[To Index]

Experimental Investigation of a Molecular Gate Membrane for Separation of Carbon Dioxide from Flue Gas

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Abstract

Commercial-sized modules of the PAMAM dendrimer composite membrane with high CO_2/N_2 selectivity and CO_2 permeance were developed according to the In-situ Modification (IM) method. This method utilizes the interfacial precipitation of membrane materials on the surface of porous, commercially available polysulfone (PSF) ultra-filtration hollow fiber membrane substrates. A thin layer of amphiphilic chitosan, which has a potential affinity for both hydrophobic PSF substrates and hydrophilic PAMAM dendrimers, was employed as a gutter layer directly beneath the inner surface of the substrate by the IM method. PAMAM dendrimers were then impregnated into the chitosan gutter layer to form a hybrid active layer for CO_2 separation. Permeation experiments of the PAMAM dendrimer composite membrane were carried out using a humidified mixed CO_2 / N_2 feed gas at a pressure difference up to 97 kPa at ambient temperature. When conducted with CO_2 (5%) / N_2 (95%) feed gas at a pressure difference of 97 kPa, the PAMAM composite membrane exhibited an excellent CO_2/N_2 selectivity of 150 and a CO_2 permeance of 1.7×10^{-7} m^3(STP) m^{-2} s^{-1} kPa^{-1}. The impact of various process parameters on the permeability and selectivity was also examined.

Keywords: CO_2 separation, membrane module, dendrimer, molecular gate

Introduction

The concentration of carbon dioxide (CO_2), a greenhouse gas, has been increasing in the atmosphere. Several methods have been devised to reduce the amount of CO_2 emissions into the atmosphere. Most notably, the sequestration of CO_2 underground or in the oceans is seen as a novel means to mitigate carbon dioxide emissions and has great promise in the near future from both technological and economic standpoints [1, 2, 3]. One problem with the sequestration is the cost of recovering CO_2 from emissions. The best-known method of separating and recovering CO_2 to date is chemical absorption,

which, while expensive, accounts for more than seventy percent of the entire cost of carbon sequestration [3].

One promising means of lowering the cost of CO_2 separation is the development of new, high-performance CO_2 separation membranes that allow CO_2 recovery via membrane separation. Cardo polyimide membranes was found to show good CO_2 separation properties, demonstrating the ability to separate CO_2 from exhaust gas at steel works at a cost comparable to that of the conventional amine solution method [4, 5]. Kovvali and Sirkar recently reported an excellent CO_2/N_2 selectivity for the viscous and nonvolatile liquid poly(amidoamine) (PAMAM) dendrimer, as an immobilized liquid membrane at isobaric test conditions of atmospheric pressure [6, 7]. Interestingly, when the feed contained saturated water vapor, the PAMAM dendrimers showed excellent CO_2 selectivity. They claimed that the facilitated transport membrane of PAMAM dendrimer functioned as a CO_2-selective molecular gate at low CO_2 partial pressures and high feed relative humidities [6]. Since exhaust gases usually contain water vapor near saturation, this excellent CO_2 selectivity would seem to be effective in CO_2 separation from fossil fuel emissions. However, this immobilized liquid membrane has insufficient tolerance to handle the large pressure differences required for obtaining sufficiently large gas fluxes. Providing the liquid PAMAM dendrimer can be successfully fabricated into a stable membrane configuration having suitable tolerances to cope with practical pressure differences, the resulting composite membrane will present a promising CO_2 separation material. In this regards, PAMAM dendrimer composite membranes comprising a gas selective layer on a porous substrate are widely expected to have application as pressure tolerant selective layers. As such, a number of composite membranes have been prepared and examined [8-10].

The research with these type membranes has initially focused on CO_2 separation from flue gases. It is realized that the low pressure separation may be a challenge with respect to overall energy needs. The next step for this membrane development could be recovering CO_2 from a pressurized mixture of CO_2 and H_2 produced after water-gas shift reaction in gasification processes using coal or natural gas [1]. If a new, high-performance separation membrane applicable to CO_2 capture from a pressurized gas stream is developed, the membrane separation will reduce the cost drastically compared to existing technologies. The membrane technique could be used with pressurized gas sources, such as those found in IGCC and NGCC, where CO_2 should be separated from a mixture of CO_2 and H_2. Lin and Freeman recently reported a CO_2/H_2 selectivity of 30 at -20 °C for cross-linked poly(ethylene oxide) membrane [11]. Recently, RITE reported newly synthesized hydroxyl PAMAM dendrimer with a CO_2/H_2 selectivity of 700 at 25 °C [12].

RITE is currently developing a CO_2 molecular gate membrane with the goal of producing a new, high-performance membrane for separating CO_2 from H_2 or N_2. The development is a part of Carbon Sequestration Leadership Forum (SCLF) project where the U.S. DOE/ NETL in collaboration with RITE evaluated the membrane performance for CO_2 separation.

In this study, in advance of CO_2 separation from a pressurized gas stream, commercial-sized modules of the PAMAM dendrimer composite membrane for an ambient flue gas were developed. Specification of the membrane module was length (1 m), diameter (1 inch) and membrane area (0.4 m^2). The module was made using the In-

situ Modification method. CO_2 separation properties of the PAMAM composite membrane at ambient pressure were determined. The impact of various process parameters on the permeability and selectivity of the membrane were also examined with a pencil module prior to the bench scale testing.

Concept of CO_2 molecular gate

Figure 1 shows the concept of CO_2 molecular gate function along with the solution-diffusion model for conventional polymeric separation membrane. The separation membrane (separation function layer) has pathway through which gas molecules pass. In general macromolecular membranes, nitrogen (N_2) or hydrogen (H_2) was able to negotiate this pathway along with the CO_2. As a result, N_2 or H_2 ended up outside the membrane with the CO_2, making it difficult to obtain a high concentration of CO_2. In RITE's proposed CO_2 molecular gate membrane, as suggested previously by Sirkar et al. [6], the pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the passage of other gases. Consequently, the amount of the other gas penetrating to the other side of the membrane is greatly limited and high concentrations of CO_2 can be obtained. The molecular gate membrane can even separate CO_2 from a mixture of CO_2 and H_2, which is very difficult for any existing membrane. The molecular gate membrane will work even under high CO_2 partial pressure.

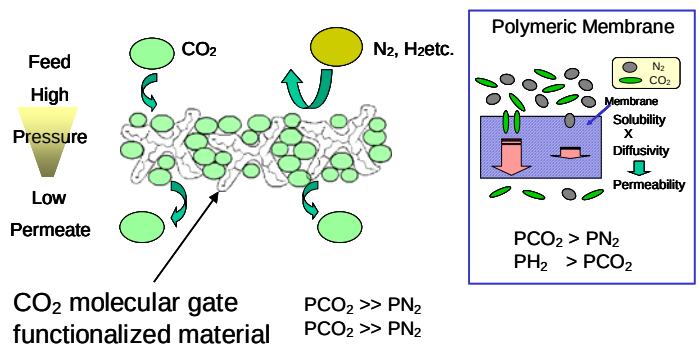

Figure 1. Conceptual diagram of CO_2 molecular gate function.

Poly(amidoamine) (PAMAM) dendrimers show an excellent CO_2 selectivity and would be one of the promising candidate materials that possess the CO_2 molecular gate function. Actually, a novel hydroxyl PAMAM dendrimer developed by RITE showed a CO_2 selectivity over H_2 of 700 as mentioned above [12]. The excellent CO_2/H_2 selectivity is derived from a H_2 permeation blockage by CO_2 existing in the dendrimer.

Experimental

1. Initial RITE membrane

A commercial ultrafiltration membrane module (NTU-3250-C1R, Nitto Denko Co.) was modified to produce PAMAM dendrimer composite membrane module. Wet hollow fiber polysulfone (PSF) membranes (molecular weight cutoff: 6,000) in the module were dried

at ambient temperature for 8 h, followed by further drying for 8 h at 60 °C. This membrane substrate is referred to as the 'PSF- substrate'.

Chitosan was selected as a gutter layer material due to its amphiphilic chemical structure based on the hydrophobic principal chain and hydrophilic hydroxyl and amino moieties. The amphiphilic chitosan exhibits a strong affinity for both the hydrophobic PSF-substrate and hydrophilic PAMAM dendrimers. Chitosan (deacetylation rate: 84-86 %) was purchased from Tokyo Kasei Kogyo Co., Ltd. and used as received.

Poly(amidoamine) (PAMAM) dendrimer molecules with amino surface groups and ethylenediamine core (Generation 0, MW=516), as shown in Figure 2, were obtained as a 20 wt% methanol solution from Aldrich Chemical Co. and used without further purification.

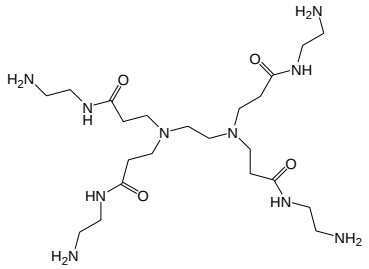

Figure 2. Chemical structure of PAMAM dendrimer (Generation 0).

Figure 3 shows the concept of the In-situ Modification (IM) method. Here, a solution containing the membrane materials was circulated in the lumen side of the hollow fiber membrane, while the opposite (shell) side was evacuated using a vacuum pump. This method can be directly used to modify the surface of the substrate situated inside a module, and is applicable to any size of module, ranging from pencil to large sized commercial modules. In the IM method, if a hydrophobic porous substrate and hydrophilic solution are applied, the hydrophilic solution would be unable to penetrate into the pores of the substrate, resulting in the formation of a gas-liquid interface at the surface of the substrate. Evacuating the opposite side of the substrate causes evaporation of the solvent at the interface, resulting in a solute rich state. Finally, the precipitation of the membrane materials at the interface occurs.

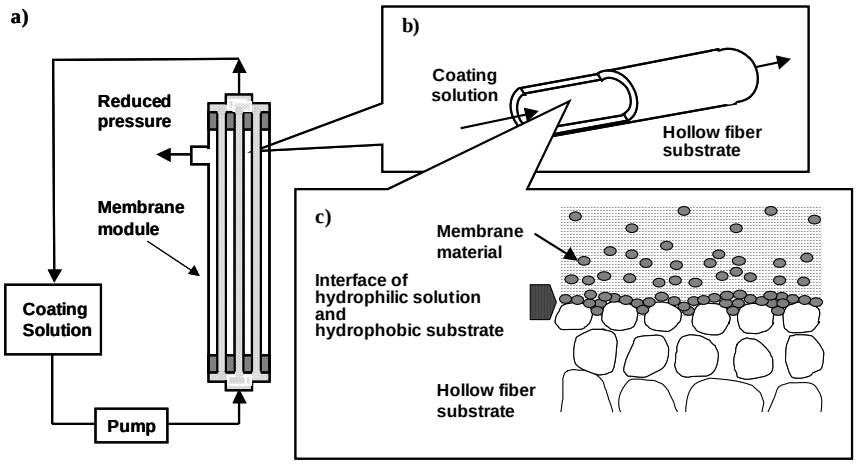

Figure 3. Schematic diagram of In-situ Modification method.

Chitosan was fabricated into a thin gutter layer using the IM method. An aqueous solution containing chitosan (0.5 wt%), acetic acid (2 wt%) and additives was circulated through the lumen side of the hollow fiber substrate using a feed pump. While on the shell side, this was evacuated with a vacuum pump to about 10 kPa at room temperature for 30 min, followed by neutralization of the ammonium ions with 0.1 M aqueous NaOH solution. After rinsing with a mixture of ethanol/H_2O=50/50 (wt/wt), the substrate was dried at 60 ºC for 120 min. The resulting chitosan modified substrate in the module is represented by CTS-substrate.

PAMAM dendrimer was hybridized into the chitosan gutter layer by circulating an aqueous methanol solution containing 10 wt% of PAMAM dendrimer through the lumen side of the CTS-substrate without evacuation of the shell side. After treatment, the membrane module was dried at 60 ºC for 8 h to produce a PAMAM dendrimer composite membrane.

A mixed CO_2 (5 %) / N_2 (95 %) feed gas of about 80% relative humidity was supplied to the lumen side of the hollow fiber membrane in a module at atmospheric pressure at ambient temperature, while the shell side was being evacuated. The permeate flow rate was measured with a soap bubble gas flow meter (SF-1, Estec Co., Ltd.), while its composition was determined with gas chromatography (TCD-GC 323, GL Sciences Inc.). The permeance and selectivity were calculated from the flow rate and composition of the permeate.

2. NETL apparatus and experimental condition

As part of a mutual collaboration between RITE and NETL, the membrane unit developed by RITE was air-freighted to NETL for additional evaluation of the membrane system to remove carbon dioxide from simulated flue gas mixtures. The system was evaluated within an existing, modified packed-bed reactor system located at NETL in Pittsburgh, PA. Simulated flue gas mixtures were passed through the membrane modules to ascertain the performance of the system to separate carbon dioxide from the other components of the gaseous stream.

The RITE apparatus was housed within a rectangular open metal frame support, shown in Figure 4. Five membrane modules were plumbed in parallel flow arrangement. There is one main inlet valve for the gas feed and two main exit valves: one for the retentate and the other for the permeate streams. The permeate stream is operated under vacuum pressure to facilitate the selective transport of carbon dioxide across the membrane interface. Gas isolation valves for the inlet and exit of each membrane module allowed for the number of modules on-line to be varied. The modules were uninsulated with no heat-tracing and therefore experiments were conducted at ambient temperature.

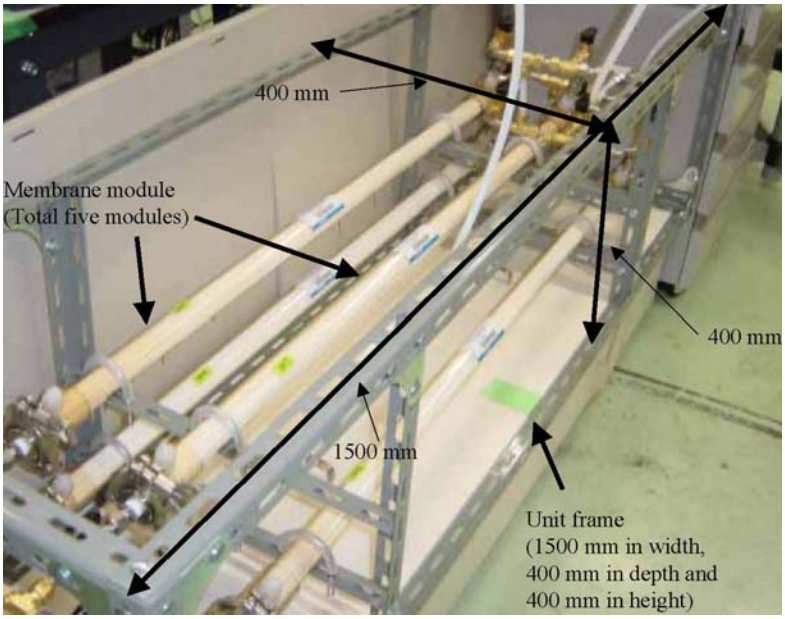

Figure 4. RITE membrane module system.

The RITE system was installed into an existing packed-bed reactor system, shown in Figure 5. The reactor system has been previously described [13] during the investigation of potassium carbonate based sorbents for CO_2 removal. Modifications were made to the reactor system to accept the installation of the membrane modules. The quartz tube reactor was removed from the system and the membrane module was plumbed into the existing tubing. Secondary temperature controls for heater tapes along the gas inlet path served to control the temperatures of several gas mixing chambers and a water humidification chamber. A gas composition was established by blending from gas cylinders using thermal mass flow controllers; water was added to the feed by bubbling the gas stream through two, in-series, water-filled spargers equipped with metal frits. The water bath temperature was measured with an immersed thermocouple in the second sparger. The packed-bed system is configured with gas analyzers for continuous monitoring of flue gas components (SO_2, NO_2, O_2, CO_2, hydrocarbons, etc.), but for the current study, only the CO_2 gas analyzer was required to monitor gas composition. The retentate process gas passed through a Perma Pure drying tube to remove moisture prior to the stream entering the gas analysis train. The reactor system operated slightly above atmospheric pressure (1-2 psig); positive system pressure is necessary to maintain sufficient gas flow to the gas analyzer train. Data are acquired using an automated data logger instrument manufactured by Linseis (model LSB 36 III). Instrument outputs from thermocouple readouts, mass flow controllers, and continuous emission monitors (CEM) for gas analysis are acquired and recorded to computer disk at 1-minute sampling interval. The data file is converted into a format compatible for importing into spreadsheet software (EXCEL).

Figure 5. NETL packed-bed reactor with RITE membrane system installed.

A process flow diagram for the modified reactor system is shown in Figure 6. Additional instrumentation was required to monitor those aspects associated with the membrane process. A mass spectrometer (MS) was used to monitor gas composition of the permeate stream. The MS was connected to a PC-based data acquisition and control system. The MS data file is converted into a format compatible for importing into spreadsheet software (EXCEL). A Vaisala humidity/temperature probe was used to monitor the moisture in the retentate stream. Brooks mass flow meters were used to measure the flow rates of the retentate and permeate streams. WIKA pressure transmitters were utilized to measure of the pressure of the membrane inlet feed and the membrane exit streams (retentate and permeate). A vacuum pump was used on the permeate stream, and a needle valve was throttled upstream of the pump to set the vacuum pressure of the permeate leg of the membrane system.

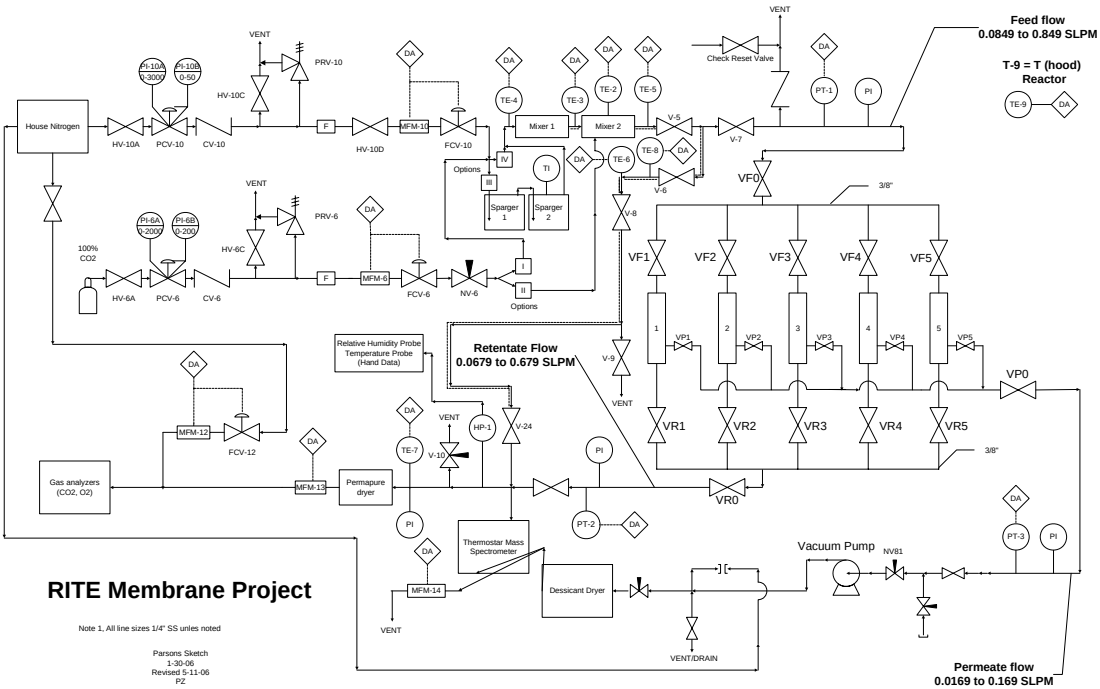

Figure 6. Process flow diagram of NETL reactor system with RITE membrane system.

The experimental procedure and test conditions employed for the membrane tests were chosen such that a material balance for the CO_2 could be monitored and quantified for the three process streams (feed, retentate, and permeate). The membrane system was isolated (i.e., bypass of gas flow) while the inlet gas composition (blended CO_2/N_2 humidified at ambient temperature) was established to simulate a typical flue gas composition. The MS sampling location was in the retentate position during this phase and served as redundant measurement of CO_2 (by the CEM) and H_2O (by the humidity probe). Upon attainment of steady state, the bypass would be halted and the flow was then introduced to the membrane system. This phase of testing would allow the membrane to be "conditioned" under the humidified feed gas at ambient pressure and temperature, but the permeate vent would remain closed and no vacuum was applied. Upon reaching steady state, the MS sampling location was switched from the retentate to the permeate location. A nitrogen purge was initially applied to the permeate leg downstream of the vacuum pump to purge residual gas within the line, and then discontinued. The vacuum pump was turned on with the throttle valve initially closed to keep the membrane isolated from sudden change in vacuum pressure. The needle valve would be slowly opened, gradually exposing the membrane to increasing vacuum. The permeate pressure would be slowly lowered to the vacuum pressure of interest (usually 0.5 psia) and the throttle valve adjusted as necessary to maintain constant permeate pressure. The flow rate and composition of gas in the retentate and permeate eventually would reach steady state and a material balance for CO_2 could be performed. The throttle valve would then be completely opened to attain maximum vacuum (near 0.3 psia) for a second test condition, followed by raising the permeate pressure to 2.2 psia for a third condition. Several hours were required at each condition to reach steady state, and thus a typical day of operation was limited to three vacuum pressures for the same gas feed conditions.

The parametric conditions examined were feed gas composition (5, 15, and 25% CO_2 in N_2), permeate vacuum pressure (0.5, 0.3 and 2.2 psia) and feed gas flowrate (0.3 and 0.8 lit/min). Testing also examined the effect of additional modules and increased surface area. Module #5 was extensively characterized individually, and the additional modules were added one at a time such that the total number of modules on-line ranged between one through five. A total of seven modules were shipped to NETL, but only a maximum of five could be simultaneously tested.

The membrane morphologies were observed using scanning electron microscopy (SEM, S-5000, Hitachi Ltd.) at an accelerating voltage of 7.0 kV. A thin Pt-Pd layer was sputtered on the SEM specimens to enhance conductivity.

Results and Discussion

1. A commercial-sized module of the PAMAM dendrimer composite membrane

A commercial-sized module of the PAMAM dendrimer composite membrane was developed using the In-situ Modification method. Figure 7 shows the membrane module.

A length and diameter of the module were 1.1 m and 1 inch, respectively, and effective membrane area was $0.4m^2$.

Figure 7. PAMAM dendrimer composite membrane module whose dimension is 1.1 m in length and 1 inch in diameter.

2. Permeance and selectivity of dendrimer composite membrane module

Figure 8 shows CO_2/N_2 separation properties of five different membrane modules, Module #1- #5 tested initially at RITE. Their CO_2 permeance and CO_2/N_2 selectivity ranged from 1.5 to 2.2 x 10^{-7} $m^3(STP)m^{-2}$ s^{-1} kPa^{-1} and 110 to 169, respectively. The CO_2 selectivity was much higher than that of about 30 for a polymeric membrane. Here, the large CO_2/N_2 selectivity of 110 to 169 is believed to derive from possible interactions between the CO_2 molecules and the PAMAM dendrimer.

Regarding a pencil module (membrane area is 17 cm^2), CO_2/N_2 selectivity of the PAMAM composite membrane was 230, while the Q_{CO2} value was 4.6×10^{-7} m^3 (STP) m^{-2} s^{-1} kPa^{-1} (61 GPU, 1 GPU = 7.5×10^{-9} m^3 (STP) m^{-2} s^{-1} kPa^{-1}). Accordingly, a 1 m long module did not perform as good as a pencil module with respect to CO_2 separation. This result implies an optimal condition would improve CO_2 separation performance.

As shown in Figure 8, the values of CO_2 separation performance was steady. IM method succeeded in modifying the surface of PSF substrate with PAMAM dendrimer in a housing to produce PAMAM dendrimer composite membrane modules.

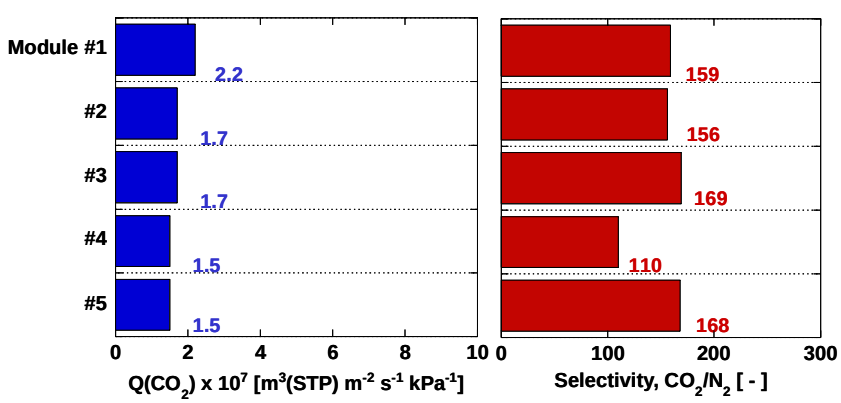

Figure 8. PAMAM dendrimer composite membrane module whose dimension is 1 m in length and 1 inch in diameter.

3. Results at NETL

Results obtained at NETL indicated some degradation in system performance of the RITE modules. After the testing campaign at NETL, all of the modules were returned to RITE and on-going characterizations are taking place to further elucidate possible causes of decreased performance. Data were still being reduced at the time of publication, but some observations can be gathered from the preliminary data.

The effect of varying the CO_2 concentration in the feed is shown in Table 1. The first three columns of data were conducted with only the N_2 feed gas being passed through the water spargers with the CO_2 feed being added downstream of the sparger system. Hence the relative humidity of the feed mixture was lower at higher CO_2 mole fractions. The last two columns of data reflect both feed gases being passed through the spargers to maintain high relative humidity. The CO_2 in the permeate is increased with higher CO_2 feed fraction and the total permeate flow rate also increases. Higher relative humidity, from sparged CO_2, also enhances separation. As could be expected, lower vacuum pressure enhances performance.

It must be noted that the presented data are still preliminary in nature. Separation factors have been approximated assuming only binary gas composition of CO_2 and N_2. Higher separation factors are attained for lower CO_2 feed fraction. Further refinement of the information will be detailed in a future publication.

Membrane testing at NETL indicated lower performance of CO_2 separation versus RITE studies. Additional studies will help confirm the cause of degradation, including the possible effect of air freight transport.

Table 1. Effect of CO_2 concentration and relative humidity in feed gas on membrane system.

Run	4/7	4/19	4/12	4/20	4/24
Module #	5	5	5	5	5
Feed					
Flow rate (lit/min)	0.8	0.8	0.8	0.8	0.8
CO_2 (dry, %)	5	15	25	15	25
Gases thru spargers	N_2	N_2	N_2	N_2 & CO_2	N_2 & CO_2
Rel Hum (%)	91	80	67	98	97
H_2O (%)	2.07	1.93	1.50	2.09	2.01
Retentate					
Rel Hum (%)					
0.5 psia	62	57	55	62	60
0.3 psia	60	55	54	58	56
2.2 psia	65	60	55	63	62
CO_2 (dry, %)					
0.5 psia	4.46	14.5	24.4	14.3	24.2
0.3 psia	4.31	14.5	24.3	14.3	24.5
2.2 psia	5.22	15.0	24.8	14.9	25.0
Flow meter (% full scale)					
0.5 psia	95.0	99.5	102.3	99.3	102.1
0.3 psia	94.1	99.4	102.5	99.0	102.4
2.2 psia	91.9	100.1	103.2	100.3	103.6
Permeate					
CO_2 (dry, %)					
0.5 psia	58.8	65.0	72.8	70.6	77.0
0.3 psia	62.8	64.6	72.0	69.7	73.7
2.2 psia	21.6	40.8	56.8	46.0	60.7
Flow meter (% full scale)					
0.5 psia	4.1	4.6	6.3	5.4	8.0
0.3 psia	4.9	4.3	5.9	5.6	6.6
2.2 psia	1.2	1.8	2.8	2.0	3.2
CO_2/N_2 separation factor (%)					
0.5 psia	27.1	10.5	8.03	13.6	10.0
0.3 psia	32.1	10.3	7.71	13.0	8.41
2.2 psia	5.23	3.91	3.94	4.83	4.63

4. Morphology of PAMAM dendrimer composite membrane

SEM observation was performed to have an insight into the morphology of PAMAM dendrimer composite membrane. A pencil module was used to observe surfaces and cross-sections of chitosan modified PSF substrate and PAMAM dendrimer composite membrane [14].

Figure 9 shows SEM images of the membrane surfaces and cross-sections of the PSF-, CTS-substrate and PAMAM dendrimer composite membrane. The inner surface of the PSF-substrate revealed a large number of pores (1a in Figure 9). After treatment with chitosan, the distinct pore openings on the inner surface were found to disappear (2a). In the cross-sectional image of the CTS-substrate, a uniform layer was observed beneath the surface of the original PSF-substrate of thickness of ca. 200 nm (2b). The SEM observation indicated that the IM method was successfully employed in the preparation of a thin uniform layer of chitosan by controlling precipitation at the interface between the hydrophobic PSF-substrate and the hydrophilic aqueous solution of chitosan. After treatment of the PAMAM dendrimer, no observable pores existed on the surface (3a), and the thickness of the uniform layer was observed to be about 300 nm (3b). Hybridization of the PAMAM dendrimer into the chitosan gutter layer is believed to be responsible for the observed increase in membrane thickness up to 300 nm.

A commercial-sized module of the PAMAM dendrimer composite membrane, with length (1 m), diameter (1 inch) and membrane area ($0.4m^2$), has a structure similar to Figure 3b. However, a thickness of the hybrid layer of chitosan and PAMAM dendrimer in the commercial-sized module was uneven and larger than that of the pencil module. The thicker selective layer may cause the smaller CO_2 permeance in a commercial-sized module of the PAMAM dendrimer composite membrane.

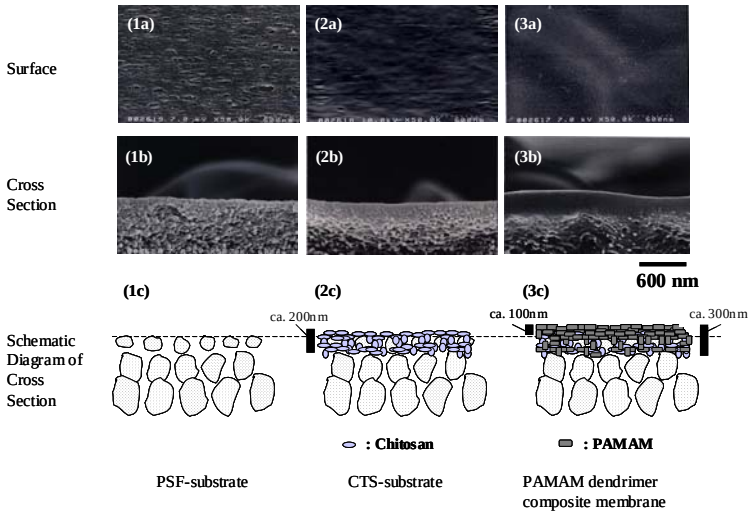

Figure 9. SEM images of PAMAM dendrimer composite membrane and substrate.
Surface image: (1a) PSF-substrate, (2a) CTS-substrate, (3a) PAMAM dendrimer composite membrane
Cross sectional image: (1b) PSF-substrate, (2b) CTS-substrate, (3b) PAMAM dendrimer composite membrane
Schematic diagram of cross section: (1c) PSF-substrate, (2c) CTS-substrate, (3c) PAMAM dendrimer composite membrane

5. Nature of PAMAM dendrimer composite membrane

To understand the nature of PAMAM dendrimer composite membrane itself, properties of the composite membrane were investigated.

Figure 10 shows 1,000 hour long durability of PAMAM dendrimer composite membrane. The test was carried out using a real exhaust gas at a steel manufacturing plant. In the test, a pencil membrane module (length: 80 cm, membrane area: 189 cm^2) was used because of only a small available flux of flue gas. As shown in the figure, PAMAM dendrimer membrane shows stable CO_2/N_2 selectivity and CO_2 permeance during a term of 1,000 hour, even though a slight decline in CO_2 permeance was observed at the first period of the experiment.

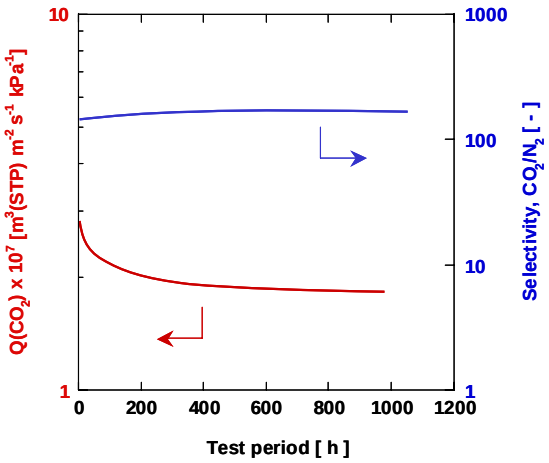

Figure 10. Long term stability of PAMAM dendrimer composite membrane.

Feed gas mixture: CO_2/N_2 (32/68 v/v%) containing saturated water vapor,

Measured temperature: 14-25°C, Pressure difference between feed and permeate: 0.1MPa

Figure 11 shows an operating temperature effect on CO_2 permeance and CO_2/N_2 selectivity. In the experiment, a pencil module (length: 20 cm, membrane area: 17 cm^2) was placed in a thermostat. Temperature of the water bubbler was kept at 40 °C. From the figure, both CO_2 permeance and CO_2/N_2 selectivity increased as a module temperature increased. The phenomenon is quite different from conventional polymeric membrane where the higher temperature yields smaller selectivity. The unique temperature dependence for the PAMAM dendrimer membrane is important and useful to get high performance in CO_2 separation at elevated temperature.

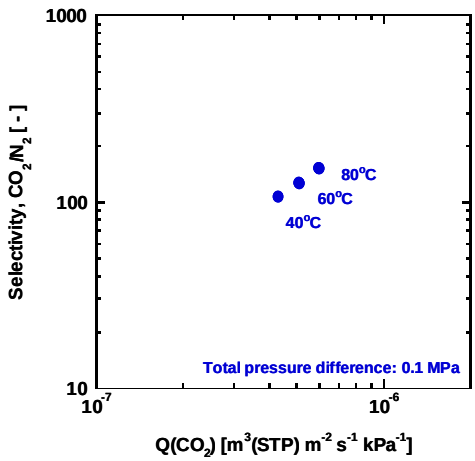

Figure 11. Effect of module temperature on CO_2 permeance and CO_2/N_2 selectivity.

6. Future possibility of CO_2 separation from pressurized gas stream

The driving force of gas permeation through the membrane is the pressure difference across the membrane. For example, membrane systems for capturing CO_2 from a flue gas of atmospheric pressure need vacuum pumps for producing reduced pressure in permeate. The electricity cost of the vacuum pumps exceeds 50 % of the total cost of CO_2 separation with membrane. CO_2 separation from a pressurized gas stream will have great potential in reducing CO_2 separation cost. One of the pressurized gas sources is in a gasification scheme after the water-gas shift reaction where there is a high partial pressure of CO_2. CO_2 molecular gate membrane that shows excellent CO_2 selectivity over H_2 will be advantageous for economical CO_2 separation in H_2 production from fossil fuel.

Some cost estimates indicated that molecular gate membrane would reduce CO_2 capture cost from a pressurized gas stream of 4 MPa to the range of $ 2 to $12 [12]. In the estimates, CO_2 permeance and CO_2/H_2 selectivity are 1.0 x 10^{-6} m^3(STP) m^{-2} s^{-1} kPa^{-1} and 500, respectively, and membrane price range from $100 to $500 per unit area ($m^2$).

In the future, PAMAM dendrimer composite membranes will be developed as CO_2 molecular gate membranes for CO_2 separation from a pressurized gas stream such as those found in FutureGen or NGCC.

Conclusions

A commercial-sized module of the PAMAM dendrimer composite membrane, with length (1 m), diameter (1 inch) and membrane area (0.4m^2) was developed using the In-situ Modification method. The membrane module showed an excellent CO_2/N_2 selectivity of 150 and a CO_2 permeance of 1.7×10^{-7} m^3(STP) m^{-2} s^{-1} kPa^{-1} (= 23 GPU) at a pressure difference of 97 kPa at room temperature.

SEM observations revealed that a commercial-sized module has a thin hybrid layer of chitosan and PAMAM dendrimer. The hybrid CO_2 selective layer was somewhat uneven and thick compared to the hybrid layer of 300 nm for a pencil module with length (20 cm) and membrane area (17 cm^2).

Membrane testing at NETL indicated lower performance of CO_2 separation versus RITE studies. Additional studies will help confirm the cause of degradation, including the possible effect of air freight transport. Higher CO_2 feed concentration increased permeate flow rate and CO_2 concentration in the permeate. Higher relative humidity and lower permeate vacuum both enhanced CO_2 separation. Higher separation factors were obtained at lower CO_2 feed concentration. The effect of increased surface area by increasing the number of membrane modules on-line yielded mixed results but generally indicated higher permeate flow and lower retentate flow.

PAMAM dendrimer composite membrane demonstrated durability over 1000 hr testing using real combustion gas. Both CO_2 permeance and CO_2/N_2 selectivity is increased as the membrane module temperature is increased.

Disclaimer

References in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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