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HAN et al.(10) **Pub. No.: US 2017/0191173 A1**(43) **Pub. Date: Jul. 6, 2017**(54) **METHOD FOR PREPARING CARBONATE****Publication Classification**(71) Applicants: **KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY**, Daejeon (KR); **SAUDI ARAMCO**, Dhahran (SA)(51) **Int. Cl.**
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C25B 1/16 (2006.01)(52) **U.S. Cl.**
CPC . **C25B 1/14** (2013.01); **C25B 1/16** (2013.01)(72) Inventors: **Jongin HAN**, Daejeon (KR); **Jieun SON**, Daejeon (KR); **Jane CHUNG**, Daejeon (KR); **Dongsu SONG**, Daejeon (KR)(57) **ABSTRACT**

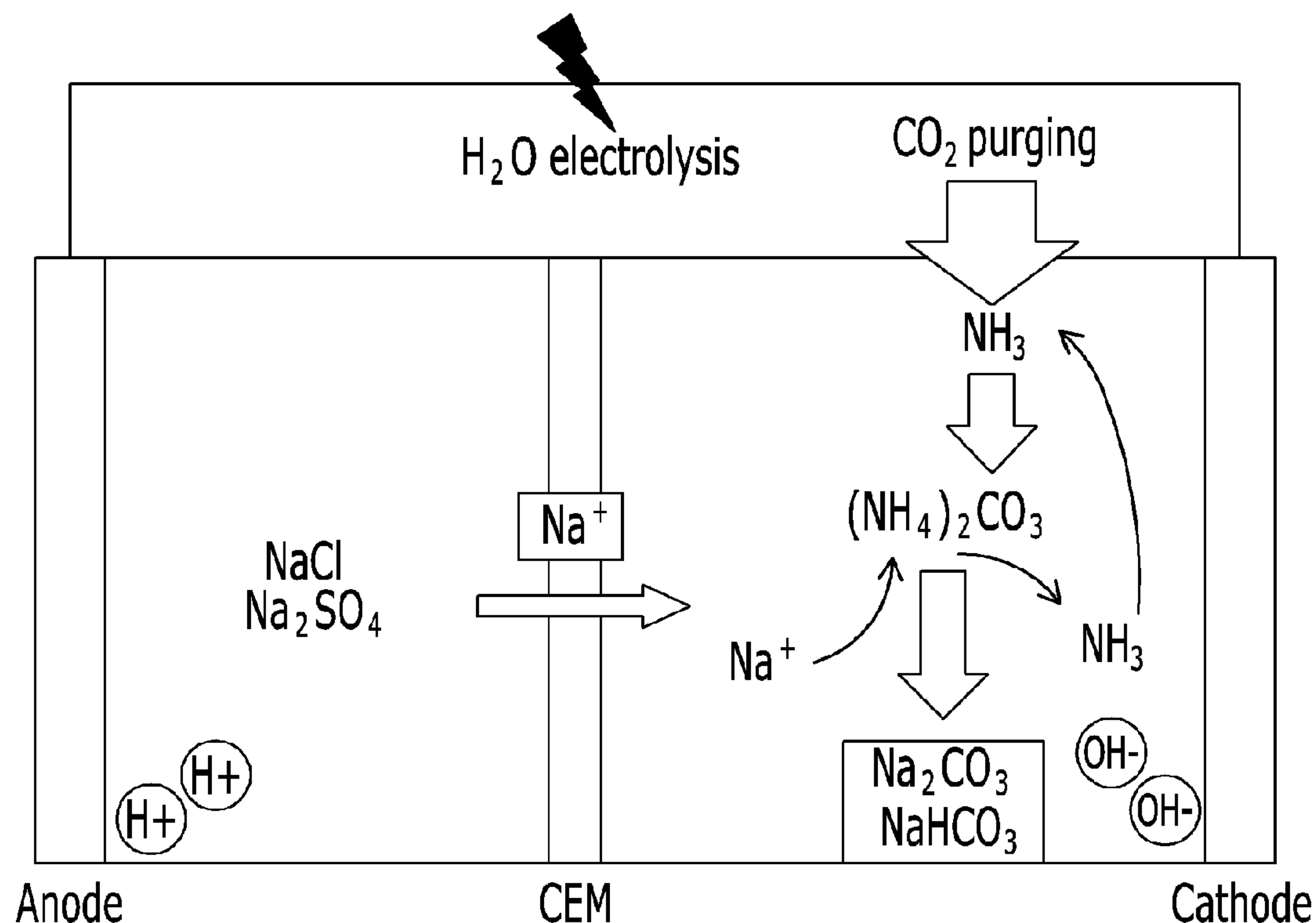
The present invention relates to a method for preparing a carbonate salt. The method for preparing a carbonate salt can provide a useful material by implementing a carbon dioxide capture method via a capturing agent such as ammonia with an electrolytic device to produce a carbonate salt, and thus capturing carbon dioxide from the atmosphere. Further, the preparation method may purely produce a carbonate salt without generating by-products using electric energy, and at the same time, the capturing agent may be reused without any additional process. Furthermore, the preparation method may selectively provide a carbonate salt in the desired form by adjusting the pH of a solution containing the carbonate salt using the electrolysis of water.

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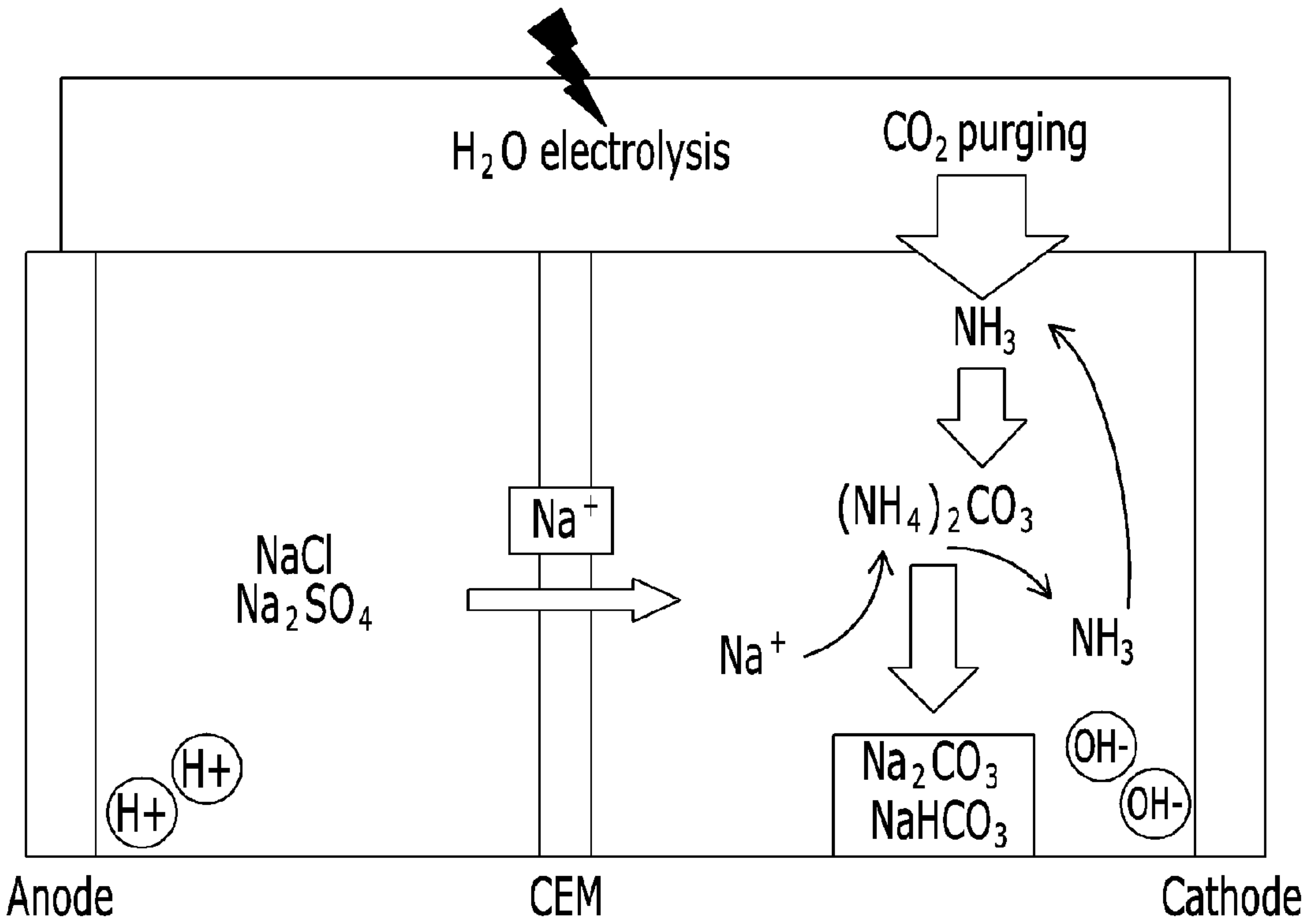
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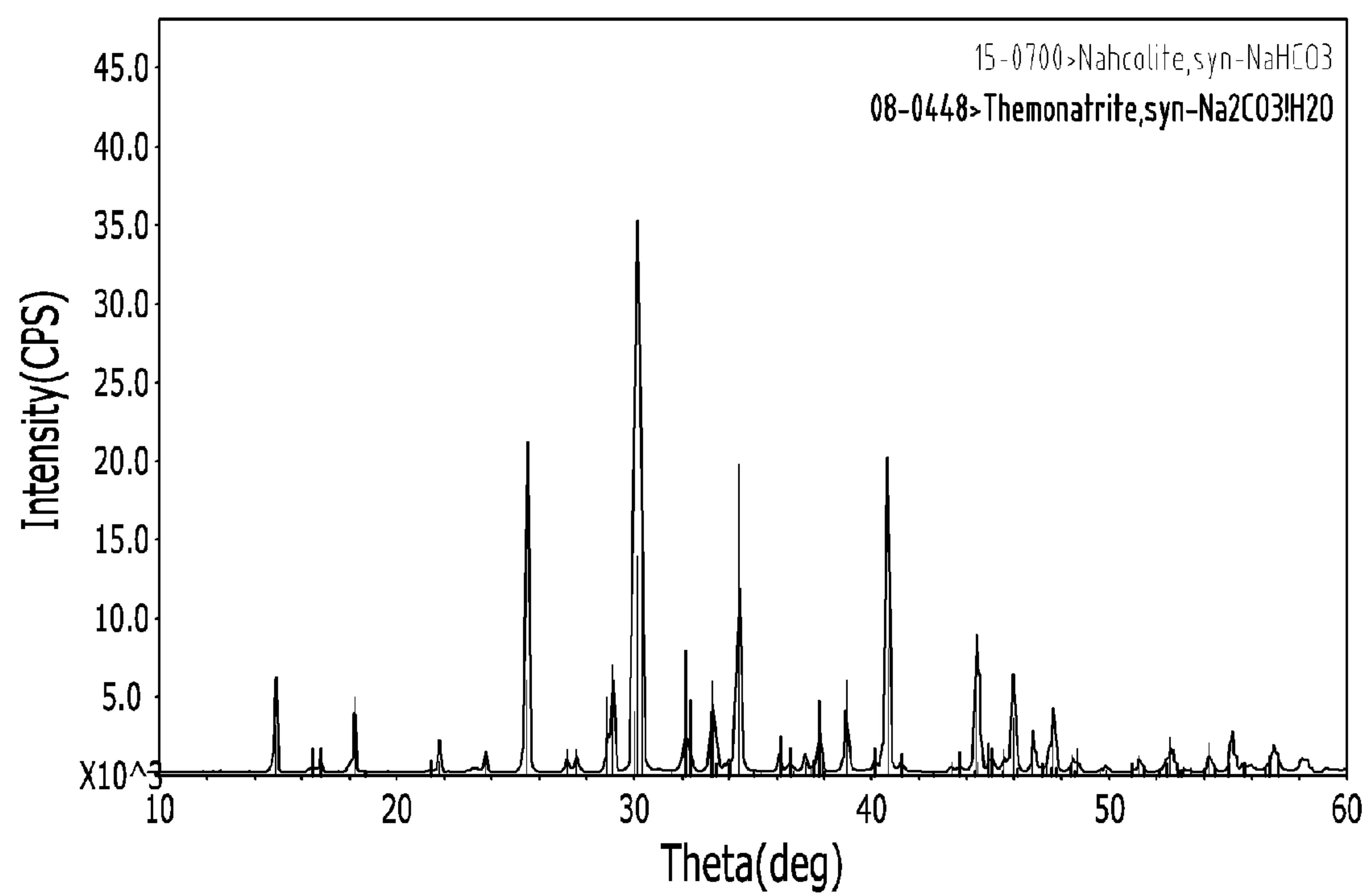
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【FIG. 1】



【FIG. 2】



METHOD FOR PREPARING CARBONATE

TECHNICAL FIELD

[0001] The present invention relates to a method for preparing a carbonate salt which can provide a pure carbonate without by-products by capturing carbon dioxide from the atmosphere.

BACKGROUND OF ART

[0002] Carbon dioxide is a typical greenhouse gas. Recently, most countries including Korea are committed to reducing carbon dioxide emission into the atmosphere to mitigate the global warming.

[0003] As one of the methods for capturing atmospheric carbon dioxide, there is a method for ionizing carbon dioxide into a carbonate ion by injecting carbon dioxide into an aqueous solution containing a dissolved catalyst having an amine group. The typical catalyst materials to increase the reaction rate of such ionization include MEA (monoethanolamine) or ammonia, etc. Among them, the research on carbon dioxide capture using ammonia solution has been in progress for a long time, and this process is particularly referred to as ammonia scrubbing. When carbon dioxide gas is injected into ammonia solution, the carbon dioxide ionizes into carbonate ions and binds to ammonium cations to produce ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$, ammonium bicarbonate $(\text{NH}_4\text{HCO}_3)$ or ammonium carbamate $(\text{NH}_2\text{COONH}_4)$.

[0004] Although it is not practically applied for carbon dioxide reduction from the atmosphere, a process of converting gaseous carbon dioxide into sodium carbonate using an ammonia solution, which is useful for carbon dioxide ionization, is widely used in industrial fields. This is often referred to as ammonia-soda process (Solvay process). In this process, (1) carbon dioxide is first injected into an ammonia solution. As a result, carbon dioxide is ionized to be in a state of being capable of binding to cations. (2) Sodium chloride is then added to the solution.

[0005] In this case, the carbonate ions generated from the carbon dioxide binds to the sodium ions dissociated from the sodium chloride, thereby obtaining sodium bicarbonate (NaHCO_3) as a precipitate. During this process, ammonium chloride (NH_4Cl) is produced as a by-product. (3) The solid sodium bicarbonate is converted to sodium carbonate (Na_2CO_3) , which is a desired product, by calcination at high temperature. (4) Then, ammonia can be reused by regenerating ammonia by reacting ammonium chloride produced from step (2) with calcium oxide (CaO) . However, calcium chloride (CaCl_2) is produced as a by-product during this process. (5) When the above process is used in industrial fields, calcium oxide and carbon dioxide used in the process can be supplied by calcinating calcium carbonate at high temperature.

[0006] This process can be applied to the actual atmospheric carbon dioxide capture to convert carbon dioxide into sodium carbonate, but it has disadvantages in that (a) calcium chloride is produced as a final by-product, and (b) pretreatment with high heat energy for reuse of ammonia and additional compounds such as calcium carbonate are necessary. Therefore, research on a new system which can compensate these disadvantages is desperately needed.

PRIOR ART DOCUMENTS

Non-Patent Documents

[0007] H. Bai and A. Yeh, Removal of CO_2 Greenhouse Gas by Ammonia Scrubbing, Industrial & Engineering Chemistry Research, 36: 2490-2493, 1997.

[0008] G. Steinhauser, Cleaner production in the Solvay Process: general strategies and recent developments, Journal of Cleaner Production 16: 833-841, 2008.

DETAILED DESCRIPTION OF THE INVENTION

Technical Problem

[0009] The present invention provides a method for preparing a carbonate salt which can produce a pure carbonate salt without by-products by capturing carbon dioxide from the atmosphere.

Technical Solution

[0010] One embodiment of the present invention provides a method for preparing a carbonate salt using an apparatus that comprises an anode chamber; a cathode chamber, which is separated from the anode chamber by a cation exchange membrane; an anode disposed in the anode chamber; and a cathode disposed in the cathode chamber, the method comprising the steps of:

[0011] supplying an aqueous solution containing an alkali metal salt or an alkaline earth metal salt to the anode chamber;

[0012] supplying a carbon dioxide and a capturing solution to the cathode chamber; and

[0013] applying a voltage to the anode and the cathode such that the cations separated from the aqueous solution containing an alkali metal salt or an alkaline earth metal salt move toward the cathode chamber through the cation exchange membrane

[0014] In the above, the capturing solution having a molar concentration of 2 M to 10 M may be used. In addition, an ammonia solution may be used as the capturing solution.

[0015] In the above, an external voltage of 2 V to 10 V may be applied to the anode and the cathode.

[0016] The preparation method above may further comprise discharging a precipitate from the cathode chamber.

Advantageous Effects

[0017] The method for preparing a carbonate salt according to one embodiment of the present invention can provide a useful material by implementing a carbon dioxide capture method via a capturing agent such as ammonia with an electrolytic device to produce a carbonate salt, and thus capturing carbon dioxide from the atmosphere. Further, the preparation method may produce a pure carbonate salt without generating by-products using electric energy, and at the same time, the capturing agent may be reused without any additional process. Furthermore, the preparation method may selectively provide a carbonate salt in the desired form by adjusting the pH of a solution containing the carbonate salt using the electrolysis of water.

BRIEF DESCRIPTION OF DRAWINGS

[0018] FIG. 1 is a schematic diagram showing an apparatus for producing carbonate salt according to one embodiment.

[0019] FIG. 2 is data showing XRD (X-ray diffraction) analysis results of precipitates generated in the cathode chamber when aqueous solutions of sodium chloride and sodium sulfate are used as an aqueous solution containing an alkali metal salt or an alkaline earth metal salt, and an ammonia solution is used as a capturing solution.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0020] Hereinafter, the method for preparing a carbonate salt according to one embodiment of the present invention will be described in detail with reference to the accompanying drawings. However, these Examples are presented for illustrative purposes only and the scope of the invention are not intended to be limited by these Examples.

[0021] The method for preparing a carbonate salt according to one embodiment of the present invention may provide a carbonate salt by using an apparatus for producing carbonate salt with the application of an electrolytic device. As used herein, the term carbonate salt refers to all salts including CO_3^{2-} , and therefore, the carbonate salt includes all salts including carbonate ions (CO_3^{2-}) and bicarbonate ions (HCO_3^-).

[0022] With reference to FIG. 1, the apparatus for producing carbonate salt includes two chambers separated by a cation exchange membrane (CEM). Among the two chambers, a chamber disposed with an anode is referred to as an anode chamber, and a chamber disposed with a cathode is referred to as a cathode chamber.

[0023] Various types of electrodes applicable to an electrolytic device or a fuel cell, etc. can be used as the anode and the cathode. For example, an electrode including an electrode substrate and a catalyst coated onto the electrode substrate may be used as the anode and the cathode. A carbon cloth and the like may be used as the electrode substrate, and the catalyst may be selected from the group consisting of platinum (Pt), ruthenium (Ru), osmium (Os), palladium (Pd), iridium (Ir), carbon (C), other transition metals, and a mixture thereof.

[0024] In addition, various types of cation exchange membranes applicable to an electrolytic device or a fuel cell, etc. may all be used as the cation exchange membrane. As for such cation exchange membranes, for example, Nafion available from DuPont or CMX ion exchange membranes available from Tokuyama Co., Ltd., both of which are commercially available, may be used.

[0025] The apparatus for producing carbonate salt may further include a component commonly employed in an electrolytic device and the like, in addition to the component described above.

[0026] The method for preparing a carbonate salt includes first supplying an aqueous solution containing an alkali metal salt or an alkaline earth metal salt (hereinafter, referred to as an aqueous solution of a salt) to the anode chamber, and supplying carbon dioxide and a capturing solution to the cathode chamber.

[0027] The aqueous solution of the salt supplied to the anode chamber is an aqueous solution containing cations to be supplied to the cathode chamber. Therefore, an aqueous

solution of a suitable salt may be selected according to cations of a carbonate salt to be produced. The aqueous solution of the salt may be any water source containing salts such as seawater, sewage, wastewater or industrial water, as long as it contains the desired cations. As a result, a high-value-added carbonate salt can be produced from carbon dioxide simultaneously with the desalination of the aqueous solution of the salt such as seawater, sewage, wastewater or industrial water.

[0028] Specifically, an aqueous solution containing a sodium salt, a magnesium salt, a potassium salt, a calcium salt and a mixture thereof may be used as the aqueous solution of the salt. When preparing sodium carbonate used as a pretreatment agent for biofuels by the method for preparing a carbonate salt according to one embodiment, an aqueous solution of sodium chloride, an aqueous solution of sodium sulfate and a mixture thereof may be used as the aqueous solution of the salt.

[0029] The cathode chamber is a chamber in which carbon dioxide is captured and ionized.

[0030] This cathode chamber is supplied with an aqueous solution in which a capturing agent capable of capturing carbon dioxide is dissolved. The cathode chamber may be supplied with an aqueous solution in which a previously prepared capturing agent is dissolved, or may be independently supplied with a capturing agent and water.

[0031] The capturing solution may be prepared at an appropriate concentration depending on the amount of carbon dioxide to be supplied and the amount of carbonate salt to be produced. The capturing solution may be prepared at a molar concentration of, for example, 2 M to 10 M or 3 M to 6 M, thereby preparing a carbonate salt in an appropriate time. If the molar concentration of the capturing solution is beyond the above range, there is a possibility that the production time of the carbonate salt is excessively long, or that a salt containing the cation of the capturing agent is generated, thereby reducing a production amount of the carbonate salt containing an alkali metal or an alkaline earth metal.

[0032] Any capturing agents known in the art to which the present invention pertains may be used without limitation as long as they can selectively capture carbon dioxide. For example, ammonia may be used as the capturing agent.

[0033] Carbon dioxide gas may be injected into the cathode chamber. The order of supply of the capturing solution and carbon dioxide described above is not limited. The capturing solution may be first supplied, and subsequently carbon dioxide gas may be injected into the capturing solution, or the capturing solution and carbon dioxide gas may be simultaneously supplied to the cathode chamber.

[0034] When the capturing solution and carbon dioxide meet, the capturing agent can capture and ionize carbon dioxide to form carbonate ions and the like. In one example, when an ammonia solution is used as the capturing solution, carbon dioxide ionizes to carbonate ions and binds to ammonium cations to produce ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$), ammonium bicarbonate (NH_4HCO_3) or ammonium carbamate ($\text{NH}_2\text{COONH}_4$).

[0035] In a conventional process, when an ammonium carbonate-based compound is produced, sodium bicarbonate was obtained along with ammonium chloride as a by-product by adding a solution of sodium chloride containing both cations and anions. However, the method for preparing a carbonate salt according to one embodiment can prepare a

carbonate salt without generating by-products by supplying pure cations into the cathode chamber, in which carbonate ions and the like are formed, using electric energy.

[0036] Specifically, the aqueous solution of the salt is supplied to the anode chamber, carbon dioxide and the capturing solution is supplied to the cathode chamber, and then an appropriate voltage is applied to the anode and the cathode, thereby producing a pure carbonate salt without generating by-products.

[0037] When the appropriate voltage is applied to the anode and the cathode, the cations separated from the aqueous solution of the salt present in the anode chamber move toward the cathode due to the electrical property thereof, and the anions separated from the aqueous solution of the salt move toward the anode. Therefore, the cations separated from the aqueous solution of the salt move toward the cathode chamber through the cation exchange membrane. Here, since the anions of the aqueous solution of the salt cannot pass through the cation exchange membrane, by-products derived from the capturing agent, for example, an ammonium salt and the like are not formed in the method for preparing a carbonate salt. The cations moved toward the cathode chamber may form a carbonate salt with a carbonate ion or a bicarbonate ion ionized from carbon dioxide.

[0038] The voltage applied to the anode and the cathode may be appropriately adjusted such that the cations separated from the aqueous solution of the salt move toward the cathode chamber through the cation exchange membrane. In one example, the external voltage applied to the anode and the cathode may be adjusted to 2 V or higher, 2 V to 10 V or 5 V to 10 V.

[0039] As described above, when a voltage is applied to the anode and the cathode such that the cations of the aqueous solution of the salt move toward the cathode chamber through the cation exchange membrane, the electrolysis of water may occur in the anode and the cathode. When the electrolysis of water occurs in the anode and the cathode, in the cathode, water is reduced and converted into hydrogen gas and hydroxide ion (OH^-), and in the anode, water is oxidized, and oxygen gas and hydrogen ion (H^+) are generated.

[0040] On the other hand, the carbonate ions or bicarbonate ions ionized from carbon dioxide in the cathode chamber may predominantly exist depending on the pH of the solution in which they are dissolved. Specifically, when the pH of the solution is 10 or higher, the carbonate ions predominantly exist, and when the pH of the solution is 10 or less, the bicarbonate ions may predominantly exist.

[0041] Therefore, the desired form of the carbonate salt may be selectively obtained by adjusting the concentration of hydroxide ions (OH^-) generated by electrolysis in the cathode chamber. Specifically, when the pH of the cathode chamber is adjusted to 10 or higher by controlling the concentration of hydroxide ions generated by electrolysis, a salt containing carbonate ions in the form of M_2CO_3 and $\text{M}'\text{CO}_3$ may be predominantly obtained, and when the pH of the cathode chamber is adjusted between 6 to 10, a salt containing bicarbonate ions in the form of MHCO_3 and $\text{M}'(\text{HCO}_3)_2$ may be predominantly obtained. Here, M is a monovalent cation of an alkali metal, and M' is a divalent cation of an alkaline earth metal.

[0042] Since the desired form of the carbonate salt may be obtained by the concentration of the hydroxide ions generated by electrolysis in the cathode chamber as described

above, the desired form of the carbonate salt may be selectively prepared by controlling the voltage applied to the anode and the cathode.

[0043] In a conventional method for preparing carbonates, calcination by which sodium bicarbonate and the like is treated at a high temperature was required in order to obtain the desired form of a carbonate salt. However, in the method for preparing a carbonate salt according to one embodiment above, the desired form of the carbonate salt can be selectively obtained by merely adjusting the pH of the cathode chamber. The method for preparing a carbonate salt according to one embodiment of the present invention may include adjusting the pH by adding a hydroxide to the cathode chamber, separately from adjusting the range of voltages applied to the anode and cathode.

[0044] On the other hand, the hydrogen ions generated by the electrolysis of water in the anode chamber may bind to the anions of the aqueous solution of the salt to generate an acid product of hydrochloric acid or sulfuric acid, etc.

[0045] When the appropriate voltage is applied to the anode and the cathode disposed respectively in the anode chamber to which the aqueous solution of the salt is supplied and the cathode chamber to which the capturing solution and carbon dioxide are supplied as described above, a carbonate salt may be produced. Here, the capturing agent forms a salt by capturing and ionizing carbon dioxide, and is regenerated without any additional process as a carbonate salt is produced, and thus is able to continuously capture and ionize carbon dioxide.

[0046] In one example, if the aqueous solution of ammonia is used as the capturing solution, ammonia captures and ionizes carbon dioxide and then is regenerated back to ammonia without any additional process, thereby being able to continuously capture and ionize carbon dioxide.

[0047] Specifically, when ammonia solution and carbon dioxide are supplied to the cathode chamber, ammonia captures and ionizes carbon dioxide, and thus, ammonium carbonate or ammonium bicarbonate in a state of being dissolved in water may be formed. Thereafter, a carbonate salt is formed as the ammonium cations of the ammonium carbonate or ammonium bicarbonate are replaced by the cations supplied from the anode chamber, and the ammonium cations are deprotonated and may be regenerated back to ammonia. The regenerated ammonia may again be used for capturing and ionizing carbon dioxide.

[0048] In a conventional process, when an ammonium carbonate-based compound was produced, an ammonium cation which is substituted by a sodium cation formed an ammonium chloride with a chloride ion by adding a solution of sodium chloride and the like containing both cations and anions. In order to regenerate ammonia from such ammonium chloride, additional processes of adding calcium oxide, which is an additional compound, to ammonium chloride, and reacting at a high temperature were required. Specifically, the reaction between ammonium chloride and calcium oxide also caused a problem of forming calcium chloride as a by-product in addition to ammonia. However, in the method for preparing a carbonate salt according to one embodiment, by-products derived from the capturing agent are not formed as pure cations are supplied to the cathode chamber using electric energy, and thus, the capturing agent may be reused without any additional process, thereby effectively providing a carbonate salt.

[0049] When the appropriate voltage is applied to the anode and the cathode while injecting carbon dioxide as described above, the produced carbonate salt may be precipitated. The method for preparing a carbonate salt according to one embodiment above may include discharging the precipitate from the cathode chamber in order to separate the produced carbonate salt from the capturing solution. For this purpose, the cathode chamber having a discharge port formed at the bottom may be used.

[0050] In one example, a precipitate was obtained from the cathode chamber using the apparatus for producing carbonate salt shown in FIG. 1 by supplying aqueous solutions of sodium chloride and sodium sulfate to the anode chamber as the aqueous solution of the salt, supplying the ammonia solution and carbon dioxide to the cathode chamber, and subsequently applying the appropriate voltage to the anode and the cathode such that the cations separated from the aqueous solution of the salt move toward the cathode chamber through the cation exchange membrane. An XRD (X-ray diffraction) analysis was performed to identify the components of the precipitate. As a result of the XRD analysis, it was confirmed that the solid materials precipitated in the cathode chamber were sodium bicarbonate and sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). Sodium carbonate has recently been used as a pretreatment agent in the production of biofuels. Therefore, it was confirmed that a high-value-added carbonate salt can be prepared without generating by-products from carbon dioxide by using the above-described method.

1. A method for preparing a carbonate salt using an apparatus that comprises an anode chamber; a cathode chamber, which is separated from the anode chamber by a cation exchange membrane; an anode disposed in the anode chamber; and a cathode disposed in the cathode chamber, the method comprising the steps of:

supplying an aqueous solution containing an alkali metal salt or an alkaline earth metal salt to the anode chamber;

supplying a carbon dioxide and a capturing solution to the cathode chamber; and

applying a voltage to the anode and the cathode such that the cations separated from the aqueous solution containing an alkali metal salt or an alkaline earth metal salt move toward the cathode chamber through the cation exchange membrane.

2. The method for preparing a carbonate salt of claim 1, wherein the capturing solution has a molar concentration of 2 M to 10 M.

3. The method for preparing a carbonate salt of claim 1, wherein the capturing solution is an ammonia solution.

4. The method for preparing a carbonate salt of claim 1, wherein an external voltage of 2 V to 10 V is applied to the anode and the cathode.

5. The method for preparing a carbonate salt of claim 1, further comprising discharging a precipitate from the cathode chamber.

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