Article

CO₂ Fixation by Membrane Separated NaCl Electrolysis

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Abstract: Atmospheric concentrations of carbon dioxide (CO_2), a major cause of global warming, have been rising due to industrial development. Carbon capture and storage (CCS), which is regarded as the most effective way to reduce such atmospheric CO_2 concentrations, has several environmental and technical disadvantages. Carbon capture and utilization (CCU), which has been introduced to cover such disadvantages, makes it possible to capture CO_2, recycling byproducts as resources. However, CCU also requires large amounts of energy in order to induce reactions. Among existing CCU technologies, the process for converting CO_2 into $CaCO_3$ requires high temperature and high pressure as reaction conditions. This study proposes a method to fixate $CaCO_3$ stably by using relatively less energy than existing methods. After forming NaOH absorbent solution through electrolysis of NaCl in seawater, $CaCO_3$ was precipitated at room temperature and pressure. Following the experiment, the resulting product $CaCO_3$ was analyzed with Fourier transform infrared spectroscopy (FT-IR); field emission scanning electron microscopy (FE-SEM) image and X-ray diffraction (XRD) patterns were also analyzed. The results showed that the $CaCO_3$ crystal product was high-purity calcite. The study shows a successful method for fixating CO_2 by reducing carbon dioxide released into the atmosphere while forming high-purity $CaCO_3$.

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1. Introduction

Increases in energy consumption due to population growth and industrial development have had a large effect on global warming by raising carbon dioxide (CO_2) concentrations in the atmosphere [1]. CO_2 is one of the six major gases causing global warming (CO_2, CH_4, N_2O, HFCs, PFCs, SF_6) [2], accounting for an estimated 80% of the greenhouse gases by amount [3]. For this reason, many researchers have focused on studies to reduce atmospheric concentrations of CO_2.

Among the various worldwide attempts to reduce atmospheric CO_2 concentrations, carbon capture and storage (CCS) technology, which captures released CO_2 and storages underground or underwater, is considered the most effective and efficient technology. In CCS technology, CO_2 can be captured before, during, or after coal or gas combustion [4]. CO_2 content in flue gas is reduced by physical, chemical, or biological means, and CCS industries, which process CO_2 after combustion, use chemical solvents [5,6]. From an energy and climate policy point of view, this type of CCS technology is theoretically the most effective method to reduce amount of CO_2 released but also entails the possibility of resistance from the general public due to high investment costs, limitation and uncertainty of potential storage capacity of CO_2. According to Nicholas *et al.* [7], over 80% of energy used in CCS is consumed in the CO_2 desorption process. In addition, according to Baciocchi *et al.* [8], CO_2 capture mechanisms require considerable energy and costs. Yu *et al.* [1] and Gough [9] have noted possible safety problems (due to earthquake or volcanic activity) from long-term CO_2 storage, while Holloway [10] reported on its risks, citing the example of a CO_2 leak case in Cameroon's Nyos Lake. Damen *et al.* [11] reported on five types of risks for underground carbon dioxide storage (CO_2 and CH_4 leakage, seismicity, ground movement, displacement of brine) [12]. In addition to these problems, according to Mazzoldi *et al.* [12], there is a possibility of CO_2 leakage caused by corrosion or external damage of pipeline of high-pressure transportation system, which was reported in the oil industry literature [13].

Because of these problems, studies related to the carbon capture and utilization (CCU) technology that recycles carbon dioxide as a resource has attracted attention. Existing CCU technologies for the production of calcium carbonate can be divided into direct and indirect reactions between solid chemicals and CO_2 gas, and aqueous system methods. Solid calcium carbonate production processes use relatively greater energy than liquid production processes. For example, according to research by Lackner *et al.* [14], Stasiulaitiene *et al.* [15] and Fagerlund *et al.* [16–18], the carbonation process for magnesium hydroxide obtained from serpentine requires high temperature (over 500 °C) and high-pressure (over 20 bar) conditions. In contrast, the liquid method according to Gerdemann *et al.* [19] and Khoo *et al.* [20] requires relatively lower carbonation temperature and pressure conditions of 185 °C and more than 40 bar, and 170 °C and 1 bar, respectively. However, the method which uses an aqueous system to produce carbonate also requires a reaction condition of high temperature and pressure. As with the solid calcium carbonate production method, it clearly requires great amounts of energy for processes such as cool-down in high-temperature and high-pressure

conditions, compared to CCS separation methods [21]. For these reasons, existing methods cannot be considered as optimal alternatives for reducing atmospheric CO_2 concentrations. For optimal CO_2 reduction, methods that (1) satisfy environmental considerations by addressing possible CO_2 leaks, and (2) reduce energy consumption compared to existing carbonation processes conducted at high-temperature and in high-pressure conditions must be devised.

This study proposes a carbonation process which uses relatively less energy than traditional process, through an electrolysis technology using ceramic membrane. CO_2 usually reacts with alkaline solutions as absorbent, with NaOH (Sodium Hydroxide) and NH_4 (Ammonium) solution, MEA (Mono-ethanol Amine), DEA (Di-ethanol Amine), and MDEA (N-methyl Diethanolamine) being the most common examples [22]. Previous studies use magnesium hydroxide ($Mg(OH)_2$) in order to absorb CO_2. Existing processes such as the one by Nduagu *et al.* [23] require the use of ammonium magnesium salt heated to over 500 °C in order to extract magnesium from serpentine or other magnesium silicates. They also require high temperature reaction conditions for the separation process of magnesium oxide (MgO) and silicon dioxide (SiO_2) from serpentine, and the hydration process after separation. Accordingly, this study uses NaOH (Sodium Hydroxide) as absorbent for CO_2 through electrolysis of NaCl in seawater. The proposed method enables formation of NaOH using low voltage of 1–4 amperes.

This technology was proven to produce alkaline solution at low voltages by CALERA Corporation of the US [24]. Furthermore, the electrolysis process using a ceramic membrane requires no additional pressure or temperature. Additionally, the carbonation process does not require a separate process for the separation of the absorbed CO_2. This enables it to reduce energy consumed in the process of CO_2 desorption, and to significantly reduce energy consumption through reaction at room pressure and room temperature. Moreover, the chemical conversion solution produced after the carbonation reaction can be recycled as feed solution for the electrolysis to produce NaOH. Accordingly, this study may find its significance in overcoming the problems of existing CO_2 reduction technologies (CCS and CCU technology) by stably fixating CO_2 at room temperature and room pressure with relatively less energy, while producing a metal carbonate to generate income.

2. Experimental Section

2.1. Materials and Electrolysis Device

Sodium chloride (NaCl), 99.5% (Mn = 58.43 g/mol) used as feed for electrolytic reaction was purchased from Samchun chemical (Gyeonggi-do, Korea). Calcium chloride ($CaCl_2$), 95.9% (Mn = 110.98 g/mol) was purchased from Kanto (Tokyo, Japan) to produce the carbonate, carbon dioxide (CO_2) gas was purchased from Samheung (Gyeonggi-do, Korea). Calcium carbonate ($CaCO_3$), ≥99.0% (Mn = 100.09 g/mol) used to determine formation of final product purity of $CaCO_3$ was purchased from Sigma-Aldrich (St Louis, MO, USA), and de-ionized water was used as solvent in the experiment.

Figure 1 is a schematic diagram of the electrolysis device designed for the experiments. The device was built with 10 mm acrylic material. In general, ion-exchanged membrane or ceramic membrane is used for electrolysis device. Ferro *et al.* [25] reported that an ion-conducting ceramic membrane around the graphite anode is necessary in electrolytic cells where reactive metals, such as calcium, magnesium and sodium, are produced to minimize the possibility of back reactions. Therefore, in this

study ceramic membrane (Korea Material scientific, Changwon, Korea) which has less than 0.2 μm pore size of alumina material, was used. The ceramic membrane used in this experiment has excellent physical properties and can be used semi-permanently, compared with MF membrane. Electrolytes in the acrylic water tank are divided into cathodes and anodes by a ceramic membrane, a negative electrode was used as the stainless steel, a positive electrode was used as the graphite. To increase the contact area between CO_2 bubbles and absorbent produced by electrolysis, a high-pressure air stone (DAE Yang Air Stone Ind., Co, Busan, Korea) was used, which generates fine CO_2 bubbles.
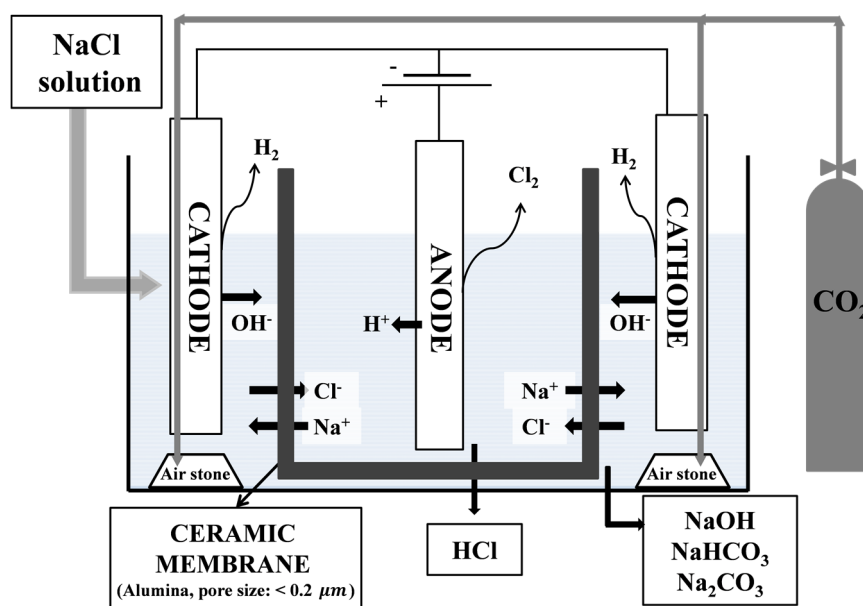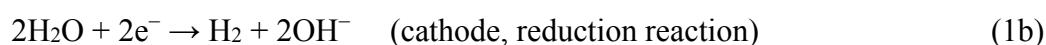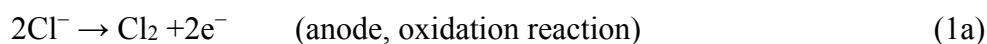
Figure 1. Schematic diagrams of the electrolysis device for the electrolysis of NaCl solutions.

2.2. Electrolysis of NaCl Solution

The method used in this study is based on chemical absorption and conversion method in CCS technology. Among the alkali solutions used as CO_2 absorbents, amine-family absorbents were excluded due to toxicity, while magnesium hydroxide ($Mg(OH)_2$) used in existing processes was excluded due to high temperature and high pressure reaction conditions. For these reasons, NaOH, which does not require high temperature and high pressure reaction conditions, was obtained through electrolysis of seawater and used as an absorbent. In the case of the NaCl solution used as feed for electrolysis, various concentration ranges were used based on concentrations (NaCl 2%–6%, 5L volume) in seawater and seawater concentrate. The NaCl solutions were prepared in the electrolysis device as in Figure 1, changes in pH over time were checked using pH electrodes (ORION 3-STAR Benchtop pH/ISE meter, Thermo Scientific Korea, Seoul, Korea), and the electrolysis was conducted using even an current of 1–4 amperes. Electrolysis was conducted for 10–15 min at a temperature of around 25 °C and atmospheric pressure, and the underlying reaction is as follows:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{(anode, oxidation reaction)} \tag{1a}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \text{(cathode, reduction reaction)} \tag{1b}$$

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2 \tag{1c}$$

2.3. CO₂ Gas Capture Using Sodium Hydroxide

NaOH is produced at the "negative" electrode as CO_2 absorbent. CO_2 gas was injected at an even flow rate into the NaOH feed solution through the CO_2 generator. The weak acidic CO_2 gas combined with alkaline NaOH to form the intermediate compound of sodium bicarbonate ($NaHCO_3$) form needed for the generation of calcium carbonate ($CaCO_3$). This is represented by the following neutralizing reaction:

$$NaOH + CO_2 \rightarrow NaHCO_3 \tag{2}$$

2.4. Precipitation of CaCO₃ by the Titration

$CaCO_3$ was generated through precipitation by adding $CaCl_2$ feed solution to sodium bicarbonate ($NaHCO_3$) produced in this study.

According to Henry's law and the solubility constant, the pH value affects the distribution of ionic CO_2; in order to increase the conversion rate to $CaCO_3$, bicarbonate should be turned into carbonate by adjusting pH level. Figure 2 shows changes of carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) compositions in accordance with pH at 25 °C. Sodium bicarbonate ($NaHCO_3$) is converted into sodium carbonate (Na_2CO_3) when pH level is higher than 12. Converted Na_2CO_3 is precipitated as $CaCO_3$ by adding $CaCl_2$ solution. The reaction by which the highly reactive Ca^{2+} and Na^+ form $CaCO_3$ through substitution reaction is as follows:

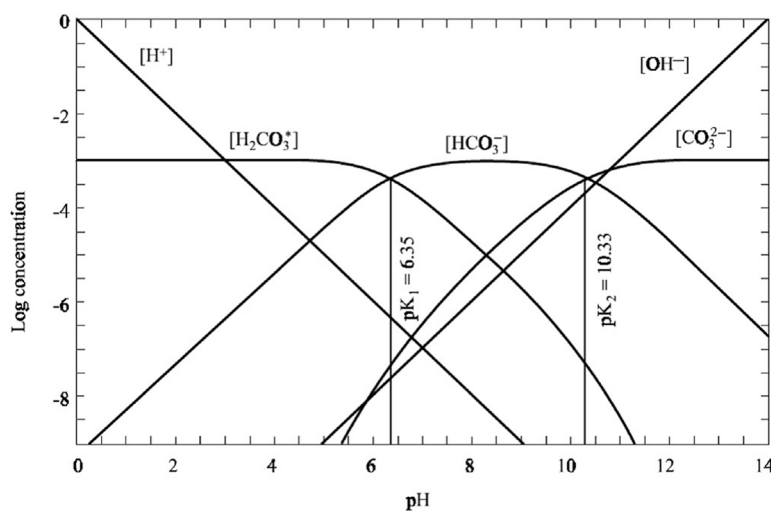$$Na_2CO_3 + CaCl_2 \rightarrow 2NaCl + CaCO_3 \tag{3}$$

Figure 2. Carbonate-bicarbonate speciation in water v. pH at 25 °C (Reproduced with permission from [26]. Copyright 2012, John Wiley & Sons).

Reaction was conducted by the titration method, and the Ca^{2+} ion selective electrode (orion ionplus calcium electrode, Thermo Scientific Orion, Beverly, MA, USA) was used in order to confirm the end of the carbonate reaction. Changes in the concentration of the Ca^{2+} ion selective electrode were observed by adding $CaCl_2$ solution in prepared concentrations. $CaCl_2$ feed solution added by the titration method is fully consumed through substitution reaction, so the concentration at the Ca^{2+} ion selective electrode was close to zero as the reaction was in progress. When the CO_3^{2-} was fully

reacted, Ca^{2+} ion selective electrode concentration also changed, and the reaction was deemed as completed and terminated. The precipitate after the reaction was filtered using a GF/C film (Whatman® Glass microfiber filters, Whatman, Clifton, NJ, USA). It was dehydrated in a vacuum oven for 24 h at room temperature. After dehydrating, the output was a white powder form.

2.5. Characterization of CaCO3

Fourier transform infrared spectroscopy (Spectrum 100 FT-IR Spectrometer, PerkinElmer, Norwalk, CT, USA) was used to confirm molecular structure of $CaCO_3$, the final product of the experiment. Each sample spectrum was measured in the 4000–600 cm^{-1} wavenumber ranges after drying for over 24 h in a vacuum oven. The particles of the product in the form of powder was applied on carbon tape, and then coated with platinum for several minutes. Shape and size of the coated particles was confirmed by using field emission scanning electron microscopy (FE-SEM, JEOL-6701F, JEOL, Tokyo, Japan). Measurements of confirmed particles were done through X-ray diffraction (XRD, Ultima IV, RIGAKU, Tokyo, Japan) pattern analysis at 40 kV/30 mA output.

3. Results and Discussion

3.1. The Metal Carbonate Produced by the CO2 Fixation.

In Figure 1, as electrolysis is conducted in the electrolysis device, Na^+ and OH^- ions, and H^+ and Cl^- ions are separated into the "negative" and "positive" electrodes, respectively, to form alkaline NaOH and acidic HCl. Figure 3 shows the changes in pH over time measured with a pH installed in the "negative" electrode. Feed solution of electrolysis using a NaCl solution (2%–6% concentration) of five liters. Figure 3 shows that regardless of concentration, NaCl solution approaches a pH of 12 over time at 1–4 A conditions (8–20 V voltage, approx. 25 °C and atmospheric pressure). The time to end the electrolysis was determined when the pH value was no longer increased. Electrolysis was completed over 10–15 min in all cases, and reaction time decreased as ampere was increased. It was shown that sodium bicarbonate, a CO_2 absorbent, could be produced without high temperature, high pressure conditions. The NaOH produced through electrolysis satisfied the reaction conditions through pH control, after which reaction took place over 2–3 h with CaCl2 in feed solution form, representing a substantial reduction in reaction time over naturally-occurring $CaCO_3$ composite reaction.
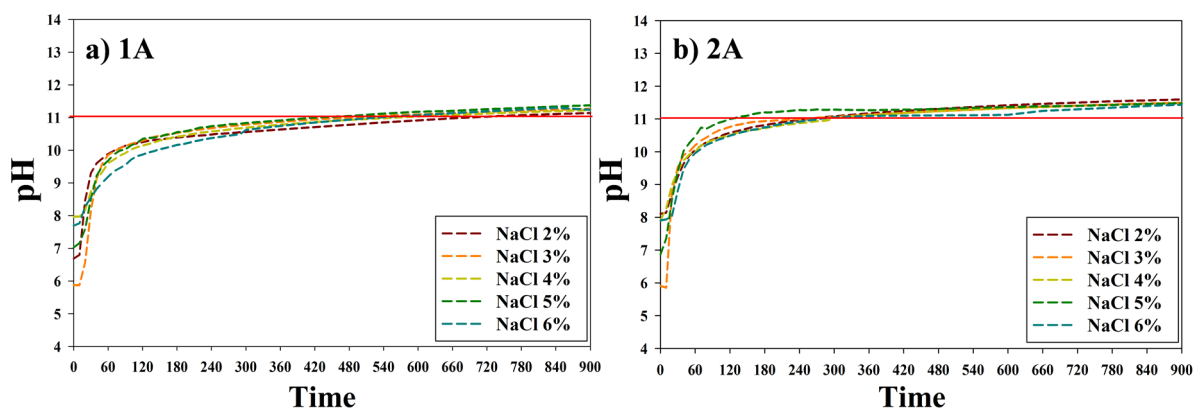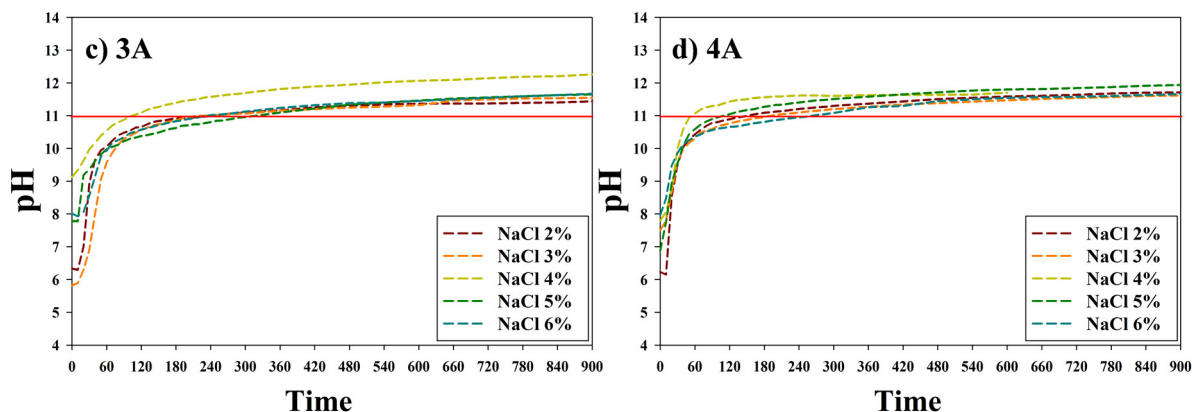

Figure 3. *Cont.*

Figure 3. Result of the electrolysis of NaCl solution. (**a**) 1A condition; (**b**) 2A condition; (**c**) 3A condition; (**d**) 4A condition.

3.2. Characteristics of the Metal Carbonate: FT-IR Analysis

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the molecular structure of the white-powder form precipitate obtained through the experiment. Figure 4 shows a comparison between FT-IR spectra of pristine $CaCO_3$ and those of experiment-derived $CaCO_3$ particles. Figure 4 shows that the characteristic peaks of the pristine $CaCO_3$ and those of experiment-derived $CaCO_3$ particles are consistent. Table 1 shows the FT-IR peak values of $CaCO_3$ particles, which confirms that they are consistent with characteristic peaks values of 1418 cm^{-1} (C–O function group, stretching mode in calcite), 876 cm^{-1} (C–O function group, In-plan bending), and 713 cm^{-1} (C–O function group, Out-plan bending in calcite) for $CaCO_3$ in calcite form. This is also consistent with research by Tlili *et al.* [27] and Wu *et al.* [28] on FT-IR spectra for $CaCO_3$.
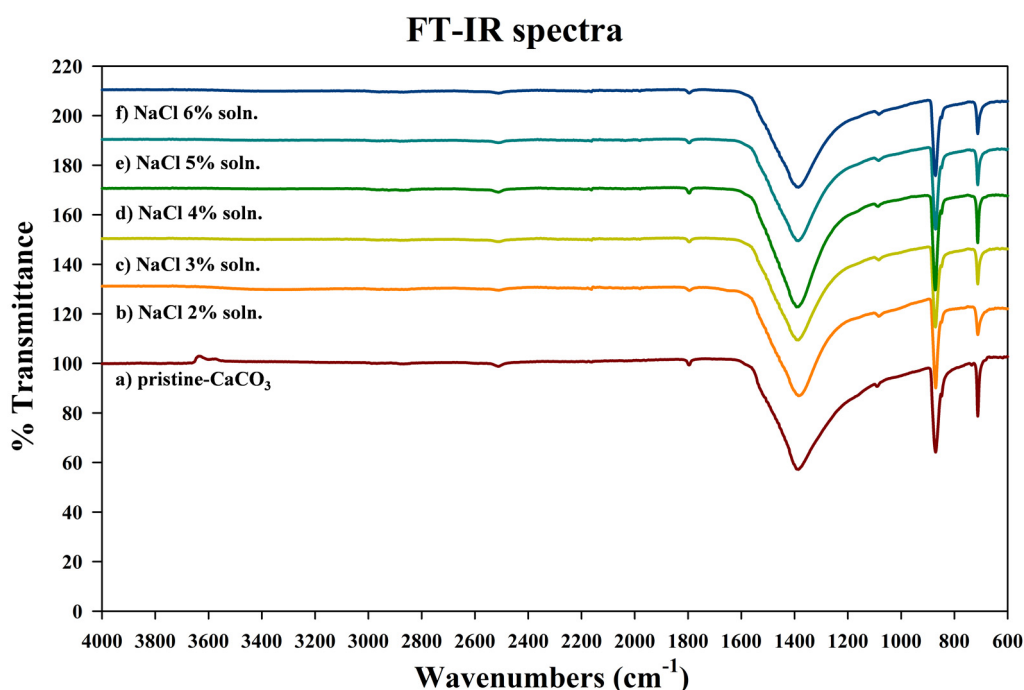

Figure 4. FT-IR spectrum of (**a**) pristine-$CaCO_3$; (**b**) NaCl 2% soln; (**c**) NaCl 3% soln; (**d**) NaCl 4% soln; (**e**) NaCl 5% soln; (**f**) NaCl 6% soln.

Table 1. Assignment of peaks for $CaCO_3$.

Wavenumber (cm^{-1})	Function Groups	Vibration
2513	Combination	1080 cm^{-1} and 1440 cm^{-1}
1796	Combination	1080 cm^{-1} and 713 cm^{-1}
1418	C–O	Stretching mode (1490 cm^{-1}, 1420 cm^{-1} in vaterite; 1418 cm^{-1} in calcite; 1465 cm^{-1} in aragonite)
1080	O–C–O	Stretching mode
876	C–O	In-plane bending
848	C–O	In-plane bending (only appeared in vaterite and aragonite)
713	C–O	Out-plane bending (750 cm^{-1} in vaterite; 713 cm^{-1} in calcite; 707 cm^{-1}, 692 cm^{-1} in aragonite)

3.3. Characteristics of the Metal Carbonate: FE-SEM Image Analysis

In general, $CaCO_3$ is known to exist in three crystals forms—cubic (calcite), spherical (aragonite), and columnar (vaterite) [29–31]. Through comparative analysis with FT-IR spectra of pristine $CaCO_3$, the molecular structure of the precipitate obtained through the experiment was confirmed as being that of calcite. However, when compared with values in Table 1, it was confirmed as having the vibration of $CaCO_3$ in cubic form. Accordingly, field emission scanning electron microscopy (FE-SEM) images were taken in order to get a more clear confirmation of the crystal form. The FE-SEM images in Figure 5 show that the $CaCO_3$ obtained through the experiment were observed to be of cubic form. Other crystal forms of calcite were not identified, and changes in crystal form did not vary with increases in feed solution concentrations.
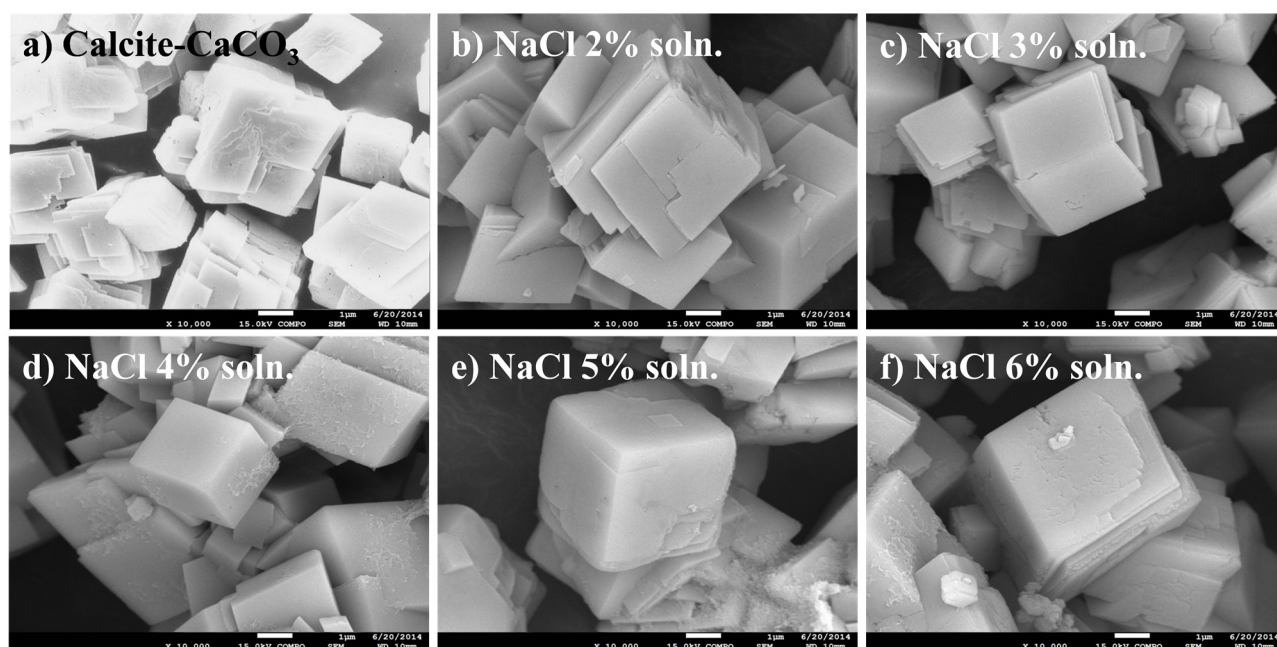

Figure 5. SEM images of the sample precipitated by the carbonation. (×10,000) (**a**) Calcite-$CaCO_3$; (**b**) NaCl 2% soln; (**c**) NaCl 3% soln; (**d**) NaCl 4% soln; (**e**) NaCl 5% soln; (**f**) NaCl 6% soln.

3.4. Characteristics of the Metal Carbonate: The XRD Pattern Analysis

While FT-IR and SEM images confirmed that the precipitate calcite was $CaCO_3$, X-ray diffraction (XRD) pattern analysis was conducted on the precipitate to confirm the crystal structure. Figure 6 shows the XRD patterns of pristine $CaCO_3$ and experiment-derived samples. The XRD patterns of the selected $CaCO_3$ samples display sharp reflection lines between 20° and 70° at the characteristic 2-θ positions. A comparison with the JCPDS values in Figure 6 shows that the 2-θ values of the $CaCO_3$ obtained through the experiment are consistent with the known 2-θ values of calcite of 29.32° (d-value 3.04 Å), 39.34° (d-value 2.29 Å), and 43.08° (d-value 2.10 Å) [32]. No other 2-θ values were detected, other than those for characteristics peaks in calcite form. The XRD pattern analysis shows that the $CaCO_3$ (white-powder form precipitate) obtained through the experiment is calcite of high purity.
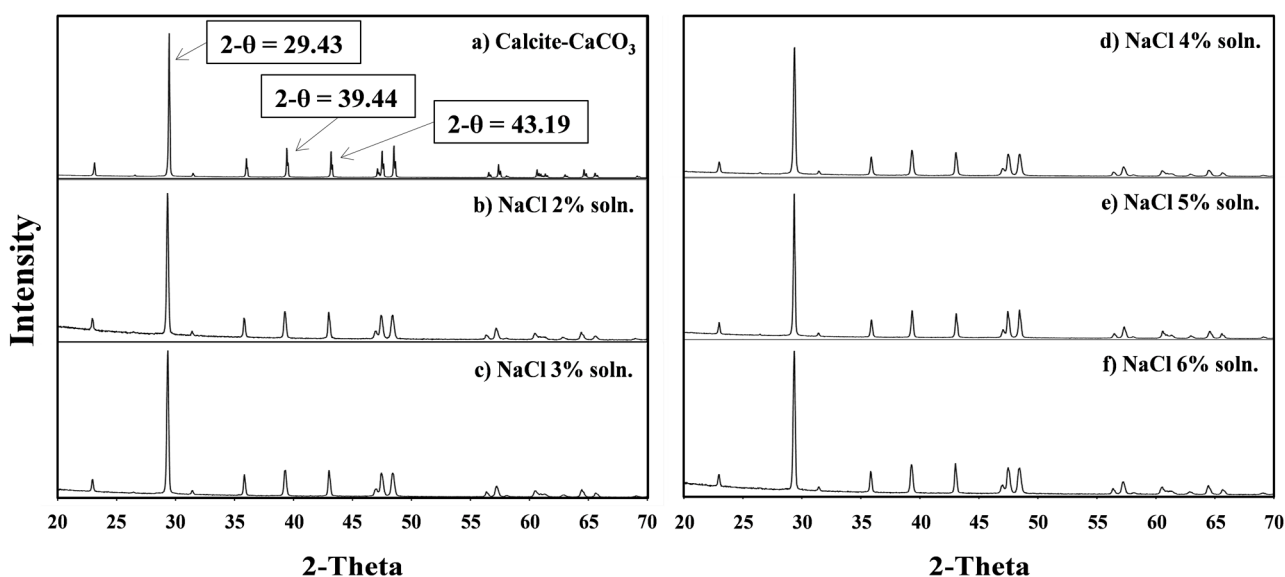

Figure 6. XRD patterns of the sample precipitated by the carbonation. (**a**) Calcite-$CaCO_3$; (**b**) NaCl 2% soln; (**c**) NaCl 3% soln; (**d**) NaCl 4% soln; (**e**) NaCl 5% soln; (**f**) NaCl 6% soln.

4. Conclusions

This study proved that $CaCO_3$ could be stably formed by absorbing CO_2 at normal room temperature and pressure conditions. Among absorbents used in existing CCS technology, a series of toxic amine was excluded, and a more environment-friendly method for CO_2 fixation was realized by using NaOH as absorbent. In addition, an electrolysis method which uses ceramic membrane at 25 °C, and atmospheric conditions with voltage of 8–24 V for 10–15 min, was used for the formation of NaOH. Through this method, NaOH was produced more effectively. In the case of the carbonation process, the precipitate was stably formed through a substitution reaction between Ca^{2+} and Na^+, by adding $CaCl_2$ at room temperature and atmospheric conditions. It was also confirmed as being calcite through FT-IR spectra measurements. Furthermore, the contents of the chemical solvent resulted from $CaCO_3$ precipitate formation consisted of sodium chloride (NaCl) and sodium hydroxide (NaOH), which can be reused as feed solution for electrolysis via an additional concentration process. Through SEM image and XRD pattern analyses, it was revealed that the precipitate $CaCO_3$ powder was high-purity calcite-$CaCO_3$ of cubic crystal form. $CaCO_3$ exists in calcite of cubic form, aragonite of

spherical form, and vaterite of columnar form, of which cubic calcite is most stable [33]. Aragonite transforms into calcite at 380–470 °C, and vaterite is the most unstable [34,35].

Natural formation of $CaCO_3$ requires extensive time and entails numerous reciprocal interactions. The method presented not only does not require high temperature reaction conditions but also makes it possible to form $CaCO_3$ in a short time. Moreover, the $CaCO_3$ produced is calcite of high purity which does not require an additional refinement process. According to Siefert and Litster [7], the most of energy used in CCS is consumed in the desorption process. However, the presented method does not use the desorption process, so the energy required to remove CO_2 does not need to be considered. According to Svensson *et al.* [36], in the transport process, in the range from 1 €/ton up to 18 €/ton of CO_2, costs arise. However, the presented method does not require a transport process of CO_2, so it can reduce the cost as much as 18 €/ton of CO_2. In order to overcome disadvantages of existing methods using serpentine or other magnesium silicate at high temperatures (over 500 °C) and high pressure (over 20 bar) conditions to produce $Mg(OH)_2$, the method which uses electrolysis at room temperature and pressure is used to produce absorbent. High temperature (over 500 °C) and high pressure (over 20 bar) conditions incurs costs, so this study provides economic benefits.

As demonstrated through this experiment, this study proposes a more stable carbonation method for more environment-friendly and economical CO_2 fixation and recycling of chemical ingredients. On the basis of the aforementioned considerations, we would like to be able to reduce the CO_2 emissions through recycling the CO_2 with the method that we have proposed.

Acknowledgments

Author Contributions

Hyun Sic Park performed the experiments, analyzed the data, and wrote first draft; Ju Sung Lee, JunYoung Han, Sangwon Park analyzed the data; Byoung Ryul Min and Jinwon Park revised the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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