

Carbon Dioxide Recovery from Carbonate Solutions by an Electrodialysis Method

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1. Introduction

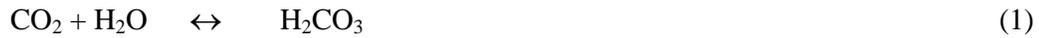
Carbon capture and sequestration (CCS) has been recognized as an effective measure to mitigate global warming. In the CCS, CO₂ generated from point sources such as thermal power plants or cement industries would be captured and separated from the flue gas, and be sequestered in an appropriate sites, e.g., underground or in the ocean. The key issue for the implementation of the CCS scenario is process cost reduction. Especially, power consumption for the capture and separation process of CO₂ accounts for a major portion of the total cost for the CCS, and therefore, it is required to develop an effective and low-cost capturing and separation method of CO₂ for the deployment of the CCS.

At the present stage, chemical absorption process is the least-cost method for capturing CO₂ from the flue gas. Liquid absorbents that have a strong affinity to CO₂ such as monoethanolamine (MEA) or alkaline metal hydroxide solutions are used for capturing CO₂ from the flue gas stream. The captured CO₂ in the absorbent will be released by heating, in which process the absorbent will be regenerated. Chemical absorption method is advantageous over other methods because the liquid absorbents have a relatively high capacity of CO₂ capture even under lower partial pressure conditions of CO₂, and the process can be operated under wet conditions. In addition, retrofit installation of the capturing plant of the chemical absorption to existing combustion units would not have much technical difficulties. A drawback is that the higher power consumption for the regeneration of the absorbents by the thermal treatment process. It is estimated that as much as 15 to 30 % net power generation efficiency of a coal-fire power plant will be reduced due to the power consumption for the thermal-regeneration process. Furthermore, the absorbent will be degraded by the cycle of the thermal treatments, and corrosive salts such as sulfate, oxalate and thiocyanate would be generated by the thermal treatment. The absorbents should be replaced after several cycles of the regeneration, which will result in an increase of the cost. Improvement of the regeneration process of the absorbent after capturing CO₂ would be most important to reduce the total cost for the capture and separation process of CO₂.

In this study, a novel process of recovery of CO₂ and regeneration of absorbents was developed based on an electrodialysis method. The process is targeting the regeneration of alkaline metal carbonate solutions after the CO₂ capture in alkaline hydroxide solutions. Electrodialysis with a combination of a bipolar membrane and ion exchange membrane enables a simultaneous recovery of CO₂ and an alkaline metal hydroxide solution from the alkaline carbonate solution. The concept was examined experimentally with a laboratory-scale electrodialysis apparatus, and effects of operating conditions for the electrodialysis on the CO₂ recovery efficiency was investigated.

2. Concept of the new process for CO₂ recovery

The following equilibrium is established in the aqueous solution of an alkaline carbonate (M₂CO₃) with CO₂ in the gas phase.



The equilibrium could be shifted to the left-hand side to increase the CO_2 partial pressure either by increasing the temperature or adding protons (in other words, decreasing pH) into the system. The former mechanism corresponds to the thermal recovery process of CO_2 from carbonate solutions. The present process corresponds to the latter mechanism. The protons can be supplied by the dissociation of water molecule.



However, there are two obstacles for the CO_2 recovery to proceed. First, it is necessary to separate hydroxyl ions from protons and supply to the feed solution. Second, the alkaline metal ions in the feed solution should be removed to keep the electroneutrality of the solution. The removed hydroxyl ions and alkaline metal ions then will form the alkaline solution that can be reused for the CO_2 absorption. To achieve the above process, the following system was developed in this study.

The concept of the system is shown in Figure 1.

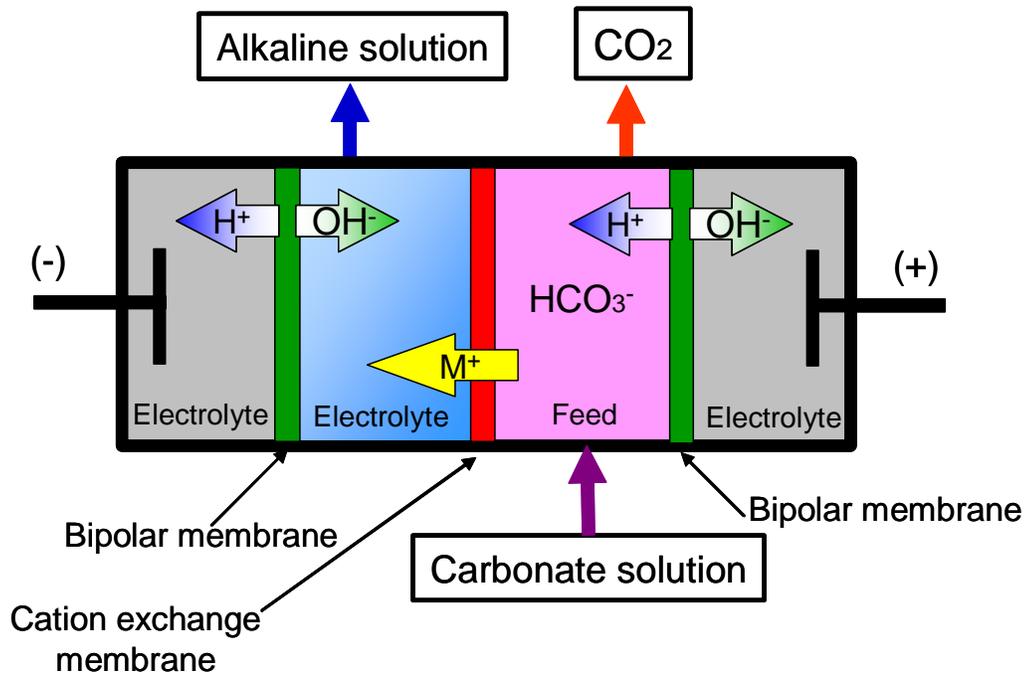


Figure 1 Conceptual drawing for the CO_2 and alkaline solution recovery system from alkaline carbonate solution with an electro dialysis method

Two cells are sandwiched with three membranes, two bipolar membranes and one cation exchange membrane. The other sides of the bipolar membranes are contacted with electrode cells, where electrodes are inserted in electrolyte solutions. A carbonated alkaline solution will be fed into the cell (feed cell) next to the anode cell, while an electrolyte solution with the same cation as the alkaline solution will be fed into the cell (base cell). Cation exchange membranes are a kind of ion exchange membrane that can exclusively transport cations. The bipolar membrane has a laminated structure of two layers; cation exchange layer and anion exchange layer.

When an electric potential difference larger than the electrolysis voltage of water is applied, the bipolar membrane will split water molecules into pairs of proton and hydroxyl ions. The produced protons will be transported into the feed cell according to the potential difference. At the same time, the alkaline metal ions in the feed cell will be transported into the base cell through the cation exchange membrane. As a result, the pH of the feed solution

was decreased, and CO₂ gas will be generated from the solution according to the following mechanism.



On the other hand, the bipolar membrane contacted with the base cell will supply hydroxyl ions to the base cell, where the alkaline solution will be regenerated with the alkaline metal ions transported from the feed cell. The regenerated alkaline solution can be reused for the CO₂ capture from the exhaust gas.

Electrodialysis is a potentially energy-saving process because it can be operated near the thermodynamic equilibrium conditions, where the process efficiency is not limited by the Carnot's principle. However, the process efficiency will be significantly reduced by the electrolysis processes in the electrode cells. For example, some part of the electric power will be consumed for producing oxygen and hydrogen gases when the sodium sulfate solution was used as an electrode solution. The effect of the electrolysis will be reduced and the efficiency will be improved by increasing the number of the pairs of the feed cell and the base cell. For a given electric current through the cell stack, the power consumed in each cell is proportional to the electric potential in the cell. With an increase in the pair of the base and feed cell units, the potential difference along each cell will be decreased, which would result in the reduction of the power consumed for the electrolysis in the electrode cells. Theoretically, the power consumption in the electrode cells will be negligible at the limit of the infinity number of the cell units of the base and feed.

3. Experimental

A CO₂ recovery experiment was carried out using a laboratory-scale electro-dialysis stack (Asahi Glass Co. Ltd., Japan) to examine the feasibility of the proposed method. An outline of the experimental is shown in Figure 2. The experimental stack has a composition that bipolar membranes and cation exchange membranes are alternately layered. Bipolar membrane and cation exchange membrane compose two-cell unit which are separated in desalination cells and concentration cells. A number of two-cell units (5~10) are placed between two electrode cells at the both ends. Neosepta BP-1 (Tokuyama Co. Ltd., Japan) was used as bipolar membrane, and Selemin AMV (Asahi Glass Co. Ltd., Japan) was used for cation exchange membrane. The membrane effective area was 210 cm² and the distance between two membranes was 0.75 mm. Sodium bicarbonate solution (0.6~1.0 M) was used as a CO₂ rich carbonate solution in the feed cell, sodium carbonate (0.1~0.5 M) was used as an electrolyte solution in the base side cell, and sodium sulfate (0.5 M) was used as electrode solution. 1000 mL of each solution was circulated in system driven by magnetic pumps. Thus, the experimental system is batch system with circulating a fixed amount of solutions. Parallel flow pattern was employed both in the feed and the base side cells. The electrical potential was applied to electrodes by a power supplying unit with keeping a constant current density in the range of 2.4 ~ 9.5 mA/cm². In other words, the electrical potential along the stack was controlled so that the current density was kept constant during one run. During the experiments, the rate of the CO₂ recovery from the feed cell was measured with a gas flow meter at the gas-liquid separator, which is installed in the downstream side of the feed cell. The pH changes of the solutions were monitored at the feed tanks. The electric potentials across the experimental stack both including and excluding electrode cells were measured.

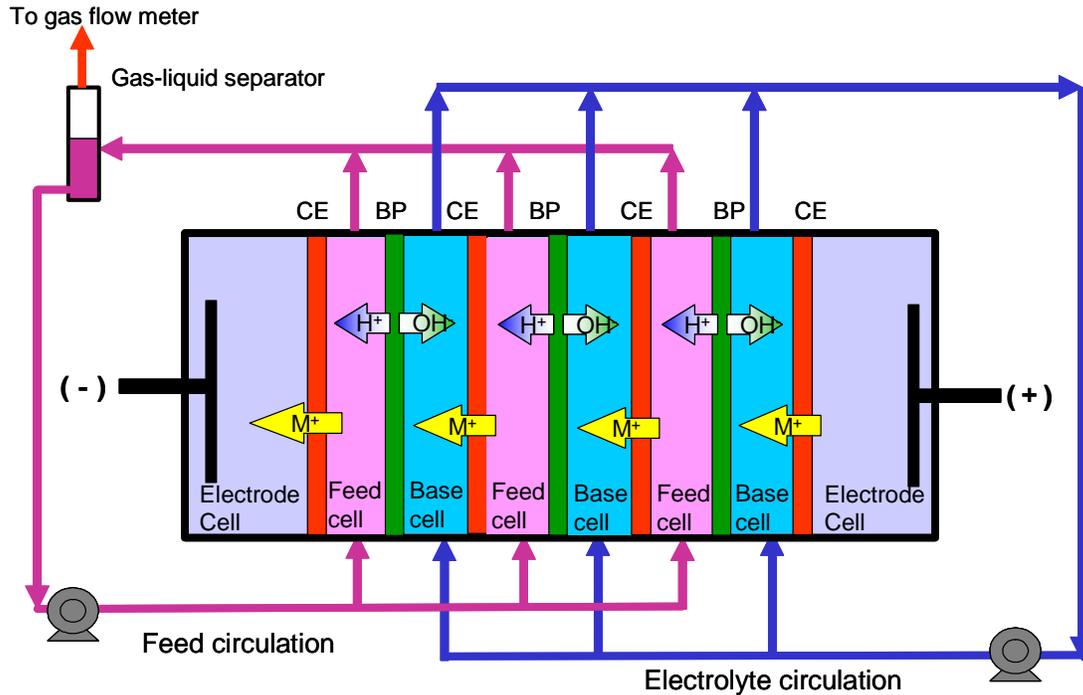


Figure 2 Outline of multi-stack CO₂ recovery experimental apparatus

4. Results and discussion

4.1. Time change of the CO₂ recovery rate, pH and voltage

The generation of CO₂ gas bubbles from the feed solution was observed immediately after applying the electric potential. An example of time change of the CO₂ recovery rate as well as the pH changes of the feed solution and that of the base solution are shown in Figure 3. In this case, the current density was set 4.8 mA/cm², and the number of the cell pairs was 10. The initial feed solution was 1.0 M NaHCO₃, and initial solution in the base cell was 0.35 M Na₂CO₃. CO₂ recovery rate was almost constant in range of 1.5×10^{-4} mol/s, and slightly decreased with time. The pH decrease in the feed solution was 0.84 (from 8.027 to 7.187) in 100 min, while the pH increase in the base cell was 1.62 (11.78 to 13.40). This result suggests that the proton increase in the feed cell was much lower than the increase in hydroxyl ions in the base solution. The bipolar membrane would produce equimolar pair of proton and hydroxyl ion. The difference can be attributed to the consumption of protons in the CO₂ recovery reactions ((2') and (3')) in the feed cell. The difference in the total mole number of proton in the feed cell and that of hydroxyl ions in the base cell was in the order of 10⁻¹ mol, which is in the same range of the cumulative CO₂ production in 100 min.

The current efficiency, η for the CO₂ recovery can be defined as the ratio of the current consumed for the CO₂ recovery to the total current, and is given by,

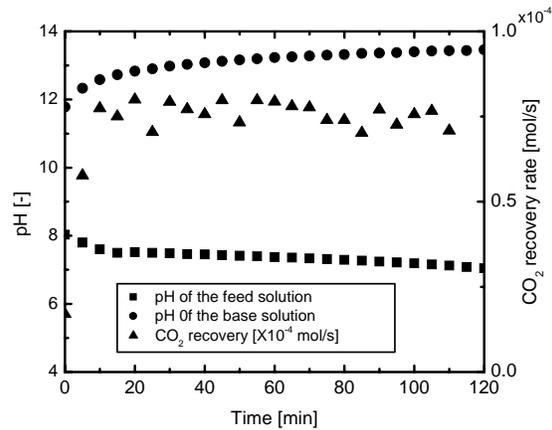


Figure 3 Time change of pH values in the cells and CO₂ recovery rate.

Number of cell pairs: 10, Feed cell: 1.0 M NaHCO₃, Base cell: 0.35 M Na₂CO₃, current density: 4.8 mA/cm²

$$\eta = \frac{r_{CO_2} F}{n \times i} \quad (5)$$

where F is the Faraday constant, n is the number of the pair cells, i is the current density, and r_{CO_2} is the CO_2 recovery rate. The current efficiency was in the range of 70~75 % for the present case. Figure 4 shows time change of electric potential across the stack, including and excluding those in the electrode cells, respectively. The potential immediately increased reached upon applying the constant current, and reached almost steady state value during the electrodialysis, although the potential was slightly increased with time. The steady-state potential value was about

10.6 V including those in the electrode cells, and about 7.5 V excluding those in the electrode cells. The increase in the potential can be explained in terms of the increased electrical resistance in the feed cells due to the decrease in the number of ions. The difference in the potentials including and excluding those in the electrode cells was about 3.1 V, indicating about 30 % ($3.1 / 10.6$) loss of the current consumed, which is consistent with the current efficiency of 70 %. The loss can be attributed to the electrolysis of water in the electrode cells, which is undesirable for the present purpose of the CO_2 recovery.

4.2. Effect of the current density

Figure 5 shows the effect of the current density on the CO_2 recovery rate during the steady-state operation. The current density was changed in the range of 2.4 ~ 9.5 mA/cm^2 (current 0.5 ~ 2.0 A), and other conditions are the same as the cases in Figure 3; number of cell pairs: 10, feed cell: 1.0 M $NaHCO_3$, base cell: 0.35 M Na_2CO_3 . The CO_2 recovery rate was increased in proportion to the current density. The electric potential differences across the stack for these runs are shown in Figure 6. The potential differences, both including and excluding electrode cells, increased linearly with the increase in the current density up to 7.1 mA/cm^2 , and leveled off after that. The difference in the potentials between the one including and excluding those in the electrode cells was almost constant.

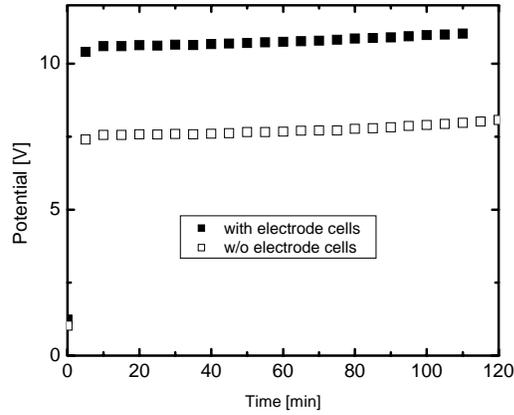


Figure 4 Time change of potential differences across the stack for the same conditions in Fig. 3.

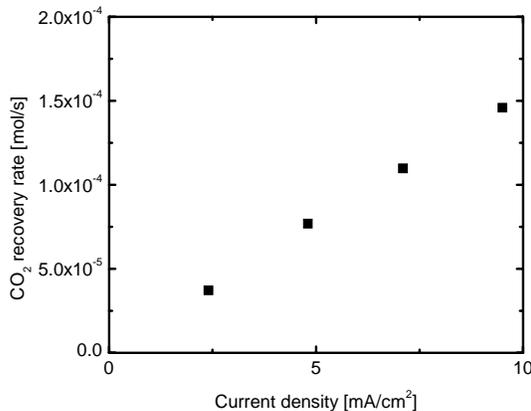


Figure 5 Effect of the current density on the CO_2 recovery rate. Conditions other than the current density were the same as those in Fig. 3.

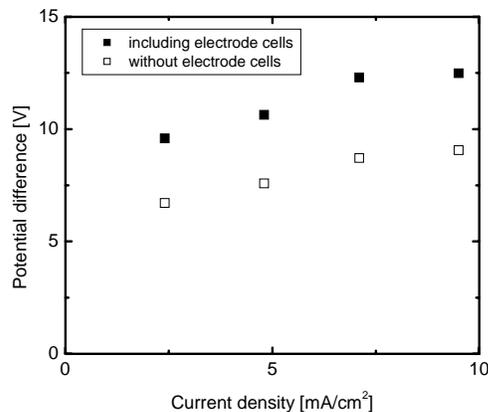


Figure 6 Effect of the current density on the potential difference across the stack.

The power consumption for the CO₂ recovery, E can be given by the following equation,

$$E = \frac{V \times i}{r_{CO_2}} \quad (6)$$

where V is the potential difference across the stack. Since all the runs in this study were conducted under the constant current density conditions, the power consumption can be directly related to the results of the potential differences applied to drive the given current. The effect of the current density on the power consumption is shown in Figure 7. The power consumption per unit amount of CO₂ recovery was in the range of 0.5 ~ 1.0 kWh/kg-CO₂, and increased with the increase in the current density. This is due to the larger loss in the cells other than the electrode cells for the higher current density. The power consumption for the CO₂ recovery for the present is reasonably low compared with the conventional processes.

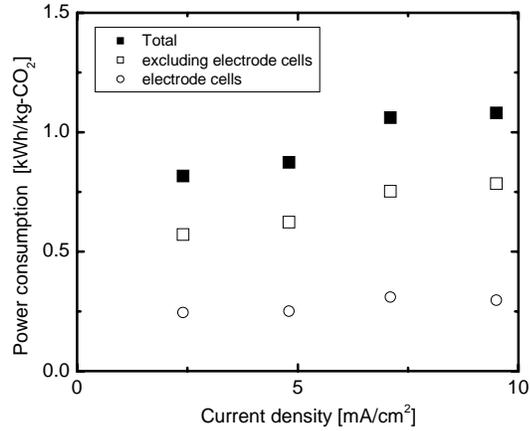


Figure 7 Effect of the current density on the power consumption for CO₂ recovery.

4.3. Effect of the number of the cell pairs

It is considered that the power loss in the electrode cells due to the electrolysis of water can be reduced by increasing the number of the cell pairs. Theoretically, the loss due to the electrolysis can be negligible at the limit of infinite number of the cell pairs. In this study the effect of the number of cell pairs was examined in the range of 5 to 10. Figure 8 shows the effect of number of the cell pairs on the CO₂ recovery rate. The CO₂ recovery rate was increased linearly with an increase in the number of the cell pairs, indicating the recovery rate per unit cell pair is constant. With an increase in the number of the cell pairs, the potential necessary to achieve a constant current density increased as shown. However, as shown in Figure 9, the power consumption per unit amount of CO₂ decreased with an increase in the number of the cell pairs.

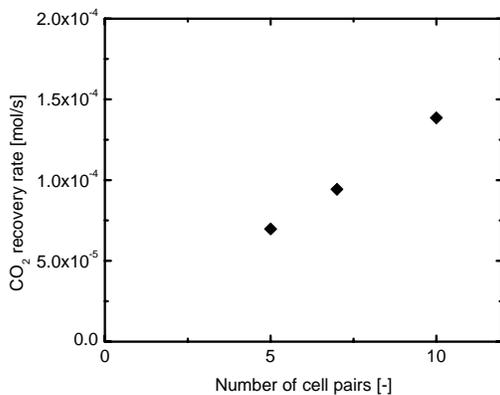


Figure 8 Effect of the current density on the CO₂ recovery rate. Conditions other than the current density were the same as those in Fig. 3.

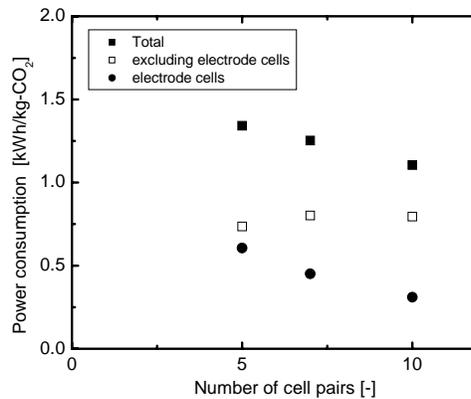


Figure 9 Effect of the current density on the power consumption for CO₂ recovery. Conditions same as those in Fig. 3.

4.4. Effect of the initial concentrations of carbonate and the electrolyte solutions

Effect of the concentration of carbonate (NaHCO_3) in the feed solution on the CO_2 recovery was examined in the range of 0.6 ~ 1.0 M. It was found that the CO_2 recovery rate was almost unaffected by the concentration in the range of studied. The potential difference was slightly decreased as the concentration increased. This is because the conductivity of carbonate solution increased with an increase in the concentration. As a result, the power consumption for unit CO_2 recovery was decreased slightly with an increase in the carbonate concentration.

Effect of the concentration of the electrolyte solution (Na_2CO_3) in the base cell on the CO_2 recovery rate was examined in the range of 0.1 ~ 0.4 M. No remarkable effect on the CO_2 recovery rate was observed. However, the potential difference was slightly decreased as the concentration increased. This is also due to the decrease in the resistance by increasing the concentration. The power consumption for unit CO_2 recovery slightly decreased with an increase in the concentration of the electrolyte solution as well.

These effects of the concentrations could be more significant when the electro dialysis operations are conducted under severer conditions such as high current densities or large numbers of cell pairs, where the electric resistances in the cell (solutions) affect on the total performance.

5. Process evaluation

The minimum power consumption within the operation conditions studied in this work was 0.57 kWh/kg- CO_2 (or 0.57 MWh/t- CO_2 equivalently), which was achieved at the current density 2.4 mA/cm². However, the CO_2 recovery rate in this case was smallest. This is due to the fact that the higher efficiency of the electro dialysis, or more generally, electrochemical process can be achieved under the conditions close to the equilibrium conditions. However, the reaction rate is also slower under such conditions. More comprehensive study will be necessary to determine the practically optimum conditions. However, the power consumption range in this study is reasonably low compared with the conventional processes along with relatively high CO_2 recovery rates.

6. Conclusions

A new type of the CO_2 recovery process with an electro dialysis method was proposed, and the feasibility of the concept was examined by laboratory-scale experimental studies. The minimum power consumption for the unit amount of CO_2 recovery from sodium bicarbonate solution was 0.57 kWh/kg- CO_2 . Thus the proposed process is both technically and economically feasible.