same time, involves carbon capture. Understandably, the present disclosure relates to a method for recovering minerals from an electrolyte with carbon capture.

[0023] The electrolyte can be any liquid waste containing such minerals. For example, the electrolyte can be any wastewater containing such minerals, e.g., brine. In the present disclosure, the terms “brine”, “brine water”, and “concentrated brine” are used interchangeably. The brine, for example, may be generated in desalination of seawater.

[0024] The minerals recoverable by the electrochemical reactor from aforesaid electrolyte may include a metal salt. The metal salt may include a metal carbonate. As non-limiting examples, the minerals recoverable (e.g., see FIG. 7) may include halite (e.g., sodium chloride), magnesite (e.g., magnesium carbonate), calcium carbonate, barium carbonate, aluminum carbonate, iron carbonate, and/or hydroxide-carbonates of such metals, etc.

[0025] The electrochemical reactor is advantageous in that it is operable at a lower voltage range of 1.0 V to 5.0 V to carry out the method. At the time of mineral recovery, the electrochemical reactor also contributes in terms of carbon abatement by CO₂ mineralization, converting carbon dioxide into stable carbonates. Hence, the electrochemical reactor and method provide an advantageous way to reduce atmospheric CO₂ levels and mitigate climate change. The method also reduces the concentration of mineral ions in wastewater discharge to environment, reducing or eliminating negative effects. For example, the electrochemical reactor can reduce or eliminate the amount of minerals in brine discharged from a seawater desalination plant.

10 [0026] Details of various embodiments of the electrochemical reactor, the method, and the system, and advantages associated with the various embodiments are described below. Where the embodiments and advantages are described in the examples section further hereinbelow, they shall not be iterated for brevity.

[0027] The present disclosure provides for an electrochemical reactor. The electrochemical reactor may include an anode and a cathode. In various embodiments, the electrochemical reactor may include an enclosure configured to house the anode and the cathode in an electrolyte. In various embodiments, the enclosure may be configured to have a gaseous mixture comprising oxygen and carbon dioxide directed into a region of the electrolyte proximal to the cathode. In various embodiments, the cathode may be configured to generate a metal carbonate from the electrolyte in the presence of the oxygen and carbon dioxide, and the anode may be configured to generate chlorine gas. Said differently, the electrochemical reactor may be configured to have the cathode render an oxygen reduction reaction (ORR) to generate hydroxide (OH⁻) species that aids recovery of metal ions, such as Ca²⁺ and Mg²⁺, from an electrolyte (e.g., brine water) with *in situ* CO₂ capture, at the same time, pure chlorine gas can be generated from the anode. This is in contrast to traditional reactors and methods that involve hydrogen evolution reaction (HER) to generate hydroxide species. For example, in certain traditional reactors and methods, the cathode is distinctly configured to generate hydroxide ions via hydrogen evolution reaction for promoting the formation of metal carbonates. Traditionally, with hydrogen evolution reaction at a cathode, which is different from oxygen reduction reaction, hydrogen gas (H₂) and hydroxide ions are generated from water (H₂O) or from protons (H⁺). With the cathode

of the present electrochemical reactor operable to render ORR, advantageously, the electrochemical reactor of the present disclosure can be operated at a lower voltage (e.g., lower by 1 V) as compared to traditional electrochemical reactors having cathode that renders HER.

[0028] In various embodiments, the anode may include a catalyst deposited on a substrate. As the catalyst and substrate are associated with the anode, such a catalyst and substrate may be referred to in the present disclosure as an “anodic catalyst” and an “anode substrate”, respectively. In other words, in various embodiments, the anode may include an anodic catalyst deposited on an anode substrate.

[0029] In various embodiments, the cathode may include a catalyst deposited on a substrate. As the catalyst and substrate are associated with the cathode, such a catalyst and substrate may be referred to in the present disclosure as a “cathodic catalyst” and a “cathode substrate”, respectively. In other words, in various embodiments, the cathode may include a cathodic catalyst deposited on a cathode substrate.

[0030] In various embodiments, the anodic catalyst may comprise iridium, iridium oxide, ruthenium, and/or ruthenium oxide. Advantageously, iridium and ruthenium (and their oxides) may exhibit excellent stability and resistance to corrosion, especially under the harsh conditions of high potential and oxidative environments at the anode in electrochemical reactions. This makes them a durable choice for long-term operation. Also, low overpotential may be involved with iridium-based and/or ruthenium-based anodic catalysts, as these materials may require lower voltage to operate at the same or more ORR efficiency with less energy input.

[0031] In various embodiments, the anode substrate and/or the cathode substrate may be gas-diffusible. Advantageously, being gas-diffusible allows, for example, carbon dioxide, air, and/or oxygen, to reach the catalyst’s surface at the cathode, i.e., maximise surface area of catalyst even when deposited on a substrate. Likewise, at the anode, more surface area of the catalyst may be available to render chlorine gas. In various embodiments, the anode substrate and/or the cathode substrate may comprise carbon paper or titanium foam, which are gas-diffusible.

[0032] In various embodiments, the cathodic catalyst may comprise a platinum/carbon composite catalyst, an iron-doped and nitrogen-doped catalyst, and/or a cobalt-doped and nitrogen-doped catalyst. Examples of (i) iron-doped and nitrogen-doped catalysts

and (ii) cobalt-doped and nitrogen-doped catalyst, may include Fe-C-N catalysts, C_3N_4 , N-doped carbon, Co-C-N catalysts, Co_3O_4 , Co-N co-doped carbon, etc. Such catalysts are advantageously economical.

[0033] In various embodiments, the electrolyte may include any liquid waste containing metal ions to be recovered. For example, the electrolyte may include any wastewater to be treated, wherein the wastewater contains metal ions. A non-limiting example of the electrolyte may include or may be brine.

[0034] In various embodiments, the anode and the cathode may be connected to an electrical source operable to render to voltage in a range of 1.0 V to 5.0 V, 2.0 V to 5.0 V, 3.0 V to 5.0 V, 4.0 V to 5.0 V, 1.0 V to 3.0 V, etc., across the anode and the cathode. The electrochemical reactor of the present disclosure is advantageous, as it is operable at these voltages that balances reaction rate and energy efficiency. If higher voltage is used, there may be higher reaction rates but energy efficiency is lower. If lower voltage is used, there may be better energy efficiency but reaction rates may be compromised. In non-limiting instances, the voltage may be 1.0 V to 3.0 V.

[0035] In various embodiments, the electrochemical reactor may further include a membrane (e.g., an ion exchange membrane) configured between the anode and the cathode.

[0036] In various embodiments, the enclosure may be configurable to be sealed air tight during operation. This renders the electrochemical reactor operable as a closed reactor. In various embodiments, the electrochemical reactor may be configured as an air tight enclosure.

[0037] In various embodiments, the electrochemical reactor may be operable as a batch reactor or a continuous reactor.

[0038] The present disclosure describes a method for recovering minerals with carbon dioxide capture. The method can be carried out using the electrochemical reactor described in various embodiments of the first aspect of the present disclosure. Embodiments and advantages described for the electrochemical reactor can be analogously valid for the method described herein, and vice versa. Where the various embodiments and advantages have already been described above and in the examples section further hereinbelow, they shall not be iterated for brevity.

[0039] The method may include directing the electrolyte into the electrochemical reactor described in various embodiments of the first aspect of the present disclosure, directing the gaseous mixture including oxygen and carbon dioxide into the region of the electrolyte proximal to the cathode in the electrochemical reactor described in various embodiments of the first aspect of the present disclosure, and operating the electrochemical reactor to generate the metal carbonate from the electrolyte at the cathode in the presence of the oxygen and carbon dioxide, and to generate chlorine gas at the anode. The minerals may be recovered as metal carbonates, which is advantageous as metal carbonates may be conveniently and easily precipitated for separation.

[0040] In various embodiments, directing the gaseous mixture may include directing oxygen from an oxygen source into the region of the electrolyte proximal to the cathode, and directing carbon dioxide from a carbon dioxide source, which may not be the oxygen source, into the region of the electrolyte proximal to the cathode.

[0041] In various embodiments, directing gaseous mixture may comprise mixing the oxygen and the carbon dioxide to form the gaseous mixture. In various embodiments, instead of oxygen, air containing oxygen may be used.

[0042] In various embodiments, the method may include operating the electrochemical to have the electrical source render a voltage in a range of 1.0 V to 5.0 V, 2.0 V to 5.0 V, 3.0 V to 5.0 V, 4.0 V to 5.0 V, etc., across the anode and the cathode.

[0043] The present disclosure further describes a system. The system may include the electrochemical reactor described in various embodiments of the first aspect of the present disclosure. The system may be operable to carry out the method described above. Embodiments and advantages described for the electrochemical reactor and the method can be analogously valid for the system described herein, and vice versa. Where the various embodiments and advantages have already been described above and in the examples section further hereinbelow, they shall not be iterated for brevity.

[0044] The system may include the electrochemical reactor described in various embodiments of the first aspect of the present disclosure. In various embodiments, the system may include a separation unit in fluid communication with the electrochemical reactor. In various embodiments, the separation unit may be operable to receive precipitates generated by the cathode and separate the precipitates from the electrolyte.

[0045] In various embodiments, the separation unit may include or may be a sedimentation tank (or a centrifugal separation unit (e.g., a centrifuge), a filtration unit, etc.) which may be configured to channel (i) the precipitates to a precipitate storage unit and (ii) the electrolyte, which may be separated from the precipitates, as an overflow that is recycled into the electrochemical reactor. The filtration unit may be configured with a filter that separates the precipitates.

[0046] In various embodiments, the system may further include a recycling pump in fluid communication with the electrochemical reactor and the separation unit, wherein the recycling pump may be operable to recycle the electrolyte from the separation unit to the electrochemical reactor.

[0047] In various embodiments, the system may further include a gas bubbler in fluid communication with a gas outlet of the electrochemical reactor, wherein the gas outlet may be configured proximal to the anode to facilitate exit of chlorine gas from the electrochemical reactor to the gas bubbler. The gas bubbler can house an alkaline solution, such as NaOH or KOH, to absorb any chlorine gas and prevent it from being released into the air. In certain non-limiting instances, the alkaline solution and/or the gas bubbler may not be needed, as the chlorine gas generated at the anode can be directly collected as a product or channel to another unit operable to utilise the chlorine gas to disinfect, for example, water.

[0048] In various embodiments, the system may further include a gas mixer configured to receive (i) oxygen from an oxygen source and (ii) carbon dioxide from a carbon dioxide source, which is not the oxygen source, and operable to render the gaseous mixture comprising oxygen and carbon dioxide. In various embodiments, instead of oxygen and/or oxygen source, air containing oxygen may be used.

[0049] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the present disclosure.

[0050] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0051] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[0052] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[0053] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

Examples

[0054] The present disclosure relates to an electrochemical reactor, and a method, for recovering minerals (e.g., calcium and magnesium) from brine water together with CO₂ capture. The electrochemical reactor may contain a cathode and an anode, and the brine water flows through the electrochemical reactor and a system containing the electrochemical reactor. Oxygen (or air) together with CO₂ was bubbled on the cathode. Calcium and magnesium carbonates were generated at the cathode side after applying a voltage (e.g., 1.0 V to 5.0 V) between the cathode and the anode. Pure chlorine gas was produced at the anode side, on the anode. The electrochemical reactor and method combine the advantages of CO₂ capture, minerals recovery from brine water (in the form of carbonates or hydroxides), together with the production of valuable chlorine products.

[0055] The electrochemical reactor and method of the present disclosure may differ from traditional electrochemical reactors and method in that the cathode is operable to generate generate OH⁻ species via ORR so as to recover, for example Ca²⁺ and Mg²⁺ from brine water with in situ CO₂ capture, and at the same time, pure Cl₂ gas can be generated from the anode.

[0056] The electrochemical reactor, system, and method are described in further details, by way of non-limiting examples, as set forth below.

[0057] Example 1: General discussion of electrochemical reactor and method

[0058] The present example, and the examples below, describes for an electron-assisted process to recover the minerals (e.g., mainly calcium and magnesium ions) from brine water by reacting with CO₂ and oxygen (or air). The process is depicted in FIG. 2. The electro-assisted reactor (i.e., electrochemical reactor) includes two parts, the cathode side and the anode side. The cathode side can include one or more catalysts, such as a

platinum/carbon (Pt/C) composite catalyst, a iron-doped and nitrogen-doped catalyst, and a cobalt-doped and nitrogen-doped catalyst, loaded on a substrate, such as a carbon paper or a titanium foam. Examples of (i) iron-doped and nitrogen-doped catalysts and (ii) cobalt-doped and nitrogen-doped catalyst, may include Fe-C-N catalysts, C_3N_4 , N-doped carbon, Co-C-N catalysts, Co_3O_4 , Co-N co-doped carbon, etc. The anode side can include or be made of one or more catalysts, such as an iridium catalyst, ruthenium catalyst, iridium oxide catalyst, and/or a ruthenium oxide catalyst, loaded on a carbon paper or a titanium foam. The operation of the electrochemical reactor and method are as follows (also see FIG. 2).

[0059] Electricity from 1.0 V to 5.0 V (e.g., 1.0 V to 3.0 V) range can be applied to the two electrodes (cathode and anode). Oxygen in the air is electrochemically converted to hydroxide ions (OH^-) on the cathode side via the following reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. The generated hydroxide ions react with CO_2 and Ca^{2+} (or other mineral ions such as Mg^{2+} , Ba^{2+} , Al^{3+} , Fe^{3+} , etc.) to generate carbonates (such as $CaCO_3$, $MgCO_3$, etc.) or hydroxide-carbonates (such as $Ca(OH)_x(CO_3)_y$, $Mg(OH)_x(CO_3)_y$, etc.). So, the overall reaction for the whole process is $Mg^{2+} + Ca^{2+} + 4Cl^- + 2CO_2 + O_2 \rightarrow 2Cl_2 + MgCO_3 + CaCO_3$. Sedimentation separation can be involved to separate the precipitates from brine or wastewater. The remaining chloride ions (which are balanced with the mineral ions) are electrochemically oxidized to chlorine gas on the anode via $2Cl^- \rightarrow Cl_2 + 2e^-$. Chlorine is a valuable product that is widely used in the PVC industry, organic/inorganic chemicals, chlorinated intermediates, sanitation, disinfection, and antiseptis. x and y in $Ca(OH)_x(CO_3)_y$ and $Mg(OH)_x(CO_3)_y$ can be any value which maintains charge neutrality in the compound, for example, x can be any value in the range of 0 to 2 and $y = 1 - x/2$.

[0060] The advantages and impacts of such electrochemical reactor and method include (1) much lower cell voltage compared with traditional electrochemical methods, (2) contribute greatly to carbon abatement by CO_2 mineralization, (3) produce valuable minerals which can greatly enhance economic competition, and (4) reduce the concentration of mineral ions in wastewater to eliminate its negative effects on the environment.

[0061] **Example 2A: Electrochemical Reactor Prototype – H-type batch reactor**

[0062] To demonstrate the concept, a H-type batch reactor with a cathode and anode separated by a membrane (ion exchange membrane) was set up, as shown in FIG. 3. The cathode is prepared by loading 20% Pt/C on carbon paper, and the anode side is prepared by loading commercial IrO₂ on carbon paper. Carbon paper substrate works as a gas diffusion layer, which allows the reactant gases (CO₂ and air/oxygen) to diffuse to the catalyst surface. The two electrodes are immersed in brine water. The oxygen gas and CO₂ gas were bubbled into the cathode side (left side in FIG. 3) near the cathode carbon paper. In a reaction process, an oxygen electrochemical reaction occurs on the cathode side and generates OH⁻ ($\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$). The generated OH⁻ reacts with CO₂, Mg²⁺, and Ca²⁺ to generate precipitates such as MgCO₃ and CaCO₃. On the anode side, chlorine evolution reaction ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$) occurs simultaneously and the excess Mg²⁺ and Ca²⁺ in the anode side transfer to the cathode side to replenish what has been consumed. Cl₂ gas evolves from the anode. So, the overall reaction for the whole process is $\text{Mg}^{2+} + \text{Ca}^{2+} + 4\text{Cl}^- + 2\text{CO}_2 + \text{O}_2 \rightarrow 2\text{Cl}_2 + \text{MgCO}_3 + \text{CaCO}_3$.

[0063] During the experimental process, first, a continuously increasing voltage was applied on the batch reactor to check when the reaction occurs and the current versus voltage (potential) curve is shown in FIG. 4. It can be seen that the reaction occurs when the cell voltage is higher than ~1.0 V. Increasing the potential increases the current (and reaction rate). For the sole purpose of demonstration, a voltage of 4V was selected and applied on the reactor for continuous reaction. The results are shown in FIG. 5 and FIG. 6. The current can maintain 0.03 A in 19 hours (FIG. 5) of continuous reaction, and obvious precipitates are generated on the cathode side (FIG. 6). The precipitates have a cotton-like structure, and it does not influence the reaction even though it covers the electrode's surface. When the cathode electrode is taken out of the brine, some of the precipitates were left in the cathode side cell, further suggesting the precipitates are very loose.

[0064] Example 2B: Electrochemical Reactor Prototype – H-type batch reactor

[0065] To make the entire reaction process continuous, a flow reactor is set up to further demonstrate the concept, as shown in FIG. 8. The input of the reactor includes the flow of brine, the flow of CO₂ and O₂ gases, and electricity. The output of the reactor includes brine waste, chlorine gas, and precipitates. A pump was used to introduce brine into the

reactor, while another pump is used to take the brine out after the reaction. CO₂ and O₂ gases were introduced into the reactor via a bubbler near the cathode side.

[0066] The reaction was conducted with the following conditions:

[0067] Cathode materials: 1.5 mg 60% Pt-C on 6 cm² carbon paper

5 [0068] Anode material: 1 cm * 1 cm Pt plate

[0069] The solution in the reactor: PUB brine water

[0070] Gas flow: O₂ (20 mL/min) + CO₂ (5 mL/min)

[0071] The inlet flow rate of brine water: about 1 mL/min

[0072] The outlet flow rate of brine water: about 1 mL/min

10 [0073] After continuous reaction for more than hour at ~2.6 V, obvious precipitates were observed at the bottom of the flow reactor, as shown in FIG. 9, further demonstrating feasibility of the electrochemical reactor and method.

[0074] **Example 3: Characterization of precipitates**

15 [0075] In order to determine the components of the precipitates, the precipitates were analysed and characterized. X-ray diffraction analysis (XRD) was used to identify and determine the precipitates via their crystallographic structure. The obtained precipitates were confirmed to be a mixture of CaCO₃, MgCO₃, and Mg(OH)₂ as shown in FIG. 7.

[0076] In all, the above experimental results confirm that the present electrochemical reactor and method of the present disclosure feasible.

20 [0077] **Example 4: Summary**

[0078] The present technology can be applied for all kinds of (waste) water resources containing mineral ions.

25 [0079] The electrochemical reactor and method of the present disclosure are configured to operate an electron-assisted process to recover the minerals (e.g., mainly calcium and magnesium ions) from the brine water by reacting with CO₂ and oxygen (or air). The process includes two parts: (1) the cathode side and (2) the anode side.

[0080] The cathode side comprises catalysts such as Pt/C catalysts, iron- and nitrogen-doped catalysts, and cobalt- and nitrogen-doped catalysts loaded on a substrate such as carbon paper or titanium foam.

30 [0081] The anode side is made of iridium and ruthenium catalysts loaded on carbon paper or titanium foam.

- [0082] Electricity with a 1.0 V to 5.0 V voltage range can be applied to the two electrodes (cathode and anode). Oxygen in the air is electrochemically converted to hydroxide ions (OH^-) on the cathode side via the following reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$. The generated hydroxide ions react with CO_2 and Ca^{2+} (or other mineral ions such as Mg^{2+} , Ba^{2+} , Al^{3+} , Fe^{3+} , etc.) to generate carbonates (such as CaCO_3 , MgCO_3 , etc.) or hydroxide-carbonates (such as $\text{Ca}(\text{OH})_x(\text{CO}_3)_y$, $\text{Mg}(\text{OH})_x(\text{CO}_3)_y$, etc). x and y in $\text{Ca}(\text{OH})_x(\text{CO}_3)_y$ and $\text{Mg}(\text{OH})_x(\text{CO}_3)_y$ can be any value which maintains charge neutrality in the compound, for example, x can be any value in the range of 0 to 2 and $y = 1 - x/2$.
- 10 [0083] The sedimentation separation can be used to separate these precipitates from brine or wastewater. The remaining chloride ions (which are balanced with the mineral ions) are electrochemically oxidized to chlorine gas on the anode via $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$.
- [0084] The overall reaction for the whole process is $\text{Mg}^{2+} + \text{Ca}^{2+} + 4\text{Cl}^- + 2\text{CO}_2 + \text{O}_2 \rightarrow 2\text{Cl}_2 + \text{MgCO}_3 + \text{CaCO}_3$.
- 15 [0085] While the present disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the present disclosure as defined by the appended claims. The scope of the present disclosure is thus indicated by the appended claims and all changes
- 20 which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. An electrochemical reactor comprising:
an anode;
a cathode; and
an enclosure configured to (i) house the anode and the cathode in an electrolyte, and (ii) have a gaseous mixture comprising oxygen and carbon dioxide directed into a region of the electrolyte proximal to the cathode,
wherein the cathode is configured to generate a metal carbonate from the electrolyte in the presence of the oxygen and carbon dioxide, and wherein the anode is configured to generate chlorine gas.
2. The electrochemical reactor of claim 1,
wherein the anode comprises an anodic catalyst deposited on an anode substrate;
and/or
wherein the cathode comprises a cathodic catalyst deposited on a cathode substrate.
3. The electrochemical reactor of claim 2, wherein the anodic catalyst comprises iridium, iridium oxide, ruthenium, and/or ruthenium oxide.
4. The electrochemical reactor of claim 2 or 3, wherein the anode substrate is gas-diffusible.
5. The electrochemical reactor of any one of claims 2 to 4, wherein the anode substrate comprises carbon paper or titanium foam.
6. The electrochemical reactor of any one of claims 2 to 5, wherein the cathodic catalyst comprises a platinum/carbon composite catalyst, an iron-doped and nitrogen-doped catalyst, and/or a cobalt-doped and nitrogen-doped catalyst.

7. The electrochemical reactor of any one of claims 2 to 6, wherein cathode substrate is gas-diffusible.
8. The electrochemical reactor of any one of claims 2 to 7, wherein the cathode substrate comprises carbon paper or titanium foam.
9. The electrochemical reactor of any one of claims 1 to 8, wherein the electrolyte comprises brine.
10. The electrochemical reactor of any one of claims 1 to 9, wherein the anode and the cathode are connected to an electrical source operable to render to voltage from 1.0 V to 5.0 V across the anode and the cathode.
11. The electrochemical reactor of any one of claims 1 to 10, further comprising an ion exchange membrane configured between the anode and the cathode.
12. The electrochemical reactor of any one of claims 1 to 11, wherein the enclosure is configurable to be sealed air tight during operation.
13. The electrochemical reactor of any one of claims 1 to 12, wherein the electrochemical reactor is a batch reactor or a continuous reactor.
14. A method for recovering minerals with carbon dioxide capture, the method comprising:
 - directing the electrolyte into the electrochemical reactor of any one of claims 1 to 13;
 - directing the gaseous mixture comprising oxygen and carbon dioxide into the region of the electrolyte proximal to the cathode in the electrochemical reactor of any one of claims 1 to 13; and
 - operating the electrochemical reactor to generate the metal carbonate from the electrolyte at the cathode in the presence of the oxygen and carbon dioxide, and to generate chlorine gas at the anode.

15. The method of claim 14, wherein directing the gaseous mixture comprises:
directing oxygen from an oxygen source into the region of the electrolyte proximal to the cathode; and
directing carbon dioxide from a carbon dioxide source, which is not the oxygen source, into the region of the electrolyte proximal to the cathode.
16. A system comprising:
the electrochemical reactor of any one of claims 1 to 13; and
a separation unit in fluid communication with the electrochemical reactor, wherein the separation unit is operable to receive precipitates generated by the cathode and separate the precipitates from the electrolyte.
17. The system of claim 16, wherein the separation unit comprises a sedimentation tank which is configured to channel (i) the precipitates to a precipitate storage unit and (ii) the electrolyte, which is separated from the precipitates, as an overflow recycled into the electrochemical reactor.
18. The system of claim 16 or 17, further comprising a recycling pump in fluid communication with the electrochemical reactor and the separation unit, wherein the recycling pump is operable to recycle the electrolyte from the separation unit to the electrochemical reactor.
19. The system of any one of claims 16 to 18, further comprising a gas bubbler in fluid communication with a gas outlet of the electrochemical reactor, wherein the gas outlet is configured proximal to the anode to facilitate exit of chlorine gas from the electrochemical reactor to the gas bubbler.
20. The system of any one of claims 16 to 19, further comprising a gas mixer configured to receive (i) oxygen from an oxygen source and (ii) carbon dioxide from a carbon dioxide source, which is not the oxygen source, and operable to render the gaseous mixture comprising oxygen and carbon dioxide.