

ELECTROCHEMICALLY ENHANCED PROCESS FOR NEXT GENERATION CARBON DIOXIDE CAPTURE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority to US Provisional Patent Application No. 63/175,761, filed April 16, 2021, the contents of which are incorporated herein by reference in their entirety.

BACKGROUND

The management of existing atmospheric carbon dioxide and ongoing carbon dioxide emissions is needed to limit the increase in the global average temperature and to reduce the effects of climate change. To realistically achieve this, 10–20 Gt CO₂ per year needs to be removed from the atmosphere within the next century, necessitating carbon management strategies that can be implemented at a large scale. The current state of the art in CO₂ capture technology uses amine-based absorption to remove CO₂. But these amine-based processes use between 0.8–5.0 MWh of thermal energy per tonne of CO₂ captured to desorb less than 50% of the CO₂ in the saturated amine. This high heat duty leads to (1) the use of large scale distillation equipment, (2) low working CO₂ absorption capacities of the amine solution (e.g., less than 0.3 mol CO₂ per mol monoethanolamine (MEA)), and (3) solvent loss via chemical degradation and evaporation. The existing approach to releasing the CO₂ and regenerating the amine is a thermal process in which the solution is heated to elevated temperatures (>140°C). At these temperatures, the carbamate decomposes to yield the original amine molecule and release CO₂ as a concentrated vapor^{3, 5-6}. However, large thermal duties (e.g., >5 MWh/tonne of CO₂ for a working capacity of 0.05 mol/mol for DAC applications)³ render such thermal processes economically unattractive. Furthermore, the high temperatures required for amine regeneration can result in solvent loss via chemical degradation and evaporation³. These factors can result in up to a 50% increase in capital expenditures (CAPEX) and up to 25% increase in operating expenses (OPEX) which lead to high costs of carbon capture (>\$100 per tonne CO₂)⁷⁻⁸ and restricts the use of amine-based processes to point source emitters such as fossil-fuel fired power plants.

These factors also limit the adoption of amine-based CO₂ capture by other industries including petrochemicals, steel making, cement, and direct air capture (DAC), where smaller scale and/or more energy efficient processes are desired for economic integration.

Copper electrochemistry has been attempted for amine-based CO₂ capture,⁹⁻¹⁶ using a complexation reaction between a metal (i.e., Cu²⁺ ions) and the amine which decomposes the carbamate ion and releases CO₂.^{11-12, 14-16} This complexation reaction is electrochemically driven at the anode where Cu²⁺ ions are generated from oxidation of Cu metal, with the Cu-amine complex being regenerated back to amines with Cu²⁺ being reduced to Cu metal at the cathode. The aforementioned system was extended to electrochemical CO₂ capture on solid polyanthraquinones.^{9, 13} In the foregoing system, a Faradaic electro-swing process is used to capture CO₂ via carboxylation reactions (reduction) with quinones (with polyvinylferrocene being oxidized) followed by reversing the polarity of the cell to decompose the carboxyl-quinone compound (and reduce the polyvinylferrocene), thereby desorbing CO₂ and regenerating the polyanthraquinone. While these previous electrochemical processes have exhibited high working capacities (as much as 0.62 mol CO₂ per mol amine for 12% v/v CO₂ streams) and low energy requirements (theoretical minimum requirements of ~0.60 MWh per t CO₂), they also require complicated Cu-based redox chemistry with expensive diamines or quinones. Furthermore, the electrochemistry operates directly on the amine. These features could lead to high extents of amine or electrode degradation and more expensive CAPEX/OPEX.¹⁷

Accordingly, there is a need for methods and systems to address these capacity, energy, and recyclability limitations of amine-based carbon dioxide capture processes. The present disclosure addresses these needs.

SUMMARY OF THE INVENTION

Provided herein are methods and systems for electrochemically enhanced amine-based carbon captures. In some embodiments, the present disclosure provides a method of capturing CO₂, comprising:

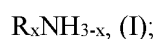
- i) reacting a CO₂ source gas with a stoichiometric excess of an amine in an aqueous solution to form an amine-CO₂ complex, thereby forming a solution comprising the amine-CO₂ complex;
- ii) electrochemically adjusting the pH of the solution comprising the amine-CO₂ complex to less than 7, thereby releasing CO₂ from the amine-CO₂ complex; and
- iii) collecting the released CO₂ as a concentrated vapor.

In some embodiments, the amine-CO₂ complex comprises carbamate ions.

In some embodiments, the step of adjusting the pH is performed using water electrolysis.

In some embodiments, the pH of the solution after adjustment is about 0.5 to about 7, about 0.5 to about 6, about 0.5 to about 5, about 0.5 to about 4, about 0.5 to about 3, about 0.5 to about 2, or preferably. In other preferred embodiments, the pH is adjusted to about 5 to about 6.

The amine may be a primary amine, a secondary amine, a tertiary amine, or a mixture thereof. In preferred embodiments, the amine is a primary amine or a secondary amine. More particularly, the amine has the structure of formula I:



wherein R is selected from an optionally substituted alkyl, ether, and hydroxyalkyl;

x is 1, 2 or 3, and;

one or more R, together with each N, optionally forms a nitrogen containing heterocycle.

Amines useful in the present methods include, in some embodiments, monoethanolamine, 2-ethylaminoethanol, 2-methylaminoethanol, ethylenediamine, benzylamine, diethanolamine, pyrrolidine, morpholine, 2,6-dimethylmorpholine, monoisopropanolamine, piperazine 2-(dimethylamino)ethanol, N-tert-butyl-diethanolamine, 3-dimethylamino-1-propanol, 3-(dimethylamino)-1,2-propanediol, 2-diethylaminoethanol, 3-diethylamino-1,2-propanediol, 3-diethylamino-1-propanol, triethanolamine, 1-dimethylamino-2-propanol, 1-(2-hydroxyethyl)pyrrolidine, 1-diethylamino-2-propanol, 3-pyrrolidino-1,2-propanediol, 2-(diisopropylamino)ethanol, 1-(2-hydroxyethyl)piperidine, 2-(dimethylamino)-2-methyl-1-propanol, 3-piperidino-1,2-propanediol, 3-dimethylamino-2,2-dimethyl-1-propanol, 3-hydroxy-1-methylpiperidine, N-ethyl-diethanolamine, 1-ethyl-3-hydroxypiperidine, and any combination thereof. Preferably, the amine is monoethanolamine, piperazine, or a mixture thereof. In certain preferred embodiments, the amine is monoethanolamine, and in certain particularly preferred embodiments, the amine is piperazine.

In some embodiments, the concentration of the amine in the aqueous amine solution is about 10% to about 50% v/v. In other embodiments, the concentration of the amine is about 15% to about 40% v/v, about 20 to about 30% v/v, or more preferably, about 22%.

The CO₂ source gas may be, in some embodiments, effluent from an industrial source. In other embodiments, the CO₂ source gas is from an atmospheric source, e.g., atmospheric air. In further embodiments, the CO₂ source gas is a mixture of effluent from an industrial

source and atmospheric air. In some embodiments, the gas from the industrial source comprises about 1 to about 12% v/v CO₂.

In particular embodiments, the step of adjusting the pH is performed at a temperature of less than 100 °C, preferably about -10 °C to about 50°C, more preferably about -10 °C to about 50°C.

In some embodiments, the method further comprises regenerating and collecting the aqueous amine solution and using the regenerated amine in step (i) of the method.

In some embodiments, the concentrated vapor comprises about 2% to about 99% CO₂.

The present disclosure further provides systems for amine-based CO₂ capture. In some embodiments, a system for capturing CO₂ from a CO₂ source gas comprises:

- a CO₂ absorption chamber configured to contain an aqueous amine solution, the CO₂ absorption chamber having a CO₂ source gas inlet, and a concentrated CO₂ vapor outlet;

- an electrochemical cell in fluid communication with the CO₂ absorption chamber and configured to receive a CO₂ rich amine solution from the CO₂ absorption chamber, the electrochemical cell comprising:

 - an anode disposed in an anode chamber,

 - a cathode disposed in a cathode chamber,

 - a first cation exchange membrane disposed between the anode chamber and a first reservoir configured to receive a CO₂-rich aqueous amine solution such that protons may flow from the anode chamber to the first reservoir,

 - an anion exchange membrane disposed between the first reservoir and a salt reservoir such that anions from the salt reservoir may flow towards the anode chamber,

 - a second cation exchange membrane disposed between the salt reservoir and the cathode chamber such that cations may flow from the salt reservoir toward the cathode chamber; and

 - an anion exchange column in fluid communication with the electrochemical cell and configured to: receive a CO₂-lean aqueous amine solution from the first reservoir, deliver a regenerated aqueous amine solution to the CO₂-absorption chamber, and receive a catholyte from the cathode chamber.

The system may further comprise a concentrated CO₂ vapor outlet. In further embodiments, the system comprises an H₂ outlet in fluid communication with the cathode

chamber. In still further embodiments, the system comprises an O₂ outlet in fluid communication with the anode chamber.

In some embodiments, the electrochemical cell is configured to perform water electrolysis.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic of an exemplary CO₂ capture process in accordance with the present disclosure. CO₂ is absorbed from a gaseous stream, such as atmospheric air or industrial process gas, into an aqueous amine solution. CO₂ is then desorbed from the amine via electrochemically induced acidification. The amine solution is regenerated using a strong base anion exchange resin so that it may be used for further CO₂ absorption. The strong base anion exchange resin may then be regenerated using the alkaline catholyte produced during the electrochemical step.

Figure 2 is a schematic of an exemplary electrochemical cell 200 useful in amine-based CO₂ capture comprising a cathode 201, an anode 202, a second cation exchange membrane 203, an anion exchange membrane 204, a first cation exchange membrane 205, a base solution 206, a salt solution 207, an amine solution 208, and an acid solution 209.

Figure 3 is a graph depicting pH values (circles) and extents of CO₂ desorption (triangles) at various proton to MEA ratios for 22 vol% aqueous MEA solutions with CO₂ loadings of 0.25 (grey) and 0.5 (black) mol CO₂ per mol MEA.

Figure 4A shows IR spectra of CO₂-rich 22% v/v MEA solutions (~0.5 mol CO₂ per mol MEA) at various pH values from an electrochemically induced acidification cell. The black line represents CO₂-rich MEA prior to acidification. **Figure 4B** shows regeneration extent for MEA solutions after acidification to pH ~6-8 followed by alkalization to pH >10. In Figure 4B, * represents the use of HCl/NaOH, # represents electrochemical acidification followed by NaOH addition, and ° represents electrochemical acidification followed by ion exchange. All experiments were carried out using a 22% v/v MEA solution with an initial loading of ~0.5 mol CO₂ per mol MEA.

Figure 5 depicts an exemplary system for a plant design 500 comprising a CO₂ absorption chamber 501, electrochemical cell 502, and anion exchange column 503. A CO₂-containing source gas is brought into a CO₂ absorption chamber 501 via inlet 504. CO₂ absorption chamber 501 is configured to contain an aqueous amine solution, where CO₂ is absorbed by the amine. The CO₂-rich aqueous amine solution flows into the electrochemical cell (505),

where protons generated at the anode (506) cross a first cation exchange membrane (508) to desorb the CO₂. The protonated, CO₂-lean amine solution next passes (515) through the anion exchange column 503, where the chlorine counter-ion is replaced with hydroxide. The regenerated amine solution completes the closed-loop and returns (518) to the CO₂ absorption chamber 501 to absorb additional CO₂.

DETAILED DESCRIPTION

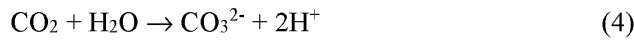
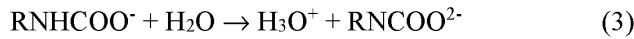
The present disclosure generally provides methods and systems for amine-based carbon capture. More specifically, the disclosure provides in some embodiments a method of capturing CO₂, comprising: reacting a CO₂ source gas with an aqueous solution comprising a stoichiometric excess of an amine to form an amine-CO₂ complex; adjusting the pH of the solution electrochemically to less than about 7, thereby releasing CO₂ from the amine-CO₂ complex; and collecting the released CO₂ as a concentrated vapor. In certain embodiments, the disclosure advantageously allows for regeneration of amine solution at ambient temperatures (e.g., less than 100 °C, preferably about -10 to about 50°C and more preferably about 10 to about 40°C and 100°C). CO₂ absorption in a basic (e.g., pH greater than about 8, greater than about 9, or preferably greater than about 10) aqueous amine solution occurs via reaction of CO₂ with the amine to form stable a carbamate ion and protons/hydronium ions. The present methods advantageously electrochemically induce a pH shift to decompose the carbamate ion via acid-hydrolysis. This pH-shift to pH ≤ 7 occurs at ambient temperature, and therefore, (1) uses simpler process equipment, (2) allows for amine regeneration and thus, maximizes working capacity and (3) reduces solvent loss. In some embodiments, the pH is adjusted to less than 7, less than 6, less than 5, less than 4, less than 3, less 2 or less than 1. In some embodiments, the pH is adjusted to about 0.5 to about 7, about 0.5 to about 6, about 0.5 to about 5, about 0.5 to about 4, about 0.5 to about 3, about 0.5 to about 2, or about 0.5 to about 1. In some embodiment, the pH is adjusted to about 5 to about 6, while in other embodiments, the pH is adjusted to about 0.5 to about 1.5.

In some embodiments, the energy intensity of the present methods is about 2x lower (e.g., 2.0 MWh per ton CO₂) than current state-of-the-art amine-based CO₂ capture processes (4.0 MWh per ton CO₂ for KOH and >5.0 MWh per ton CO₂ for MEA¹⁻³), with reduced hazardous chemical inputs and the possibility of using renewable energy. In some embodiments, the disclosure herein provides amine-based CO₂ capture processes (Figure 1), which integrate electrochemical cells for ambient-temperature regeneration of the aqueous amine solution. In some embodiments, the amine-based processes of the present disclosure

include electrochemically generated acidification to desorb the CO₂, thereby reducing heat and power requirements and to increase working solvent capacity. These process improvements may advantageously lead to reduced size, and land requirements, and environmental footprints of CO₂ capture systems.

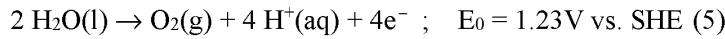
Energy-Efficient Electrochemical Regeneration of Amine Solutions

Under basic conditions (pH>10), CO₂ absorption occurs via the reaction of CO₂ with the amine (e.g., MEA; RNH₂ where R=CH₂CH₂OH) to form carbamate anions (RNHCOO⁻, RNCOO²⁻), protonated amines (RNH₃⁺), and protons/hydronium ions (H⁺/H₃O⁺), according to Equations 1-3, while other gases, such as N₂ and O₂, escape in the effluent. CO₂ also forms carbonates at high pH (Equation 4)⁴.



Electrochemically shifting the pH of the solution to acidic conditions (e.g., pH ≤ 7) favors the decomposition of the carbamate ions via acid-hydrolysis according to the reverse of Equations (1) and (3). Water electrolysis generates the protons for carbamate ion hydrolysis, thereby converting a CO₂-rich amine solution to a CO₂-lean solution, and hydroxide ions that are used to increase the pH of the CO₂-lean solution for subsequent cycles of CO₂ absorption.

In certain embodiments, protons are generated from an aqueous solution at the anode with hydroxide ions generated at the cathode in an electrochemical cell (Figure 2) according to equations 5 and 6:



In certain embodiments, the protons diffuse into the CO₂-rich amine solution across a cation exchange membrane (CEM) resulting in a decrease in the pH which leads to the decomposition of carbamate ions and release of CO₂. In certain embodiments, the CEM prevents diffusion of carbamate anions into the anode chamber, thereby preventing electrooxidation of carbamates/amine. In certain embodiments, a concentrated salt solution

(e.g., NaCl or NaNO₃) provides counter anions to the amine solution and cations to the catholyte to maintain electroneutrality. In certain embodiments, an anion exchange membrane (AEM) prevents the diffusion of the salt solution cations into the aqueous amine chamber. In certain embodiments, after CO₂ is released, the CO₂-lean amine solution is restored to high pH using a strong base anion exchange resin (see Figure 1). In certain embodiments, this resin exchanges the counterions (Cl⁻ or NO₃⁻) from the salt reservoir that have accumulated in the amine solution with hydroxide ions to increase the pH of the CO₂-lean aqueous amine solution to its original basic value. The strong base anion exchange resin is then regenerated using the hydroxide rich solution from the cathode chamber of the electrochemical cell, thereby recovering the anions used in the salt solution chamber. In certain embodiments, the regeneration process allows efficient recycling of the aqueous amine solution, thereby minimizing operating costs and preventing waste generation.

Accordingly, the present electrochemically-induced pH-swing process of the present disclosure has the advantages of replacing hazardous, expensive, and carbon-intensive reagents (e.g., mineral acids) with an abundant and benign proton source (e.g., water), while optionally leveraging renewable energy to facilitate the process.

While not being bound by theory, using water electrolysis for amine regeneration according to the present methods has at least two significant advantages. First, performing water electrolysis in isolated anode/cathode cell chambers allows for localized generation of protons without using stoichiometric or expensive/exotic reagents, catalysts, or materials, and with reduced risk of electrochemical degradation of the amines/electrodes. Second, water electrolysis at the cathode generates H₂, thereby providing an opportunity for realistic energy requirements of 2.0 MWh/tonne CO₂ by capturing and using the evolved H₂. An additional benefit of using electrochemical processes is that up to 100% of the required energy can be supplied from renewable sources. These features impact both the process equipment and energy efficiencies. Complete or near complete regeneration of the amine molecules at ambient temperature can be achieved via acid-mediated carbamate decomposition. This impacts process equipment by (1) reducing the amount of amine used by an amount that is proportional to the CO₂ working capacity increase and (2) replacing complex distillation towers with simpler, modular electrochemical cells and, in some embodiments, separate anion exchange columns. Simpler process equipment has the potential for reducing CAPEX (e.g., less than the >\$60 million investment cost for an amine stripper column⁷) and increasing the flexibility and modularity of the system, both of which would allow for the use of the process in a wider array of applications including concentrated and dilute CO₂ streams

(e.g., capture from industrial process and directly from air). In some embodiments, the concentration of the absorbed CO₂ may range from 300 ppm to 250,000 ppm. In certain such embodiments, the concentration of the absorbed CO₂ may range from 350 ppm to 20,000 ppm. In certain embodiments, preferably wherein the method of the disclosure is being used for direct air capture of CO₂, the concentration of CO₂ may range from 400 ppm to 1,000 ppm.

Realistic energy requirements for the electrochemically enhanced amine process can be estimated based on the number of protons required to desorb CO₂ and on electrolyzers operating at ~80% efficiency (e.g., 68 kWh per kg H₂ produced¹⁸ assuming a thermodynamic demand of 54.8 kWh/kg for the stoichiometric hydrogen evolution reaction and oxygen evolution reaction as shown in equations (5) and (6)¹⁹). For example, titration of a 22% MEA solution at various CO₂ loadings (Figure 3; 0.25 and 0.5 mol CO₂ per mol MEA) shows that ~1.0 mol of H⁺ per mol of amine is used for a pH decrease from 12 to 0.6, at which point all of the CO₂ is desorbed. From this information, energy requirements can be estimated for certain embodiments of disclosure: (1) Direct Air Capture with an initial MEA loading is 0.25 mol CO₂ per mol MEA²⁰ and (2) industrial effluents containing between 1-12% CO₂ (initial loading of 0.5 mol CO₂ per mol MEA).

In some embodiments, the ratio of protons to CO₂ is ~4 for complete desorption in a Direct Air Capture application. In some such embodiments, using currently available electrolyzers, the process would require 6.3 MWh/tonne CO₂ removed. In certain embodiments, if ~70% of the H₂ energy is recovered, this value decreases to 3.8 MWh/tonne CO₂ removed. At 95% cell efficiency, the energy requirements may be 5.3 and 2.8 MWh/tonne CO₂ without and with H₂ recovery, respectively. By comparison, for a traditional thermal swing process, the reboiler duty required to desorb CO₂ from a loading of 0.30 to 0.25 mol CO₂ per mol MEA is ~5.0 MWh/tonne CO₂³, and the duty required for complete desorption would be >25 MWh/tonne CO₂^{3,20}. This preliminary energy analysis indicates that, in certain embodiments, the methods or apparatuses of the disclosure could not only currently be carried out at much lower energy requirements than traditional thermal swing processes (6.3 versus 25.0 MWh/tonne CO₂), but could also potentially achieve a factor of 5x higher working capacity (0.25 versus 0.05 mol CO₂/mol MEA).

For applications with effluents containing >1% CO₂, the energy requirements decrease. In certain embodiments, e.g., assuming that the initial MEA loading is about 0.5 mol CO₂ per mol MEA, the ratio of protons to CO₂ is ~2 for complete desorption. At an 80% efficiency, the methods of certain embodiments of the disclosure would require about 3.1

MWh/tonne CO₂ removed. If ~70% of the H₂ energy is recovered, this value decreases to about 1.9 MWh/tonne CO₂ removed. In certain embodiments, at 95% cell efficiency, the energy requirements are about 2.6 and about 1.4 MWh/tonne CO₂ without and with H₂ recovery, respectively. By comparison for a traditional thermal swing process, the reboiler duty required to desorb CO₂ from a loading of 0.5 to 0.25 mol CO₂ per mol MEA is ~1.3 MWh/tonne CO₂⁵. This duty increases to >2.2 MWh/tonne CO₂ for desorption to less than 0.20 mol CO₂ per mol MEA and is >5 MWh/tonne CO₂ for desorption from less concentrated amines (i.e., from 0.3 to 0.2 mol CO₂ per mol MEA)⁵. Based on these studies, the duty required for complete desorption would be >25 MWh/tonne CO₂ because CO₂ desorption is thermodynamically un-favored at low CO₂ loadings⁵. This preliminary energy analysis indicates that the process could currently be carried out at comparable energy requirements as traditional thermal swing processes (1.9 versus 1.3 MWh/tonne CO₂) but could potentially achieve a factor of 2 higher working capacity (0.5 versus 0.25 mol CO₂ per mol MEA).

Some embodiments of the disclosure include a method of capturing CO₂, comprising: reacting CO₂ with a solvent capable of forming an anionic complex; adjusting the pH of the solution electrochemically to less than about 7; collecting the CO₂ as a concentrated vapor that is released during or after the pH adjusting step; and optionally collecting the regenerated solvent. In some embodiments, the anionic complex comprises carbamate ions and/or a hydroxide (e.g., sodium hydroxide, potassium hydroxide). In some embodiments, the solvent is an amine. In some embodiments, the amine is R_xNH_{3-x}, wherein R is selected from an optionally substituted alkyl, ether, or alcohol.

Exemplary embodiments of amines include **Primary Amines** (e.g., monoethanolamine (MEA), 2-ethylaminoethanol, 2-methylaminoethanol, ethylenediamine, benzylamine); **Secondary Amines** (e.g., diethanolamine (DEA), pyrrolidine, morpholine, 2,6-dimethylmorpholine, monoisopropanolamine, piperazine (PZ)); **Tertiary Amines** (e.g., 2-(dimethylamino)ethanol (DMAE), N-tert-butyl-diethanolamine (tBDEA), 3-dimethylamino-1-propanol (DMA-1P), 3-(dimethylamino)-1,2-propanediol (DMA-1,2-PD), 2-diethylaminoethanol (DEAE), 3-diethylamino-1,2-propanediol (DEA-1,2-PD), 3-diethylamino-1-propanol (DEA-1P), triethanolamine (TEA), 1-dimethylamino-2-propanol (DMA-2P), 1-(2-hydroxyethyl)pyrrolidine [1-(2HE)PRLD], 1-diethylamino-2-propanol (DEA-2P), 3-pyrrolidino-1,2-propanediol (PRLD-1,2-PD), 2-(diisopropylamino)ethanol (DIPAE), 1-(2-hydroxyethyl)piperidine [1-(2HE)PP], 2-(dimethylamino)-2-methyl-1-propanol (DMA-2M-1P), 3-piperidino-1,2-propanediol (3PP-1,2-PD), 3-dimethylamino-2,2-

dimethyl-1-propanol (DMA-2,2-DM-1P), 3-hydroxy-1-methylpiperidine (3H-1MPP), N-ethyldiethanolamine, 1-ethyl-3-hydroxypiperidine), and mixtures thereof.

In certain embodiments, the pH adjusting step is performed via water electrolysis. In certain embodiments, the CO₂ source gas is an effluent from an industrial source. In some embodiments, the pH adjusting step is performed at a temperature of less than 100 °C. In some embodiments, the regenerated amine is collected and used for the same process again. In some embodiments, the CO₂ source gas is from an atmospheric source. In further embodiments, the CO₂ source gas is a mixture of industrial and atmospheric sources.

In certain embodiments, the disclosure provides system, such as the one shown in Figure 5. Figure 5 depicts an exemplary system for a plant design 500 comprising a CO₂ absorption chamber 501, electrochemical cell 502, and anion exchange column 503. A CO₂-containing source gas is brought into a CO₂ absorption chamber 501 via CO₂ source gas inlet 504. CO₂ absorption chamber 501 is configured to contain an aqueous amine solution, where CO₂ is absorbed by the amine, and further includes a scrubbed gas outlet (519). The CO₂-rich aqueous amine solution flows (505) into a first reservoir 523 in the electrochemical cell (502). Protons generated at the anode (506) are disposed in anode chamber 522 and can pass a first cation exchange membrane (508) and into the first reservoir to desorb the CO₂, thereby producing a CO₂-lean amine solution. Anode chamber further includes an O₂ outlet 512. The first reservoir is further in fluid communication with a salt reservoir 524 via an anionic exchange membrane 511, such that anions can flow into the first reservoir. Electrochemical cell 502 further includes concentrated CO₂ vapor outlet 514. Salt reservoir 524 is in fluid communication with cathode chamber 525 via a second cation exchange membrane 510, such that cations can flow into the cathode chamber towards cathode 507. Cathode chamber 525 further includes H₂ outlet 513. The CO₂-lean amine solution is delivered (515) through the anion exchange column 503, where the chlorine counter-ion is replaced with hydroxide. A salt solution flows (516) back to salt reservoir 524, and catholyte flows from the cathode chamber to the anion exchange column. The regenerated amine solution completes the closed-loop and returns (518) to the CO₂ absorption chamber 501 to absorb additional CO₂. A sweep gas also may be provided to the system via inlet 519 to aid the desorbed gas flow. Finally, one-way (520) and two-way (521) valves can control flow in and out of anion exchange column 503.

The terms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to an object can include multiple objects unless the context clearly dictates otherwise.

As used herein, the terms “substantially,” “substantial,” “approximately,” and “about,” and the symbol “~,” are used to describe and account for small variations. When used in conjunction with an event or circumstance, the terms can refer to instances in which the event or circumstance occurs precisely as well as instances in which the event or circumstance occurs to a close approximation. When used in conjunction with a numerical value, the terms can refer to a range of variation of less than or equal to $\pm 10\%$ of that numerical value, such as less than or equal to $\pm 5\%$, less than or equal to $\pm 4\%$, less than or equal to $\pm 3\%$, less than or equal to $\pm 2\%$, less than or equal to $\pm 1\%$, less than or equal to $\pm 0.5\%$, less than or equal to $\pm 0.1\%$, or less than or equal to $\pm 0.05\%$. For example, a first numerical value can be deemed to be “substantially” the same or equal to a second numerical value if the first numerical value is within a range of variation of less than or equal to $\pm 10\%$ of the second numerical value, such as less than or equal to $\pm 5\%$, less than or equal to $\pm 4\%$, less than or equal to $\pm 3\%$, less than or equal to $\pm 2\%$, less than or equal to $\pm 1\%$, less than or equal to $\pm 0.5\%$, less than or equal to $\pm 0.1\%$, or less than or equal to $\pm 0.05\%$.

Additionally, amounts, ratios, and other numerical values are sometimes presented herein in a range format. It is to be understood that such range format is used for convenience and brevity and should be understood flexibly to include numerical values explicitly specified as limits of a range, but also to include all individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly specified. For example, a ratio in the range of about 1 to about 200 should be understood to include the explicitly recited limits of about 1 and about 200, but also to include individual ratios such as about 2, about 3, and about 4, and sub-ranges such as about 10 to about 50, about 20 to about 100, and so forth.

EXAMPLES

A proof-of-concept of the electrochemical pH-swing system was performed using a modified electrochemical cell containing four chambers (Figure 2). The dimensions of the cell were ~ 20 cm x ~ 14 cm x ~ 5.0 cm. The anode (~ 8 cm² of platinum immersed in ~ 0.5 M Na₂SO₄; ~ 2.9 cm thickness) and cathode (~ 8 cm² of 316 stainless steel in ~ 0.5 M NaCl; ~ 0.7 cm thickness) chambers were separated from a saturated salt (NaNO₃) solution (~ 0.7 cm thickness) and a CO₂-rich MEA solution (~ 0.5 mol CO₂ per mol MEA; ~ 0.7 cm thickness) using cation (~ 160 cm²; Fuel cell store, FAS-PET-130) and anion exchange membranes (~ 160 cm²; Fuel cell store, FAA-3-PK-75).

Next, to demonstrate the effectiveness of the electrochemical cells of some embodiments of the disclosure, ~50 mL of 22% v/v aqueous MEA solution was saturated with CO₂ via bubbling CO₂ until a liquid phase loading of ~0.5 mol CO₂ per mol MEA was achieved. The liquid phase loading was quantified by continuously measuring, via gas phase infrared (IR) spectroscopy, the CO₂ concentration in the gas phase effluent from the bubbling chamber, and then numerically integrating the resulting concentration versus time curve. The CO₂-rich MEA solution was loaded into the amine chamber with ~1 M NaNO₃ in the salt reservoir chamber and an overpotential was applied. CO₂ desorption was confirmed via infrared (IR) spectroscopy of MEA samples collected at various pH values. Figure 4A shows that the presence of carbamate ions (with characteristic peaks at 1568, 1486, 1320 cm⁻¹) decreases with a concomitant increase in the amount of protonated MEA (characteristic peak at 1517cm⁻¹) as the experiment proceeds (and as the pH decreases). Furthermore, the peak at 1340 cm⁻¹ indicates the presence of nitrate ions (NO₃⁻) accumulating in the amine solution via migration from the salt reservoir to maintain electroneutrality.

The extent of CO₂ desorption at pH = ~6, ~7, and ~8 was quantified by shifting the pH of these amine solutions (using NaOH) to ~10 followed by contacting with the gaseous CO₂ stream. This method indicated that a pH decrease from ~10 to ~6 corresponded to a >80% extent of desorption/regeneration (Figure 4B, Blue bars) at ambient temperature (~25°C). This regeneration extent was similar to that achieved by adding aliquots of ~5 M HCl followed by ~1M NaOH to achieve a similar pH shift (i.e., HCl addition to decrease from ~10 to ~6, ~7, or ~8 followed by NaOH addition to increase back to ~10; Figure 4B, *). To demonstrate the effectiveness of anion exchange resins to complete the pH-swing process, in certain embodiments, electrochemically acidified MEA (at pH = ~6, ~7, and ~8) was mixed with a commercial anion exchange resin (~200 ml of IRN78-OH) in a batch reactor for ~5 min. The solutions were then filtered to recover the resin and to test the MEA solution for CO₂ absorption. The pH of MEA solutions after exposure to the resin increased to ~11, and their capacities for CO₂ reabsorption were similar to those of the previous experiments (Figure 4B, #). Specifically, electrochemically acidifying a CO₂-rich MEA solution to pH = ~6 followed by exchange with IRN78-OH to pH = ~11 resulted in recovery of >80% of the initial absorption capacity. These results clearly demonstrate the effectiveness of the electrochemical-ion exchange pH-swing process for MEA regeneration at ambient temperature without capacity loss.

While the disclosure has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes may be made

and equivalents may be substituted without departing from the true spirit and scope of the disclosure as defined by the appended claim(s). In addition, many modifications may be made to adapt a particular situation, material, composition of matter, method, operation or operations, to the objective, spirit and scope of the disclosure. All such modifications are intended to be within the scope of the claim(s) appended hereto. In particular, while certain methods may have been described with reference to particular operations performed in a particular order, it will be understood that these operations may be combined, sub-divided, or re-ordered to form an equivalent method without departing from the teachings of the disclosure. Accordingly, unless specifically indicated herein, the order and grouping of the operations are not a limitation of the disclosure. As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present invention. Any recited method can be carried out in the order of events recited or in any other order which is logically possible.

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

This invention is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present invention will be limited only by the appended claims.

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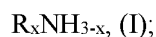
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WHAT IS CLAIMED IS:

1. A method of capturing CO₂, comprising:
 - i) reacting a CO₂ source gas with a stoichiometric excess of an amine in an aqueous solution to form an amine-CO₂ complex, thereby forming a solution comprising the amine-CO₂ complex;
 - ii) electrochemically adjusting the pH of the solution comprising the amine-CO₂ complex to less than 7, thereby releasing CO₂ from the amine-CO₂ complex; and
 - iii) collecting the released CO₂ as a concentrated vapor.
2. The method of claim 1, wherein the amine-CO₂ complex comprises carbamate ions.
3. The method of claim 1 or 2, wherein adjusting the pH is performed via water electrolysis.
4. The method of any one of claims 1 to 3, wherein the pH of the solution after adjustment is about 0.5 to about 6.
5. The method of any one of claims 1 to 3, wherein the pH of the solution after adjustment is about 0.5 to about 5.
6. The method of any one of claims 1 to 3, wherein the pH of the solution after adjustment is about 0.5 to about 4.
7. The method of any one of claims 1 to 3, wherein the pH of the solution after adjustment is about 0.5 to about 3.
8. The method of any one of claims 1 to 3, wherein the pH of the solution after adjustment is about 0.5 to about 2.
9. The method of any one of claims 1 to 3, wherein the pH of the solution after adjustment is about 0.5 to about 1.5.
10. The method of any one of claims 1 to 3, wherein the pH of the solution after adjustment is about 5 to about 6.
11. The method of any one of claims 1 to 10, wherein the amine is a primary amine, a secondary amine, a tertiary amine, or a mixture thereof.

12. The method of claim 11, wherein the amine is a primary amine or a secondary amine.
13. The method of claim 11 or 12, wherein the amine has a structure of formula I:



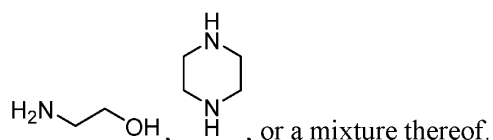
wherein R is selected from an optionally substituted alkyl, ether, and hydroxyalkyl;

x is 1, 2 or 3, and;

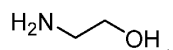
one or more R, together with each N, optionally forms a nitrogen containing heterocycle.

14. The method of any one of claims 1 to 13, wherein the amine is chosen from monoethanolamine, 2-ethylaminoethanol, 2-methylaminoethanol, ethylenediamine, benzylamine, diethanolamine, pyrrolidine, morpholine, 2,6-dimethylmorpholine, monoisopropanolamine, piperazine 2-(dimethylamino)ethanol, N-tert-butyl-diethanolamine, 3-dimethylamino-1-propanol, 3-(dimethylamino)-1,2-propanediol, 2-diethylaminoethanol, 3-diethylamino-1,2-propanediol, 3-diethylamino-1-propanol, triethanolamine, 1-dimethylamino-2-propanol, 1-(2-hydroxyethyl)pyrrolidine, 1-diethylamino-2-propanol, 3-pyrrolidino-1,2-propanediol, 2-(diisopropylamino)ethanol, 1-(2-hydroxyethyl)piperidine, 2-(dimethylamino)-2-methyl-1-propanol, 3-piperidino-1,2-propanediol, 3-dimethylamino-2,2-dimethyl-1-propanol, 3-hydroxy-1-methylpiperidine, N-ethyl-diethanolamine, 1-ethyl-3-hydroxypiperidine, and any combination thereof.

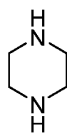
15. The method of any one of claims 1 to 14, wherein the amine is



16. The method of claim 15, wherein the amine is:



17. The method of claim 15, wherein the amine is:



18. The method of any one of claims 1 to 17, wherein the concentration of the amine in the aqueous amine solution is about 10% to about 50% v/v.
19. The method of claim 18, wherein the concentration of the amine is about 15% to about 40% v/v.
20. The method of claim 18, wherein the concentration of the amine is about 20 to about 30% v/v.
21. The method of anyone of claims 1 to 20, wherein the CO₂ source gas is an effluent from an industrial source.
22. The method of claim 21, wherein the gas from the industrial source comprises about 1 to about 12% v/v CO₂.
23. The method of any one of claims 1 to 22, wherein the CO₂ source gas is from an atmospheric source.
24. The method of anyone of claims 1 to 23, wherein adjusting the pH is performed at a temperature of less than 100 °C.
25. The method of anyone of claims 1 to 24, further comprising regenerating and collecting the aqueous amine solution and using the regenerated amine in step (i) of the method.
26. The method of claim any one of claims 1 to 25, wherein the concentrated vapor comprises about 2% to about 99% CO₂.
27. A system for capturing CO₂ from a CO₂ source gas comprising:
a CO₂ absorption chamber configured to contain an aqueous amine solution, the CO₂ absorption chamber having a CO₂ source gas inlet, and a concentrated CO₂ vapor outlet;

an electrochemical cell in fluid communication with the CO₂ absorption chamber and configured to receive a CO₂-rich aqueous amine solution from the CO₂ absorption chamber, the electrochemical cell comprising:

- an anode disposed in an anode chamber,
- a cathode disposed in a cathode chamber,
- a first cation exchange membrane disposed between the anode chamber and a first reservoir configured to receive a CO₂-rich aqueous amine solution such that protons may flow from the anode chamber to the first reservoir,
- an anion exchange membrane disposed between the first reservoir and a salt reservoir such that anions from the salt reservoir may flow towards the anode chamber,
- a second cation exchange membrane disposed between the salt reservoir and the cathode chamber such that cations may flow from the salt reservoir toward the cathode chamber; and
- an anion exchange column in fluid communication with the electrochemical cell and configured to: receive a CO₂-lean aqueous amine solution from the first reservoir, deliver a regenerated aqueous amine solution to the CO₂-absorption chamber, and receive a catholyte from the cathode chamber.

28. The system of claim 27, further comprising a concentrated CO₂ vapor outlet.

29. The system of claims 27 or 28, further comprising an H₂ outlet in fluid communication with the cathode chamber.

30. The system of any one of claims 27 to 29, further comprising an O₂ outlet in fluid communication with the anode chamber.

31. The system of any one of claims 27 to 30, wherein the electrochemical cell is configured to perform water electrolysis.