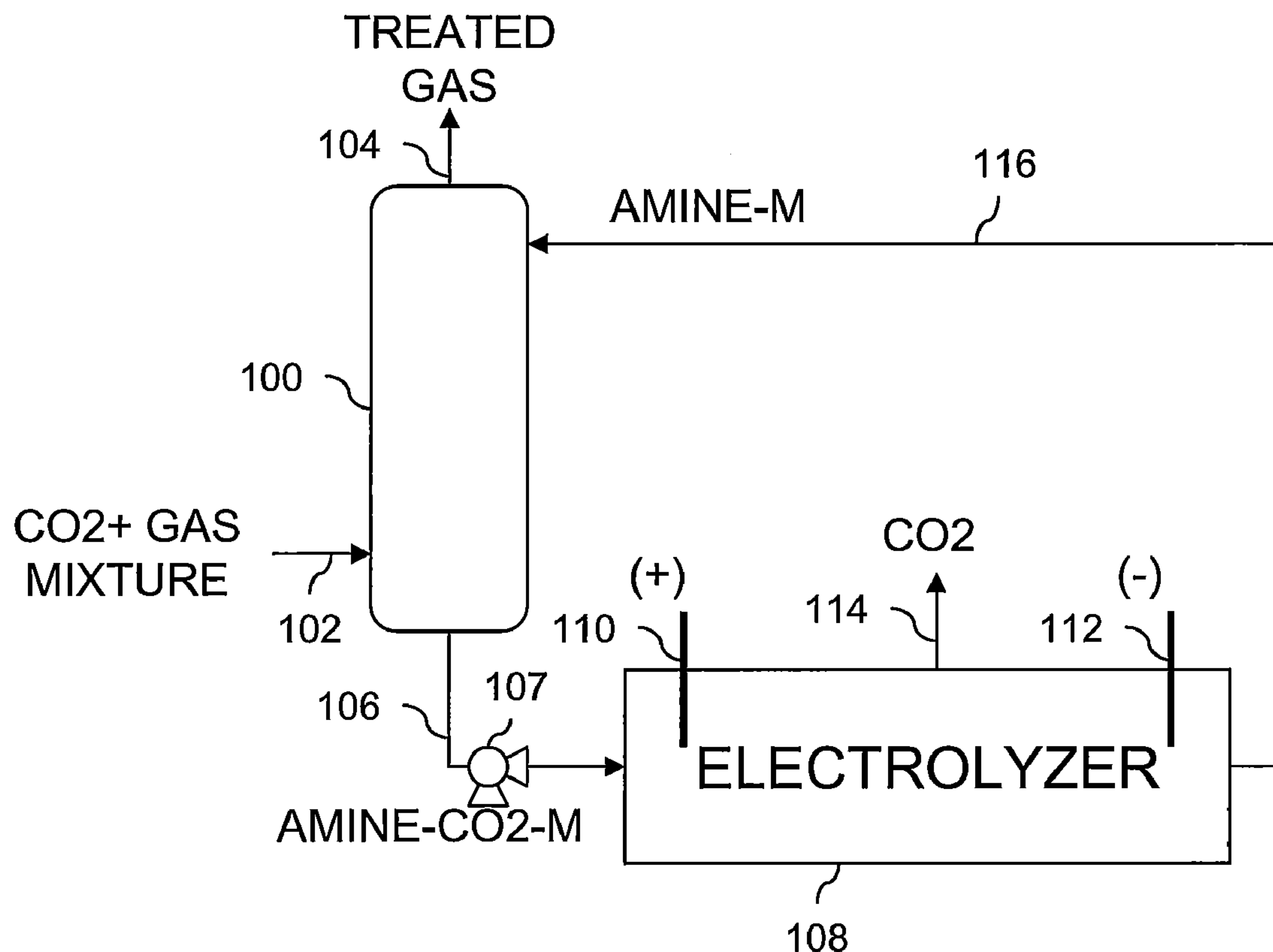


US 20110186441A1

(19) **United States**(12) **Patent Application Publication**
LaFrancois et al.(10) **Pub. No.: US 2011/0186441 A1**(43) **Pub. Date: Aug. 4, 2011**(54) **ELECTROLYTIC RECOVERY OF RETAINED
CARBON DIOXIDE****Publication Classification**(75) Inventors: **Christopher J. LaFrancois**,
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(US)(51) **Int. Cl.**
C25B 1/00 (2006.01)(52) **U.S. Cl.** **205/555**(73) Assignee: **ConocoPhillips Company**,
Houston, TX (US)(57) **ABSTRACT**(21) Appl. No.: **13/012,319**(22) Filed: **Jan. 24, 2011****Related U.S. Application Data**(60) Provisional application No. 61/299,775, filed on Jan.
29, 2010.

Methods and apparatus relate to capturing carbon dioxide. A solution formed from metal ions combined with an amine reagent absorbs carbon dioxide from gas introduced into the solution. Subsequent electrolysis of the solution results in dissociation of complexes formed upon the carbon dioxide being absorbed. The electrolysis thus liberates the carbon dioxide for capture and regenerates the solution for reuse.



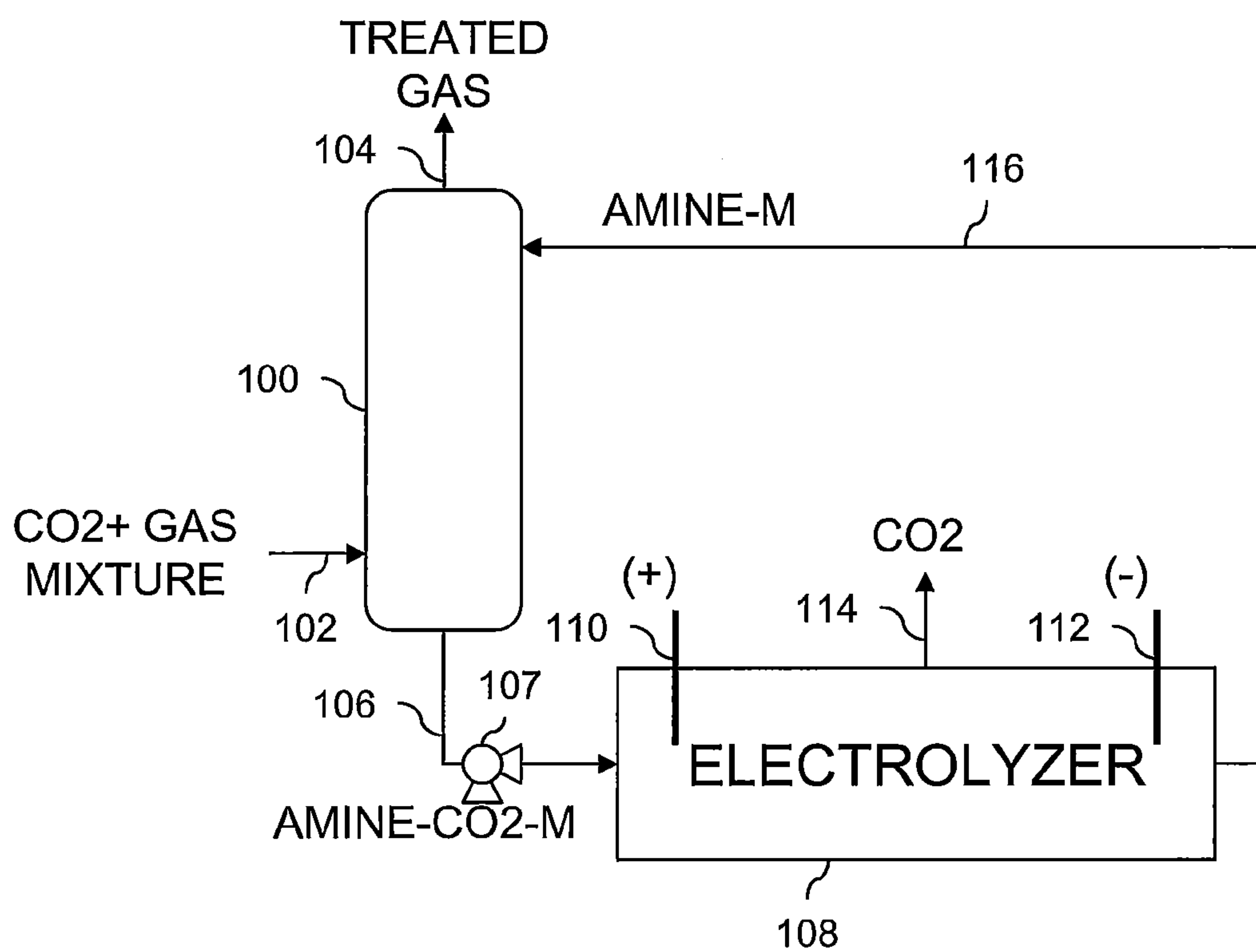


FIG. 1

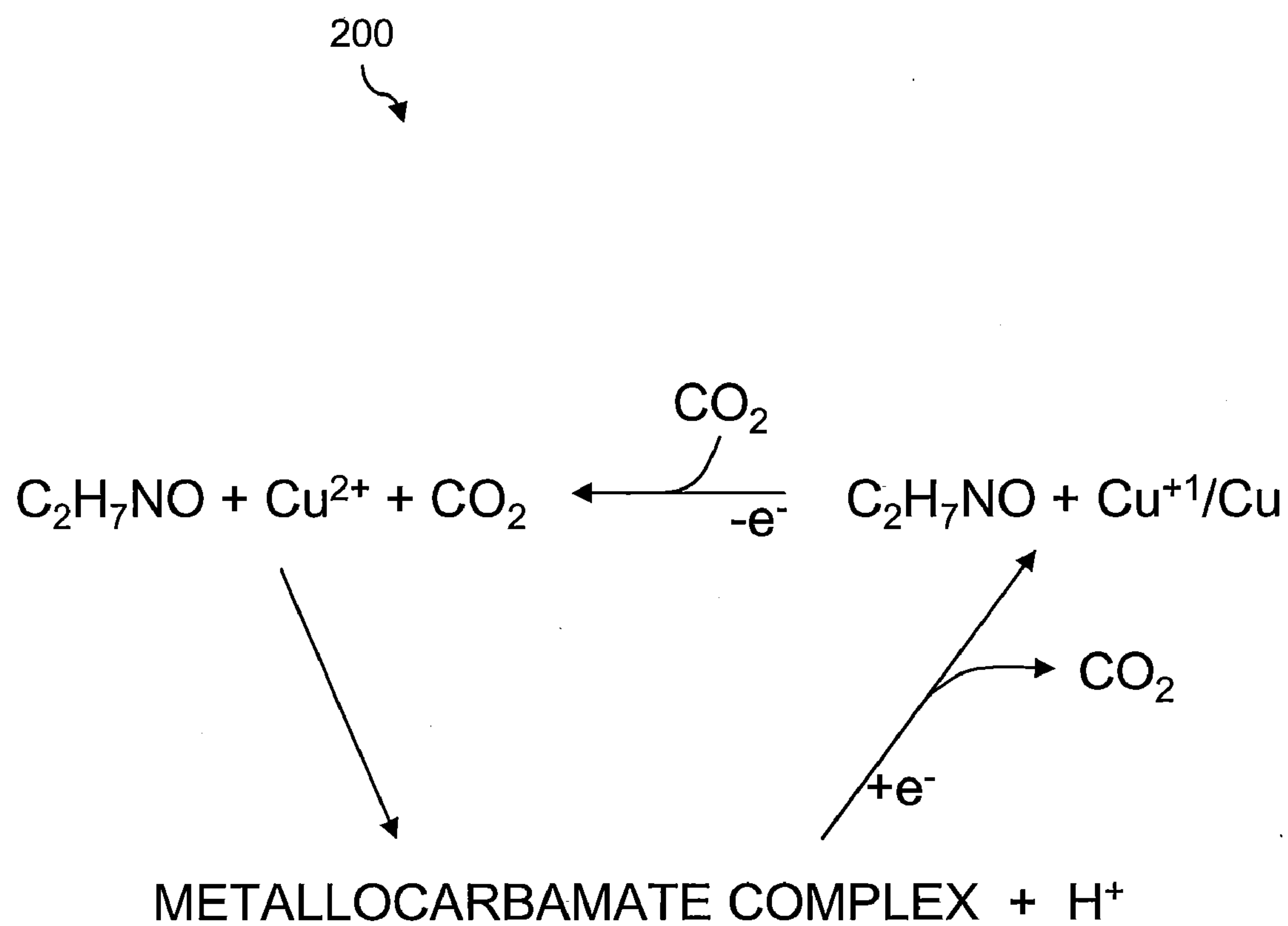


FIG. 2

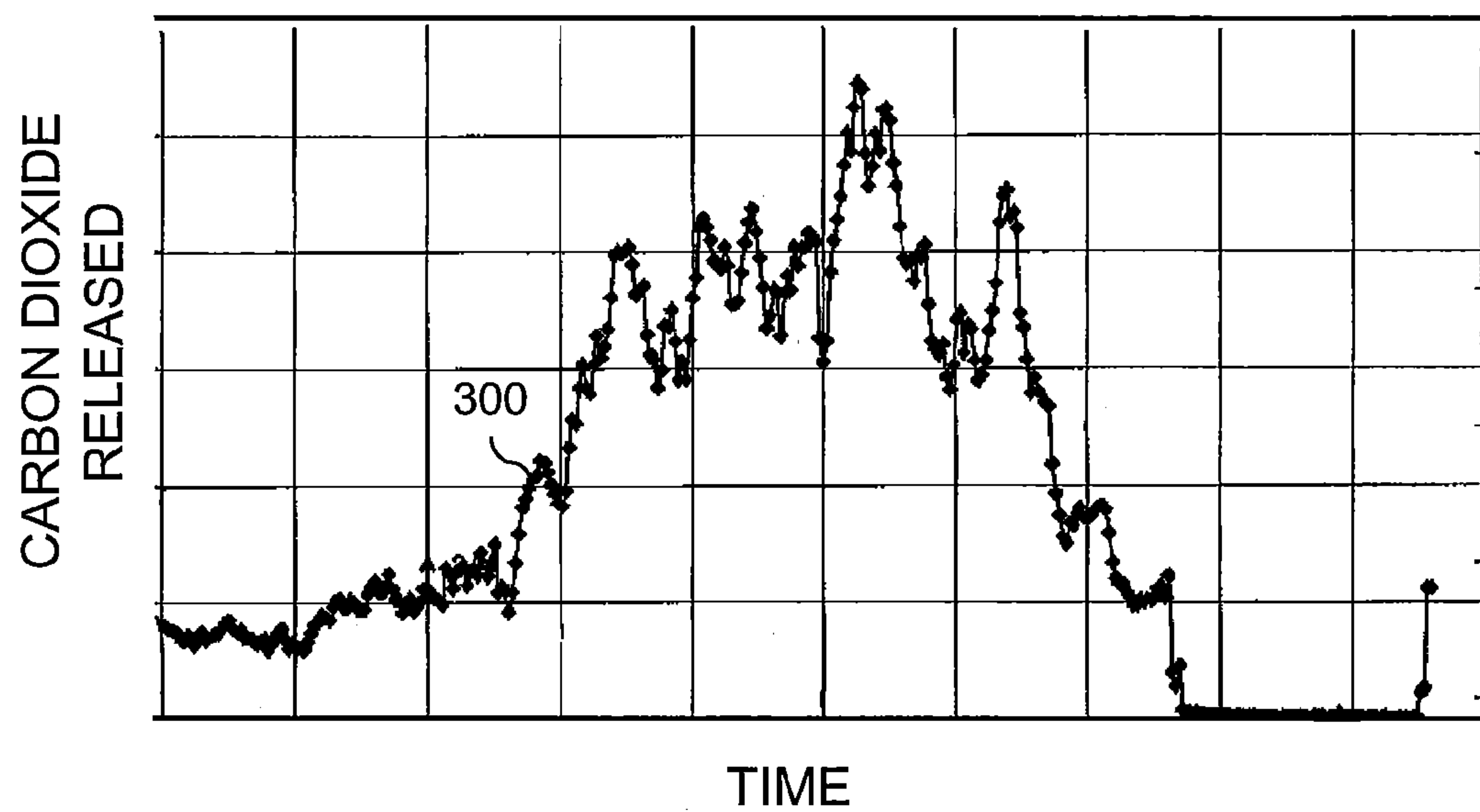


FIG. 3

ELECTROLYTIC RECOVERY OF RETAINED CARBON DIOXIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a non-provisional application which claims the benefit of and priority to U.S. Provisional Application Ser. No. 61/299,775 filed Jan. 29, 2010, entitled "Electrolytic Recovery of Retained Carbon Dioxide," which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] None

FIELD OF THE INVENTION

[0003] Embodiments of the invention relate to methods and systems for electrolytic recovery of retained gasses from absorption liquid to regenerate the absorption liquid.

BACKGROUND OF THE INVENTION

[0004] One approach to reducing emissions of carbon dioxide gas includes recovery of the carbon dioxide from power plants and other point sources. Such recovery depends on ability to remove or capture the carbon dioxide from other gasses. By example, sequestration of the carbon dioxide once captured provides ability to dispose of the carbon dioxide without creating atmospheric environmental issues.

[0005] A prior technique that enables the recovery of the carbon dioxide utilizes an amine solution that absorbs the carbon dioxide and is then regenerated by steam stripping. However, generating steam by burning fossil fuels in order to release the carbon dioxide from the amine solution produces more carbon dioxide and contributes to operational costs making the recovery expensive. Other problems associated with such prior systems include need to further purify an overhead containing the carbon dioxide released during the steam stripping to remove water and need to compress the carbon dioxide via inefficient as compression. Size of vessels required for the steam stripping can also limit ability to locate the prior systems where desired. Further, raising temperature of the amine solution with the steam stripping results in undesired increasing corrosiveness of the amine solution in contact with components of the system.

[0006] Therefore, a need exists for improved methods and systems that enable carbon dioxide capture.

SUMMARY OF THE INVENTION

[0007] In one embodiment, a method of capturing carbon dioxide from a gas mixture includes contacting an aqueous solution formed from amine and metal ions with the gas mixture thereby forming metallocarbamate complexes from the amine, the metal ions and the carbon dioxide. Separating the aqueous solution from unabsorbed constituents of the gas mixture occurs after the contacting. Applying an electric potential to the aqueous solution recovered by the separating causes dissociation of the metallocarbamate complexes in order to liberate the carbon dioxide for capture.

[0008] According to one embodiment, a method of capturing carbon dioxide from a gas mixture includes forming an aqueous solution by mixing monoethanolamine and copper ions from copper sulfate. Contacting the aqueous solution

with the gas mixture forms metallocarbamate complexes from the monoethanolamine, the copper ions and the carbon dioxide. The method further includes separating the aqueous solution from unabsorbed constituents of the gas mixture after the contacting. Pumping the aqueous solution recovered by the separating increases pressure of the aqueous solution to above a first pressure associated with the contacting prior to applying an electric potential to the aqueous solution to liberate from the aqueous solution the carbon dioxide at a second pressure above the first pressure.

[0009] For one embodiment, a method of capturing carbon dioxide from a gas mixture includes forming an aqueous solution by mixing amine and metal ions with less of the metal ions added on a mole basis than the amine. Contacting the aqueous solution with the gas mixture causes the aqueous solution to absorb the carbon dioxide. Separating the aqueous solution from unabsorbed constituents of the gas mixture occurs after the contacting. In addition, the method includes applying an electric potential to the aqueous solution recovered by the separating such that throughout the applying of the electric potential one of the metal ions reacts with more than one molecule to facilitate liberation of the carbon dioxide and regeneration of the aqueous solution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The invention, together with further advantages thereof, may best be understood by reference to the following description taken in conjunction with the accompanying drawings.

[0011] FIG. 1 is a schematic of a system for carbon dioxide capture, according to one embodiment.

[0012] FIG. 2 is an exemplary reaction pathway to enable capturing carbon dioxide, according to one embodiment.

[0013] FIG. 3 is a plot of carbon dioxide released by electrolysis from an aqueous solution, according to one embodiment.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Embodiments of the invention relate to capturing carbon dioxide. A solution formed from metal ions combined with an amine reagent absorbs carbon dioxide from gas introduced into the solution. Subsequent electrolysis of the solution results in dissociation of complexes formed upon the carbon dioxide being absorbed. The electrolysis thus liberates the carbon dioxide for capture and regenerates the solution for reuse.

[0015] FIG. 1 shows a system for carbon dioxide (CO₂ or "CO2") capture that includes an absorber vessel 100 in which a gas mixture containing carbon dioxide enters via gas input 102. The gas mixture passes through the absorber vessel 100 and contacts a liquid solution formed from amine and metal "M" ions prior to exiting the absorber vessel 100 via gas output 104 as treated gas. Unabsorbed constituents of the gas mixture thus separate in the absorber vessel 100 from the solution after the contacting to provide the treated gas.

[0016] The solution absorbs the carbon dioxide from the gas mixture such that the treated gas contains a lower concentration of the carbon dioxide than present in the gas mixture as introduced into the absorber vessel 100 at the gas input 102. In some embodiments, flue gas defines the gas mixture, which thus may include between about 3% and about 30% carbon dioxide by volume and other exhaust gasses, such as about 70% to about 95% nitrogen. For some embodiments,

passage of the gas mixture through the absorber **100** removes at least about 70%, at least about 80% or at least about 90% of the carbon dioxide from the gas mixture.

[0017] In operation, the solution in the absorber vessel **100** over time becomes saturated with the carbon dioxide and for continuous operation must therefore be replenished with new or regenerated solution. A rich liquid conduit **106** from the absorber vessel **100** couples the absorber vessel **100** with an optional pump **107** and an electrolysis cell **108**, which is used to regenerate the solution by releasing the carbon dioxide from complexes formed from the amine, the carbon dioxide and the metal ions. The electrolysis cell **108** includes a counter electrode **110** and a working electrode **112** that supply an electric potential to the solution in the electrolysis cell **108**. The working electrode **112** reduces metal in the complex resulting in release of the carbon dioxide. Alternating between positive and negative potentials ensures the metal ions are not depleted by elemental metal plating on the working electrode **112**. For some embodiments, a liquid-gas phase selective membrane may facilitate separation of the carbon dioxide from the solution upon the carbon dioxide being liberated from the complexes. A carbon dioxide recovery outlet **114** of the electrolysis cell **108** captures the carbon dioxide liberated within the electrolysis cell **108**.

[0018] Controlling voltage applied during the electrolysis and selection of the counter and working electrodes **110**, **112** can avoid competing reactions and decomposition of water concurrent with the release of the carbon dioxide from the solution in the electrolysis cell **108**. While the voltage depends on reactant concentrations in the solution and composition of the electrodes **110**, **112**, the voltage in some embodiments cycles between about -3 volts to about +3 volts. Alternating between positive and negative potentials about each minute, for example, ensures that the metal ions are not depleted from the solution as a result of precipitation or plating on the working electrode **112**.

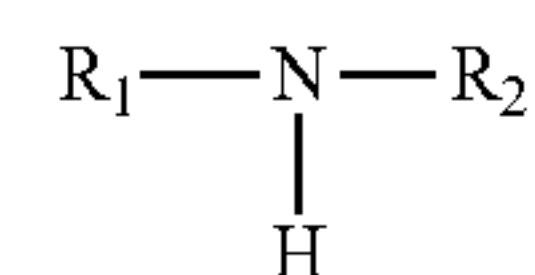
[0019] Experiments utilizing stainless steel for both the electrodes **110**, **112** liberated the carbon dioxide but also resulted in some water electrolysis. As shown by an Example herein, providing the working electrode **112** made out of carbon allows separation of the carbon dioxide without release of hydrogen, which occurs with the carbon at higher voltages relative to carbon dioxide being liberated. A conductive metal that is either inert in the solution or provides the metal ions may form the counter electrode **110**. Platinum for example may form the counter electrode **110** in order to avoid introduction of metal ions such as iron that can form undesired complexes with the amine.

[0020] The pump **107** in fluid communication with the solution inside the absorber vessel **100** and inside the electrolysis cell **108** functions to increase pressure of the solution that is fed to the electrolysis cell **108** to above a first pressure, such as ambient pressure, associated with the contacting inside the absorber vessel **100**. In some embodiments, the pump **107** maintains the solution inside the electrolysis cell **108** at sufficient elevated pressure such that the carbon dioxide is released at a second pressure, such as above about 6750 kilopascal, higher than the first pressure. The carbon dioxide output through the recovery outlet **114** may not require further compression for transport or sequestration purposes due to use of the pump **107**.

[0021] A lean liquid line **116** couples the electrolysis cell **108** to the absorber vessel **100** to resupply the solution for more carbon dioxide absorption. The lean liquid line **116**

contains the solution formed from the amine and the metal ions with the carbon dioxide removed upon the solution being regenerated in the electrolysis cell **108**. The solution thus cycles through the absorber vessel **100** and the electrolysis cell **108** for treating a stream of the gas mixture fed into the gas input **102**.

[0022] For some embodiments, the amine used to form the solution includes a linear or noncyclical amine in water such that the solution is aqueous. A general formula provided as



may represent the amine with R_1 being $C_xH_{2x}OH$ and R_2 being one of hydrogen and $C_yH_{2y}OH$, given x and y are from 1 to 8, or 2 to 4. Specific alcohol amines that were tested and demonstrated suitability include monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and diglycolamine (DGA).

[0023] In some embodiments, linearity of the amine and the amine having at least one hydrogen atom bound to nitrogen of the amine helps ensure that the nitrogen remains sterically free and available for carbamate formation. Further, noncyclical formulas of the amine lack sites where the metal ion complexes for carbonate formation preferential to the carbamate formation during the carbon dioxide absorption. In operation, complexes formed by absorption of the carbon dioxide may thus not include carbonate groups.

[0024] In some embodiments, the metal ions used to form the solution include at least one of copper, zinc, cobalt, nickel, aluminum and magnesium and may be di-cationic species. The complexes formed from the amine, the metal ions and the carbon dioxide provide ionic charged species that are influenced by the electrical potential such that reduction is achieved at the working electrode **112** of the electrolysis cell **108**. Experiments utilizing amine, such as MEA, without the metal ion proved inability for electrolytic release from the amine of the carbon dioxide absorbed. While possible to separate conductive mixtures like sodium hydroxide, the amine alone cannot achieve recovery of the carbon dioxide using electrolysis.

[0025] For some embodiments, adding a metal salt to a reagent containing the amine forms the solution with the metal ions from the metal salt. Selection of the metal salt depends on solubility of the metal salt and avoidance of anion interference with electrochemistry. Examples of the metal salt include copper sulfate ($CuSO_4$) or copper perchlorate ($Cu(ClO_4)_2$). In some embodiments, a metal electrode, such as the counter electrode **110** or a different disposable anode, within a reagent containing the amine supplies a source of the metal ions to form the solution upon electric current dissolving the metal electrode. Copper ions can for example come from use of the working electrode **110** if made from copper.

[0026] Various factors influence amount of the metal ions and the amine added to form the solution. Addition of either the amine or the metal ions enables adjusting levels of the amine and the metal ions independent of one another in the solution at any time as needed. Reaction efficiency increases with amount of the metal ions added to make the solution. Even with stabilization of the metal ions by the amine, potential for formation of metal carbonate that is not able to be

regenerated limits increasing concentration of the metal ions. Corrosion issues also limit increasing concentration of the amine.

[0027] The solution is formed on a mole basis from less of the metal ions than the amine such that there is not a 1:1 stoichiometric quantity of the metal ions to the amine. Each of the metal ions thus reacts with different molecules containing the amine throughout regeneration of the solution while applying the electric potential. In an exemplary embodiment, the forming of the solution includes mixing reagent of between about 10 percent and about 20 percent MEA in water with copper sulfate such that copper ions added are between about 1 mole percent and about 5 mole percent relative to the MEA.

[0028] FIG. 2 illustrates an exemplary reaction cycle 200 employed such as described with the system in FIG. 1. MEA, copper ions and carbon dioxide react to form metallocarbamate complexes. Reduction of copper within the metallocarbamate complexes by electrolysis liberates the carbon dioxide, which is separated from the solution. Reversing electric potential oxidizes metallic copper or reduced copper ions for further formation of the metallocarbamate complexes upon reaction with additional carbon dioxide.

EXAMPLE

[0029] A solution for absorbing carbon dioxide was prepared by adding copper sulfate to a 15 percent aqueous solution of MEA such that copper was 3 mole percent relative to the MEA. The solution was enriched with carbon dioxide through sparging. An electric potential was then applied to the solution utilizing a carbon working electrode and a stainless steel counter electrode. Effluent gasses from the solution during application of the electric potential were collected and passed through a mass spectrometer for analysis.

[0030] FIG. 3 shows the carbon dioxide released based on a plot of ion current detected with the mass spectrometer as a function of time. Data 300 corresponds to the carbon dioxide released from the solution increasing as voltage decreased from -1 volts to -5 volts prior to stopping application of the electric potential, at which point residual amounts of the carbon dioxide liberated were detected as the effluent gasses diminished to zero. The effluent gas was also monitored with the mass spectrometer for hydrogen, which was not detected in the effluent gas throughout the time plotted.

[0031] The preferred embodiment of the present invention has been disclosed and illustrated. However, the invention is intended to be as broad as defined in the claims below. Those skilled in the art may be able to study the preferred embodiments and identify other ways to practice the invention that are not exactly as described herein. It is the intent of the inventors that variations and equivalents of the invention are within the scope of the claims below and the description, abstract and drawings are not to be used to limit the scope of the invention.

1. A method comprising:

contacting an aqueous solution formed from amine and metal ions with a gas mixture containing carbon dioxide, wherein the contacting forms metallocarbamate complexes from the amine, the metal ions and the carbon dioxide;

separating the aqueous solution from unabsorbed constituents of the gas mixture after the contacting; and

applying an electric potential to the aqueous solution recovered by the separating, wherein the electric poten-

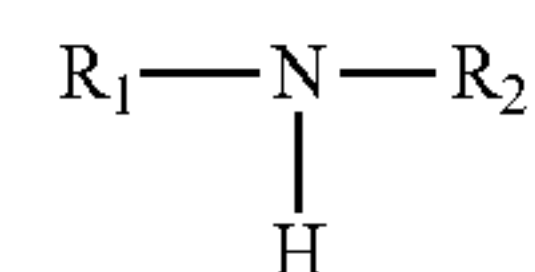
tial causes dissociation of the metallocarbamate complexes in order to liberate the carbon dioxide for capture.

2. The method according to claim 1, wherein the aqueous solution is formed on a mole basis from less of the metal ions than the amine.

3. The method according to claim 1, wherein one of the metal ions reacts with different molecules throughout regeneration of the aqueous solution by the applying of the electric potential.

4. The method according to claim 1, wherein the amine includes alcohol amine.

5. The method according to claim 1, wherein the amine has a formula



with R_1 being $C_xH_{2x}OH$ and R_2 being one of hydrogen and $C_xH_{2x}OH$ given x is from 2 to 4.

6. The method according to claim 1, wherein the amine includes at least one of monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and diglycolamine (DGA).

7. The method according to claim 1, wherein the metal ions include at least one of copper, zinc, cobalt, nickel, aluminum and magnesium.

8. The method according to claim 1, wherein the metal ions include copper.

9. The method according to claim 1, wherein the amine includes monoethanolamine and the metal ions include copper.

10. The method according to claim 1, wherein the applying of the electric potential includes cycling a working electrode between positive and negative potentials.

11. The method according to claim 1, wherein the applying of the electric potential utilizes a carbon working electrode.

12. The method according to claim 1, wherein the applying of the electric potential occurs with the aqueous solution pumped above a first pressure associated with the contacting such that the carbon dioxide is liberated at a second pressure above the first pressure.

13. The method according to claim 1, further comprising forming the aqueous solution by adding a metal salt to a reagent containing the amine, wherein the metal ions are from the metal salt.

14. The method according to claim 1, further comprising forming the aqueous solution using a counter electrode made from source metal in a reagent containing the amine, wherein the metal ions are from the source metal of the counter electrode.

15. The method according to claim 1, wherein the applying of the electric potential regenerates the aqueous solution for reuse in a cycle of more carbon dioxide absorption and liberation.

16. A method comprising:

forming an aqueous solution by mixing monoethanolamine and copper ions from copper sulfate;

contacting the aqueous solution with a gas mixture containing carbon dioxide, wherein the contacting forms metallocarbamate complexes from the monoethanolamine, the copper ions and the carbon dioxide;

separating the aqueous solution from unabsorbed constituents of the gas mixture after the contacting;
pumping the aqueous solution recovered by the separating to increase pressure of the aqueous solution to above a first pressure associated with the contacting; and
applying an electric potential to the aqueous solution to liberate from the aqueous solution the carbon dioxide at a second pressure above the first pressure due to the pumping.

17. The method according to claim **16**, wherein the forming of the aqueous solution includes mixing reagent of between 10 percent and 20 percent monoethanolamine in water with the copper sulfate such that the copper ions added are between 1 mole percent and 5 mole percent relative to the monoethanolamine.

18. A method comprising:
forming an aqueous solution by mixing amine and metal ions, wherein on a mole basis less of the metal ions are added than the amine;

contacting the aqueous solution with a gas mixture containing carbon dioxide, wherein the aqueous solution absorbs the carbon dioxide;

separating the aqueous solution from unabsorbed constituents of the gas mixture after the contacting; and
applying an electric potential to the aqueous solution recovered by the separating, wherein one of the metal ions reacts with more than one molecule to facilitate liberation of the carbon dioxide and regeneration of the aqueous solution throughout the applying of the electric potential.

19. The method according to claim **18**, wherein metal-carbamate complexes form upon the aqueous solution absorbing the carbon dioxide.

20. The method according to claim **18**, wherein the applying of the electric potential includes cycling between positive and negative voltages.

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