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DEVELOPMENT OF CARBON DIOXIDE SEPARATION PROCESS USING CONTINUOUS HOLLOW-FIBER MEMBRANE CONTACTOR AND WATER-SPLITTING ELECTRODIALYSIS

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ABSTRACT

Studies on the development of carbon dioxide (CO_2) separation process using continuous hollow-fiber membrane contactor (HFMC) and water-splitting electrodialysis (WSED) as an alternative method for the conventional processes are reported. Several experiments for CO_2 recovery and absorbent regeneration using HFMC–WSED hybrid system were performed. In this study, four widely used absorbents (KOH, NaOH, K_2CO_3, and *N*-methyldiethanolamine) were examined and compared in terms of the process efficiency. The results showed that KOH was the best absorbent for this hybrid system due to its high ionic conductivity. In addition, several

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operational problems including the proton leakage and gas molecule diffusion through the membranes were considered. The results of continuous experiments showed that the continuous recovery of CO_2-rich absorbents was reliably performed during the tests without any problem.

Key Words: Carbon dioxide; Continuous hollow-fiber membrane contactor; Water-splitting electrodialysis; Hybrid system

INTRODUCTION

Carbon dioxide (CO_2), which is produced whenever fossil fuels such as oil, coal, and natural gas are burned, is the largest contributor to the greenhouse effect. In the United States, approximately 6.6 tons of greenhouse gases are emitted per person every year. In addition, the emissions per person have increased about 3.4% between 1990 and 1997. Most of these emissions, about 82%, are from burning fossil fuels to generate electricity and power our cars (1). Since global warming problem has a significant impact on the earth's environment, there has been worldwide attention to the reduction of greenhouse gas emissions from related sources. In 1998, emissions of CO_2 in the United States resulting from the generation of electric power were 2447 million short tons, an increase of 3.7% from 1997 (1). Therefore, CO_2 removal from stack gases of power plants burning coal as a fuel is important if the greenhouse effect is to be reduced. To achieve adequate CO_2 reduction, CO_2 separation from industrial waste gases, which would otherwise be vented to the atmosphere, should become essential. With current technologies, CO_2 separation can be performed by several approaches including absorption into liquid solvents (2–5), adsorption on solids (6,7), permeation through membranes (8–10), and chemical conversion (11). For removing CO_2 from high-volume waste gas streams, absorption into liquid solvents is the most suitable process approach (2). The CO_2 absorption process generally consists of an absorption unit where CO_2 is removed from a gas phase into a liquid solvent and a regeneration unit where the absorption capability of the used solvent is recovered before being reintroduced to the absorption unit. The commonly used absorption solvents are alkanol amines (monoethanolamine (MEA), diethanolamine (DEA), and *N*-methyldiethanolamine (MDEA) etc.), mixed amine solution, alkaline solutions (KOH and NaOH etc.), potassium carbonate (K_2CO_3), and so on (2–5). The CO_2-rich absorbents are recovered by the thermal (or thermal-vacuum) processing in most cases. Since these processes are operated at high temperature, several problems occur including thermal instability of chemical absorbents, corrosion of

materials, and high-energy consumption. Therefore, the developments of novel chemicals and processes for absorbing and recovering CO_2 at low temperature are required to overcome these demerits. In this study, the feasibility of new hybrid CO_2 separation process using a Hollow-Fiber Membrane Contactor (HFMC) and a water-splitting electrodialysis (WSED) was investigated as an alternative method for the conventional CO_2 separation.

Hollow Fiber Membrane Contactor

The HFMC is a bundle of microporous hollow fibers packed into a shell similar in configuration to a shell-and-tube heat exchanger. Gas separation using HFMC has been studied for many years (12–15). The HFMC is an emerging technology for replacing conventional scrubbers for gas/liquid contacting. Conventional scrubbers for flue gas absorption and degassing processes are characterized by having huge space requirements, high capital costs, and several operational limitations such as entrainment and loading limitation (16). Moreover, the conventional processes are operated at high temperature over 100°C for CO_2 absorption and regeneration, causing significant problems such as poor thermal instability of chemical absorbents, corrosion of materials, and high-energy consumption. The HFMC, having huge specific area can potentially overcome these problems. The CO_2 absorption efficiency depends on the properties of microporous hollow-fiber membranes (hydrophobicity and pore size etc.), operating conditions (e.g., gas/liquid flow rate and absorption temperature etc.), and characteristics of chemical absorbents. High CO_2 removal efficiency can be achieved by controlling these conditions. However, the membrane resistance to mass transfer and membrane fouling are problems to be solved (3).

Water-Splitting Electrodialysis

Ion-exchange membrane processes such as WSED and diffusion dialysis, and electrodeionization exhibit great potential as efficient and economic tools for environmental pollution control in end-of-pipe treatment (17–19). These processes are successfully being used only recently in the chemical process and environmental protection industry. The WSED using bipolar membrane (BPM) is very interesting in terms of its unique electrochemical properties. Water-splitting electrodialysis is an energy efficient process for converting salts to their acids and bases (17,19–26). The BPM, which contains anion and cation exchange regions in series, has unique electrochemical properties. During current flow, all salts exchanged in the membrane are removed from the fixed charge regions, and then hydrogen and hydroxyl ions are generated in this zone. The hydrogen and

hydroxyl ions migrate out of the interface, in opposite directions, under the action of the strong electric force in the region, to the adjacent solutions. Recent developments of high performance bipolar membranes enable to further expand the potential uses of electrodialysis in the chemical industries. The WSED using BPM can realize zero-emission as a clean technology without the production of undesirable by-products.

Hybrid Systems for Separating CO_2

Water-splitting electrodialysis connected with HFMC can recover CO_2 from CO_2-rich absorbents using electricity as a driving force at low temperature without extra heating. Therefore, the equipment can be simplified, and the energy consumption is expected to decrease significantly. Moreover, hydrogen gas (H_2) produced by the electrode reaction can be used as an energy source to generate electricity using a fuel cell. Schematic drawing of new CO_2 separation process using continuous HFMC and WSED is shown in Fig. 1. The CO_2 contained in flue gas is absorbed into an absorbent in the HFMC and then degassed in the WSED stack by pH controlling. The principle of CO_2 degassing is that bicarbonate (or carbonate) ions electromigrated into the acid compartment are changed into gaseous CO_2 form at low pH (below four), and CO_2 reacted

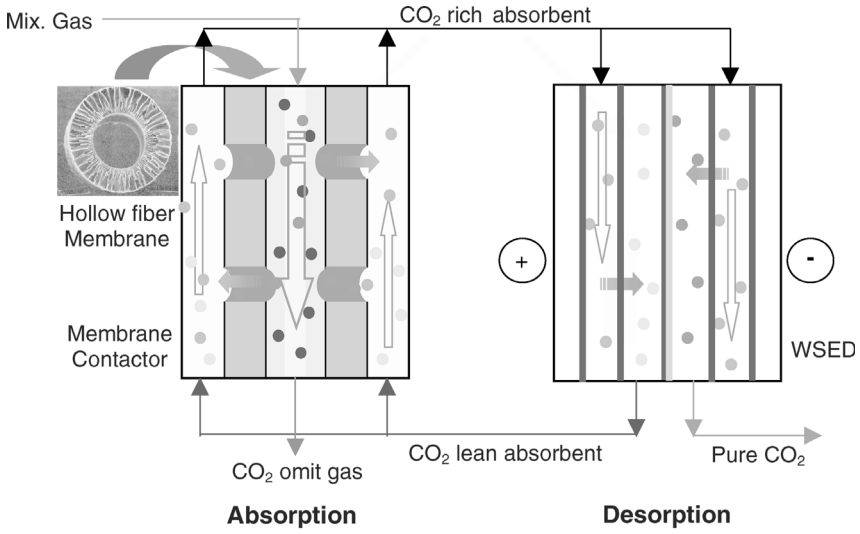


Figure 1. Schematic view of carbon dioxide separation process using continuous HFMC and WSED.

absorbents are recovered in the base compartment simultaneously. The reactions in the HFMC and WSED units are as follows:

Absorber (HFMC)

$$MDEA + CO_2 + H_2O \Leftrightarrow MDEAH^+ + HCO_3^- \quad (1)$$

$$CO_2 + 2NaOH \Leftrightarrow Na_2CO_3 + H_2O \quad (2)$$

$$H_2O + CO_2 \Leftrightarrow H^+ + HCO_3^- \quad (3)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad (4)$$

Acid compartment (WSED)

$$H^+ + HCO_3^- \Rightarrow H_2O + CO_2\uparrow \quad (5)$$

Base compartment (WSED)

$$MDEAH^+ + OH^- \Rightarrow MDEA + H_2O \quad (6)$$

$$Na^+ + OH^- \Leftrightarrow NaOH \quad (7)$$

The electrode reactions are

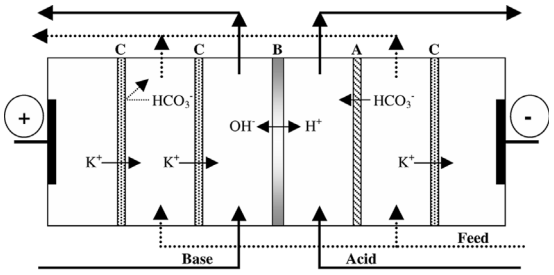
$$\text{Cathode}: \ 2H_2O + 2e^- \Rightarrow H_2\uparrow + 2OH^- \quad (8)$$

$$\text{Anode}: \ 2H_2O \Rightarrow O_2\uparrow + 4H^+ + 4e^-. \quad (9)$$

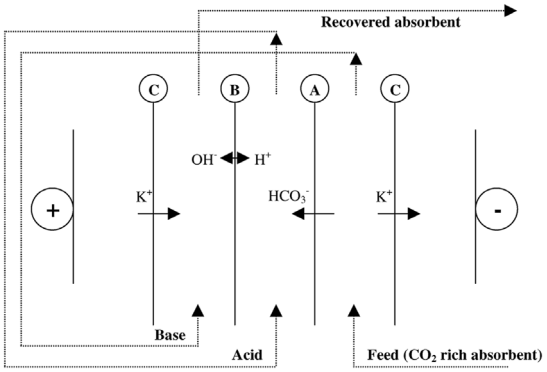
EXPERIMENTAL

Batch Water-Splitting Electrodialysis Experiments

Batch cell experiments were performed with various operating conditions and absorbents using a six-chamber electrodialytic cell. The membrane effective area was 7.07 cm^2 and the distance between the two membranes was 15 mm. During the experiments, the feed solution (absorbent fully reacted with CO_2), acid/base solutions (0.5 mol dm^{-3} NaCl), and electrode rinse solution (0.5 mol dm^{-3} Na_2SO_4) were circulated using a peristaltic pump. The feed solutions (KOH, NaOH, K_2CO_3, and MDEA) were fully reacted with CO_2 using a fine diffuser. The schematic drawing for cell configuration is shown in Fig. 2(a) and detailed experimental conditions are listed in Table 1. The constant current was supplied from the HP



(a)



(b)

Figure 2. The WSED cell configurations of batch (a) and continuous experiment (b): (A: anion-exchange membrane; B: bipolar membrane; C: cation-exchange membrane).

Table 1. Experimental Conditions for Batch Cell Experiments

Absorbent Concentration (mol dm^{-3})				Temperature (°C)	Current Density (mA cm^{-2})
NaOH	KOH	K_2CO_3	MDEA		
0.50	0.50	0.36	0.84	35.0	56.58
0.75	1.00	0.72	1.26	40.0	113.15
1.00	1.50	1.09	1.68	45.0	169.73
1.50		1.45	2.52	50.0	
			2.94	55.0	

6674A-power supply (Hewlett Packard Co. Ltd., USA) connected to two platinum plated titanium electrodes. Solution conductivity (conductivity meter, Cole-Parmer, USA), pH (250 A pH meter, Orion, USA), and recovered base concentrations were measured for investigating the process characteristics. Neosepta® CM-1 and ACM (Tokuyama Co. Ltd., Japan) were employed as the cation and anion exchange membranes, respectively. Neosepta BP-1 (Tokuyama Co. Ltd., Japan) was used as a bipolar membrane for water splitting. The CO_2 recovery rates were measured using a gas-flow meter (MKS instruments Inc., USA) and bubble-flow meter. Pure helium was used as a sweep gas. The CO_2 permeabilities for selected ion-exchange membranes were measured through gas permeation cell tests. The experimental setup was well depicted in Ito et al.'s work (8). The apparatus consisted of a flat-type membrane cell with an effective membrane area of 12.56 cm^2, a CO_2 gas flow system, a water vapor saturator, and a bubble flow meter. The membranes were wet during the gas permeation tests and the CO_2 permeabilities were measured at a steady state using a bubble flow meter. The current efficiency for recovered absorbents was calculated from the total current passing through the cell system and base concentrations determined by acid–base titration with 0.1-mol dm^{-3} HCl as follows:

$$\eta = \frac{\sum \left(\frac{m_i^o - m_i^e}{Mw_i} \right) |z_i| VF}{nIt} \tag{10}$$

where η is the current efficiency ($0 \leq \eta \leq 1$), m_i^o and m_i^e the initial and final concentration (g dm^{-3}) of ionic species, respectively, Mw_i the molecular weight of ion (g mol^{-1}), and z_i the valence of ion. V refers to the solution volume (dm^3), F the Faraday constant (96,500 C mol^{-1}), n the number of cell pair, I the current (A) applied in system, and t the operating time (sec).

CO_2 Absorption in Hollow-Fiber Membrane Contactor

Batch CO_2 absorption experiments were performed to investigate the absorption trends for various absorbents. Microporous polytetrafluoroethylene (PTFE) hollow fiber membranes (Poreflon®, Sumitomo Electric Industries Ltd., Japan) were used in this study. More detailed dimensions for the absorption module and membrane are listed in Table 2. N_2/CO_2 (80/20%) mixture was used as a feed gas and the gas flow rate was constantly controlled by a mass flow controller (MKS instruments Inc., USA). A gas chromatography (Shimadzu GC-12B, Japan) including a thermal conductivity detector and bubble flow meter were used to check the composition and flow rate of the gas mixture at the module outlet, respectively. Absorption liquid was constantly fed using a gear pump (Cole-Parmer, USA). The CO_2 absorption rates were measured at a steady state.

Table 2. Dimensions of Hollow Fiber Membrane and Module

Material	I.D. (10^{-3} m)	O.D. (10^{-3} m)	Porosity (%)	Pore Size (10^{-6} m)	Length (10^{-2} m)	No. of Fibers	Packing Fraction
PTFE	1.00	2.00	70.0	1.00	20.0	54	0.64

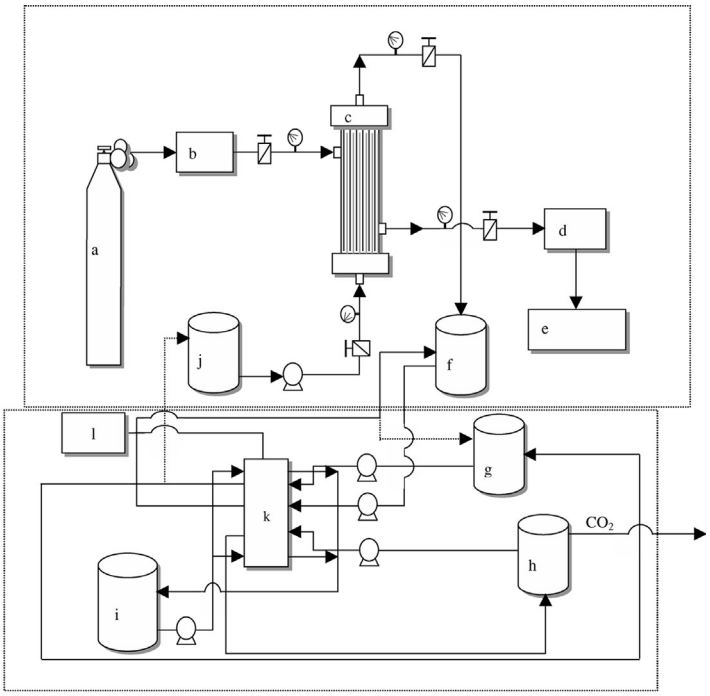
Continuous CO_2 Separation

The schematic diagram of continuous CO_2 separation system is shown in Fig. 3. Continuous experiments were carried out with a HFMC, which consists of microporous PTFE membranes (Poreflon, Sumitomo electric Industries Ltd., Japan) and a 5-compartment WSED cell. The specifications of the absorption module and hollow fiber membrane are given in Table 2. The mixture gas of N_2/CO_2 (80/20%) and potassium hydroxide were used as a feed gas and CO_2 absorbent, respectively. The absorbent reacted with CO_2 and was fed into the 5-chamber electrodialytic cell (Fig. 2(b)) for continuous CO_2 recovery. The membrane effective area was 50.24 cm^2, and Neosepta CM-1 and ACM (Tokuyama Co. Ltd., Japan) were employed as the cation and anion exchange membranes, respectively. Neosepta BP-1 (Tokuyama Co. Ltd., Japan) was used as a bipolar membrane for water splitting.

RESULTS AND DISCUSSION

Batch Experiments

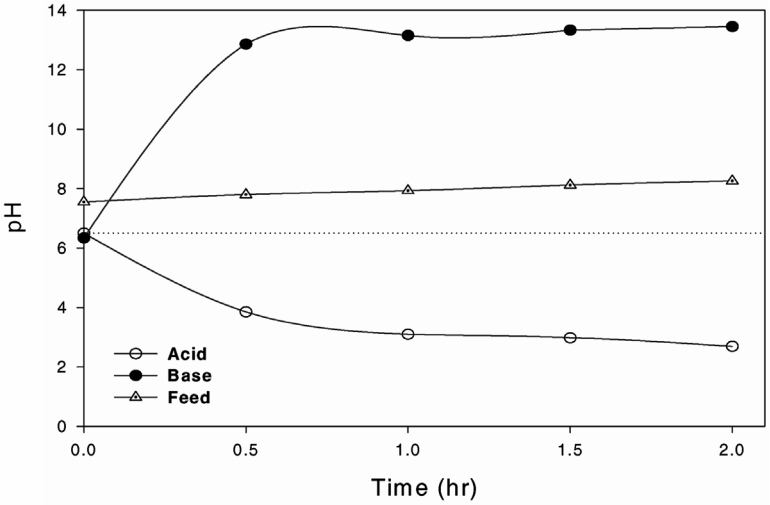
Batch WSED experiments were performed with various operating conditions and absorbents using a six-chamber electrodialytic cell. The pH and conductivity values measured in each compartment are shown in Fig. 4. On comparing the pH variations between the acid and the base compartment, it was observed that the pH changes were much more pronounced in the case of the base compartment. This observation indicates that the protons generated from bipolar membranes were consumed to form gaseous CO_2 molecules. This can also be observed in the variations of solution conductivity (Fig. 4(b)). Here it is seen that the solution conductivities in the base compartment increased as a function of time but that of the acid compartment slightly decreased. This can only be due to the removal of bicarbonates (or carbonates) combined with protons in the acid compartment. The loss in process efficiency due to the diffusion of a gas molecule from the acid compartment and H^+ ion leakage through an anion exchange membrane was reported by several researchers (21,26). In this study,



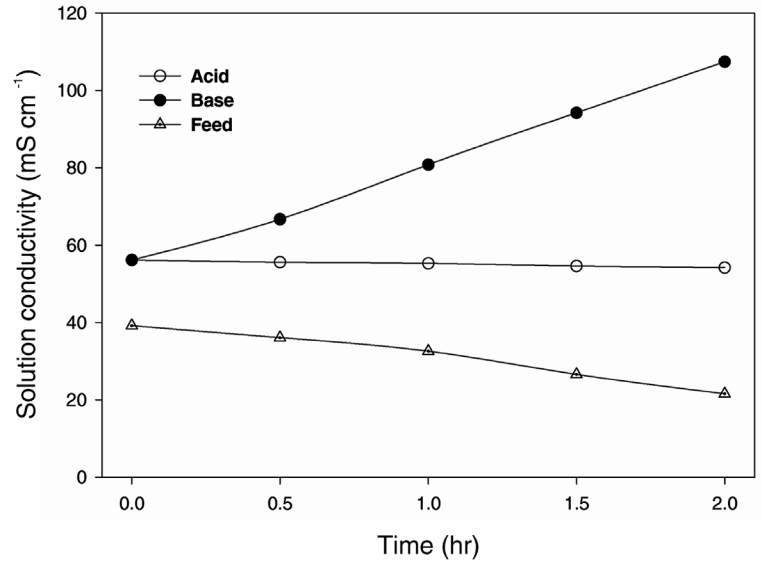
a.	Mix. gas cylinder	g.	Base reservoir
b.	Mass flow controller	h.	Acid reservoir
c.	Hollow fiber membrane module	i.	Electrode rinse solution reservoir
d.	Mass flow meter/ Bubble flow meter	j.	Absorbent reservoir
e.	Gas chromatograph	k.	Water-splitting electrodialyzer
f.	Feed reservoir	l.	D.C. power supply

Figure 3. Schematic diagram of continuous CO_2 separation system.

the Neosepta ACM having low proton permeabilities was used as an anion exchange membrane to minimize the proton leakage into the feed stream. In addition, CO_2 permeabilities for commercial ion-exchange membranes used in this study were measured by using gas permeation cell. The membranes were wet during the gas permeation tests and the CO_2 permeabilities were measured at equilibrium state. The CO_2 permeability through BPM (BP-1) was ca. 1.25×10^{-9} cc cm^{-1} sec^{-1} cmHg^{-1} and lower than those of mono-polar membranes as expected (ACM: ca. 1.38×10^{-9} and CM-1: ca. 1.65×10^{-9} cc cm^{-1} sec^{-1} cmHg^{-1}). Moreover, because the current efficiency for base compartment was over 95% in most cases, it seems that the loss of current efficiency due to the diffusion of CO_2 molecules can be neglected. Figure 5



(a)



(b)

Figure 4. Variation of pH (a) and conductivity (b) of the compartments according to time (Feed: 0.5 mol dm^{-3} NaOH; Acid/Base: 0.5 mol dm^{-3} NaCl: Electrode rinse: 0.5 mol dm^{-3} Na_2SO_4; Temperature: 35°C; Current density: 113.15 mA cm^{-2}).

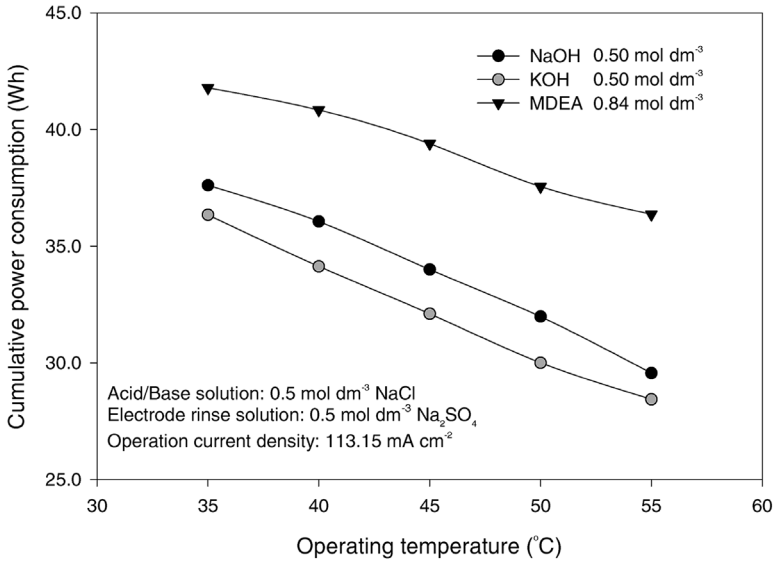


Figure 5. Effect of operating temperature on the energy consumption.

shows the cumulative power consumptions as a function of operating temperatures. Since the ionic mobility increases with increasing temperature, the cumulative power consumptions for 3 hr decreased as an increase in solution temperatures. In this study, the commonly used absorbents (KOH, NaOH, K_2CO_3, and MDEA) were examined. The relationship between the solution conductivities and the energy consumptions for the considered absorbents is shown in Figs. 6 and 7. The absorbents were reacted fully with CO_2 using a fine diffuser before the experiments. The energy consumptions decreased with an increase of absorbent concentrations due to increased solution conductivity. Since the mobility of potassium ion is higher than that of sodium, the energy consumptions for the potassium-absorbents (KOH and K_2CO_3) were lower than that of the sodium-absorbent (NaOH). The detailed ionic properties of the absorbents are shown in Table 3. Moreover, the precipitation of sodium (bi)carbonate occurred over the concentration of 1.00-mol dm^{-3} NaOH as shown in Fig. 6. The conductivity of alkanolamine (MDEA) exhibited lower values than that of other absorbents at the same concentration and decreased over 1.60-mol dm^{-3} MDEA. Although potassium carbonate revealed lowest energy consumption, it possessed relatively lower absorption capability than those of other chemicals and was also converted to hydroxide form (i.e., KOH) after regeneration. Therefore, potassium hydroxide was selected as the best absorbent among the four considered chemicals in terms of energy efficiency. The CO_2

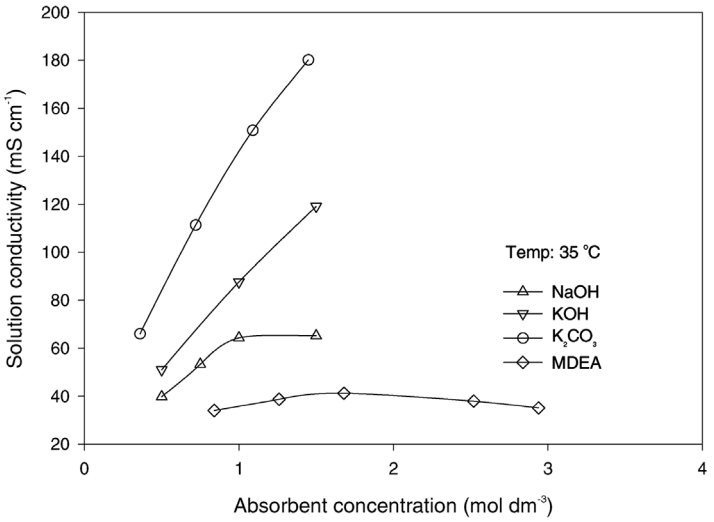


Figure 6. Variations of solution conductivities according to absorbent concentrations.

recovery rates shown in Fig. 8 were measured in batch WSED experiments. The results show that the CO_2 recovery rates reach a steady state after a certain time. The values obtained at steady states agreed with those calculated by using Eq. (11) modified from Eq. (10).

$$\frac{C_{CO_2}V}{t} = \frac{I}{F} \quad (\text{mol sec}^{-1}) \tag{11}$$

Here, C_{CO_2} is the concentration (mol dm^{-3}) of the CO_2 generated in the acid compartment. Figure 8(a) shows that the CO_2 regeneration rates converged with the estimated value at a constant current ($113.15\ \text{mA cm}^{-2}$) operation.

Table 3. Ionic Properties in Water at 25°C

Cations	Molar Conductivity[a] (10^{-4} S-m mol^{-1})	Stokes Radii[a] (nm)	Diffusion Coefficient[b] (10^5 cm^2 sec^{-1})
H^+	349.8	0.026	9.312
Na^+	50.14	0.183	1.334
K^+	73.55	0.125	1.957

[a] From Ref. (27).
[b] From Ref. (28).

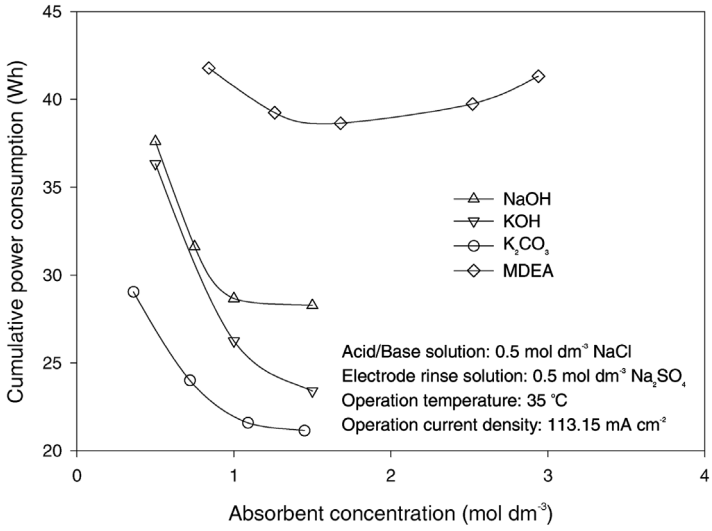


Figure 7. Effect of absorbent concentrations on energy consumption.

Moreover, the same results were obtained at different current densities as shown in Fig. 8(b). This suggests that the proton leakage through anion-exchange membrane was negligible, and also an additional process for converting CO_2 into a gaseous form is not required in this system.

Several batch absorption experiments using PTFE-HFMC were performed to investigate the effect of absorbent concentration on CO_2 removal efficiency. As mentioned previously, the CO_2 absorption efficiency of a HFMC strongly depends on membrane properties and various operating conditions such as gas/liquid flow rate and operation temperature. Accordingly, these factors must be considered in the process design of pilot scale. Although adequate experiment conditions were determined before the main experiments, in this work, however, these were fixed and only the effect of absorbents on the process efficiency was considered. An example of variation in CO_2 absorption rate as a function of the absorbent concentration is presented in Fig. 9. Although CO_2 absorption capability of NaOH was similar to that of KOH, the precipitation of sodium (bi)carbonates in hollow fiber membrane decreased the removal efficiency at high absorbent concentrations ($>$ ca. 0.50 mol dm^{-3}). It seems that the precipitated carbonate compounds blocked the membrane pore and therefore reduced the absorbent solution-CO_2 contact area. As expected, potassium carbonate revealed relatively lower absorption capability than those of other chemicals considered.

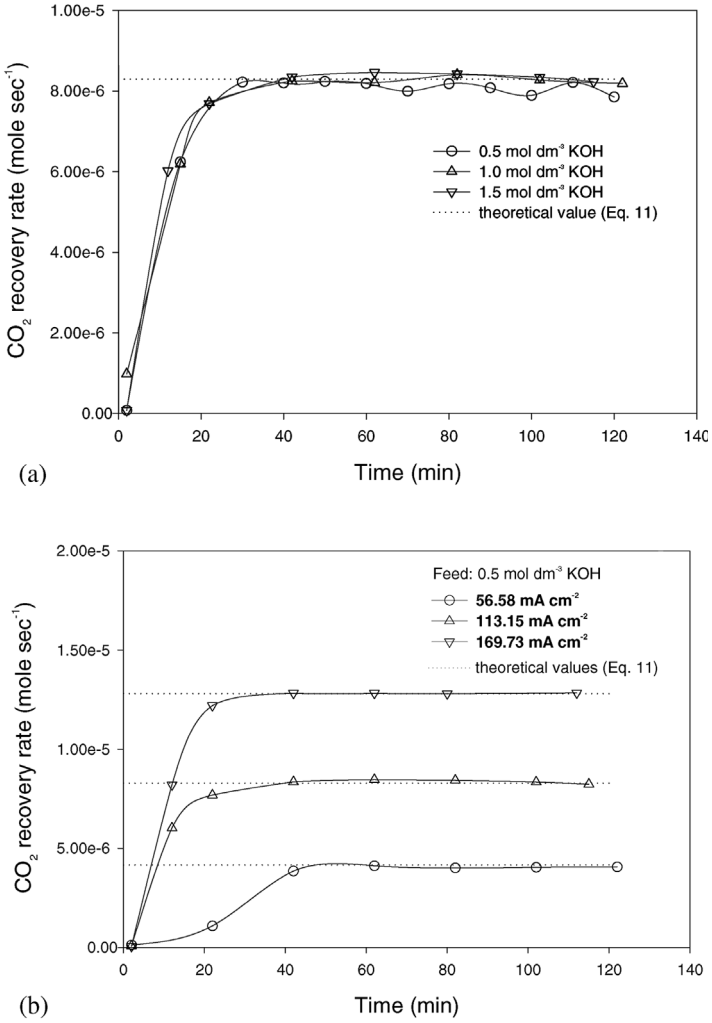


Figure 8. Variations of CO_2 recovery rate according to time (Acid/Base: 0.5 mol dm^{-3} NaCl: Electrode rinse: 0.5 mol dm^{-3} Na_2SO_4; Temperature: 35°C): (a) at constant current density (113.15 mA cm^{-2}); (b) at constant feed concentration (0.50 mol dm^{-3} KOH).

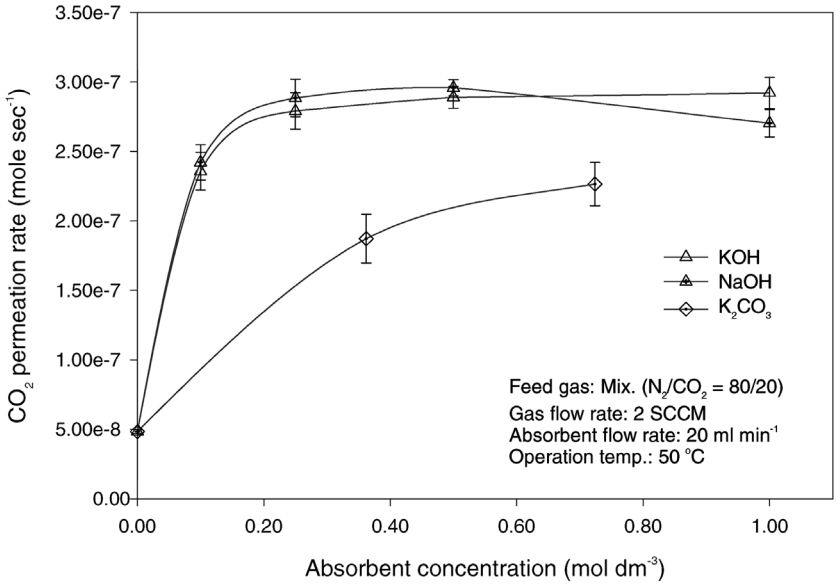


Figure 9. Variation of CO_2 absorption rate a according to absorbent concentration in batch absorption experiments.

Continuous Experiments

The WSED can be used likewise classical electrodialysis principles in different operation configurations. Three common process configurations are widely in use, i.e., batch-mode, feed and bleed-mode, and single-pass continuous flow configuration. In a feed and bleed-configuration, a concentration or depletion of a process stream is carried out, but in a continuous manner. This is accomplished by recycling the main part of the process solution and bleeding off only a small part of this stream, which is the product (29). In the case of continuous CO_2 separation, a modified feed and bleed-mode was considered as the most adaptable configuration. Continuous CO_2 separation experiments were carried out using continuous system composed of PTFE-HFMC and a five-chamber WSED cell. The experimental conditions were based on the result of the batch experiments and, therefore, potassium hydroxide was selected as the CO_2 absorbent. Two representative results of variation trend in CO_2 removal efficiencies are shown in Fig. 10 as a function of time. During the tests, the removal efficiencies were maintained steadily over 93% in both cases (run 1 and 2). However, the cumulative power consumption (for 10 hr) of run 2

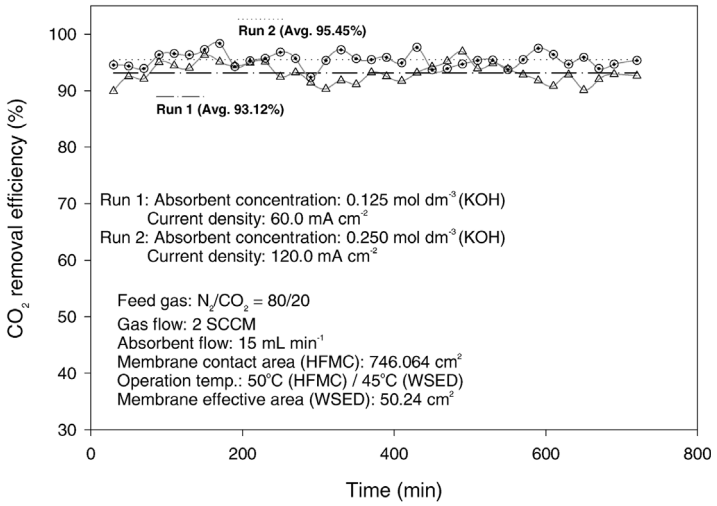


Figure 10. Variations of CO_2 removal according to time in continuous experiment.

(ca. 3.233 kWh) was much lower than that of run 2 (ca. 0.997 kWh), i.e., the removal efficiency was slightly enhanced by increasing absorbent concentration, but on the other hand the power consumption was significantly increased. Therefore, the optimum operating conditions should be considered in terms of process and economical efficiency, simultaneously. The optimization of the process as a pilot-scale is in progress. Meanwhile, the result of continuous experiments shows that a continuous recovery of absorbents combined with CO_2 in absorber was reliably performed in the WSED cell.

CONCLUSIONS

Several experiments for CO_2 removal using HFMC–WSED hybrid system were carried out. In this study, the commonly used absorbents (KOH, NaOH, K_2CO_3, and MDEA) were examined and compared in terms of the process efficiency. In conclusion, KOH was the best absorbent for this hybrid system due to its high ionic conductivity. In the case of NaOH, the precipitation of sodium (bi)carbonate was considered as the significant problem in this system. Moreover, the proton leakage could be minimized using membrane having low proton permeabilities. The continuous experiments were carried out and the results showed that continuous recovery of CO_2-rich absorbents was reliably performed during the tests.

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