GCEP Research Symposium 2008
Friday, October 3, 2008
Carbon Capture and Storage

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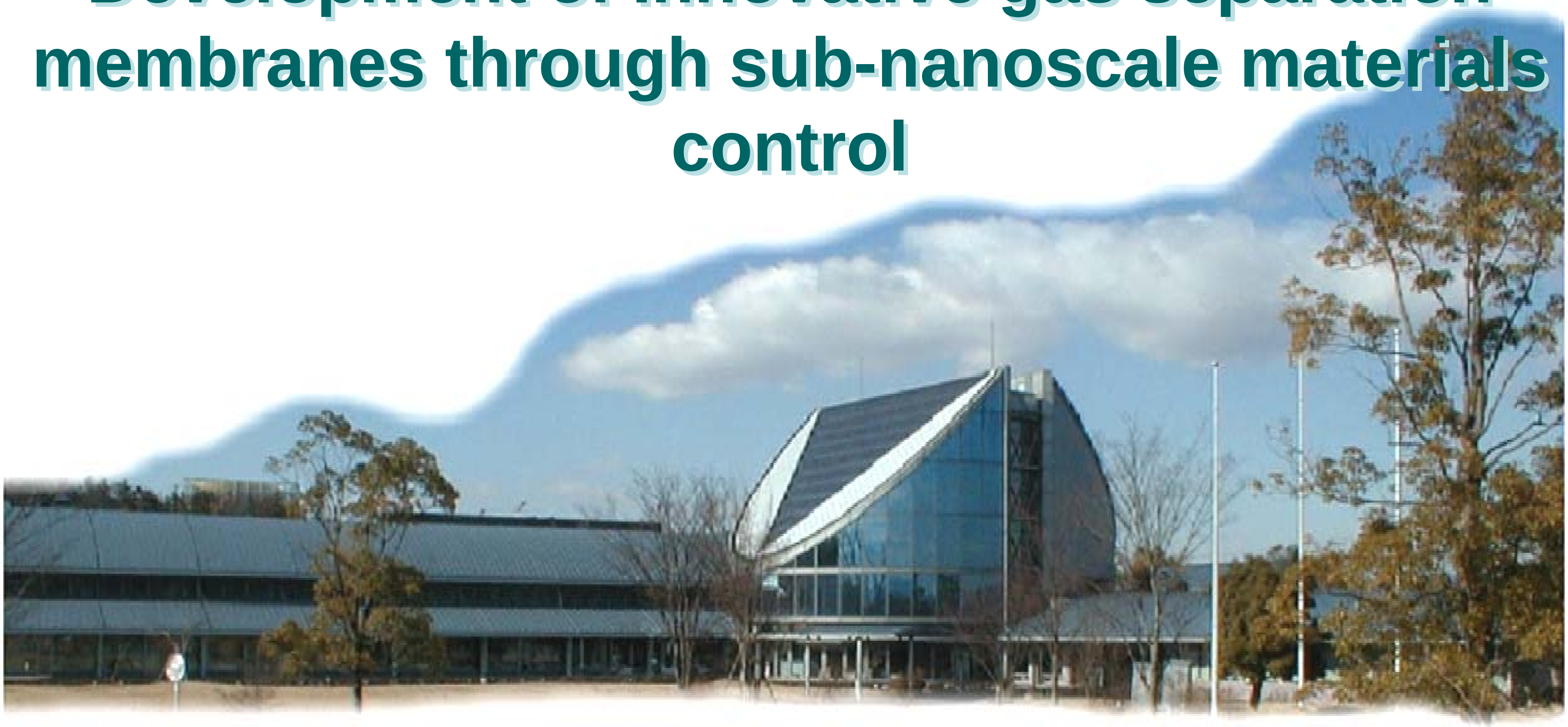
Development of Innovative gas separation membranes through sub-nanoscale materials control



Yuichi Fujioka

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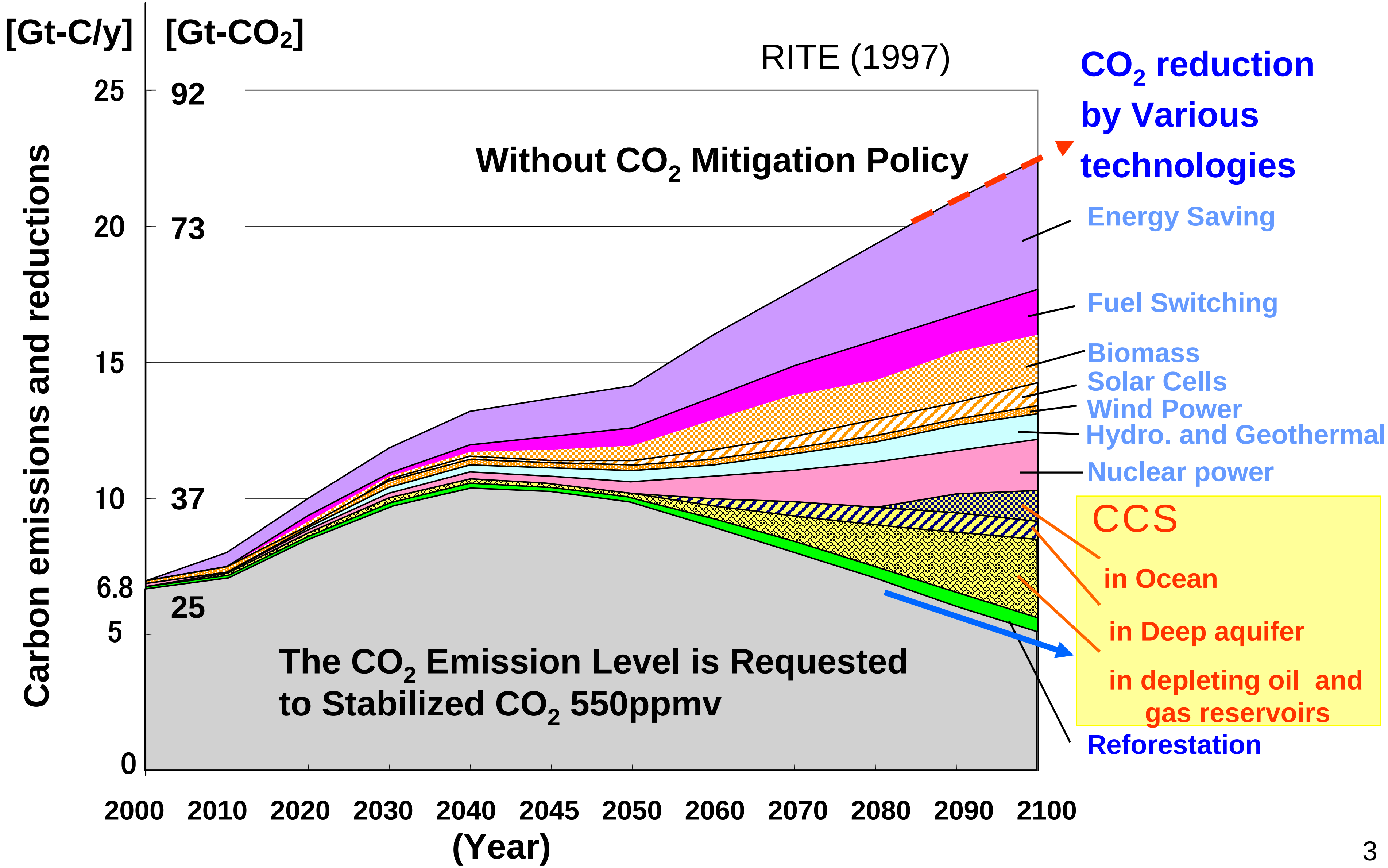
Outline

1. Background

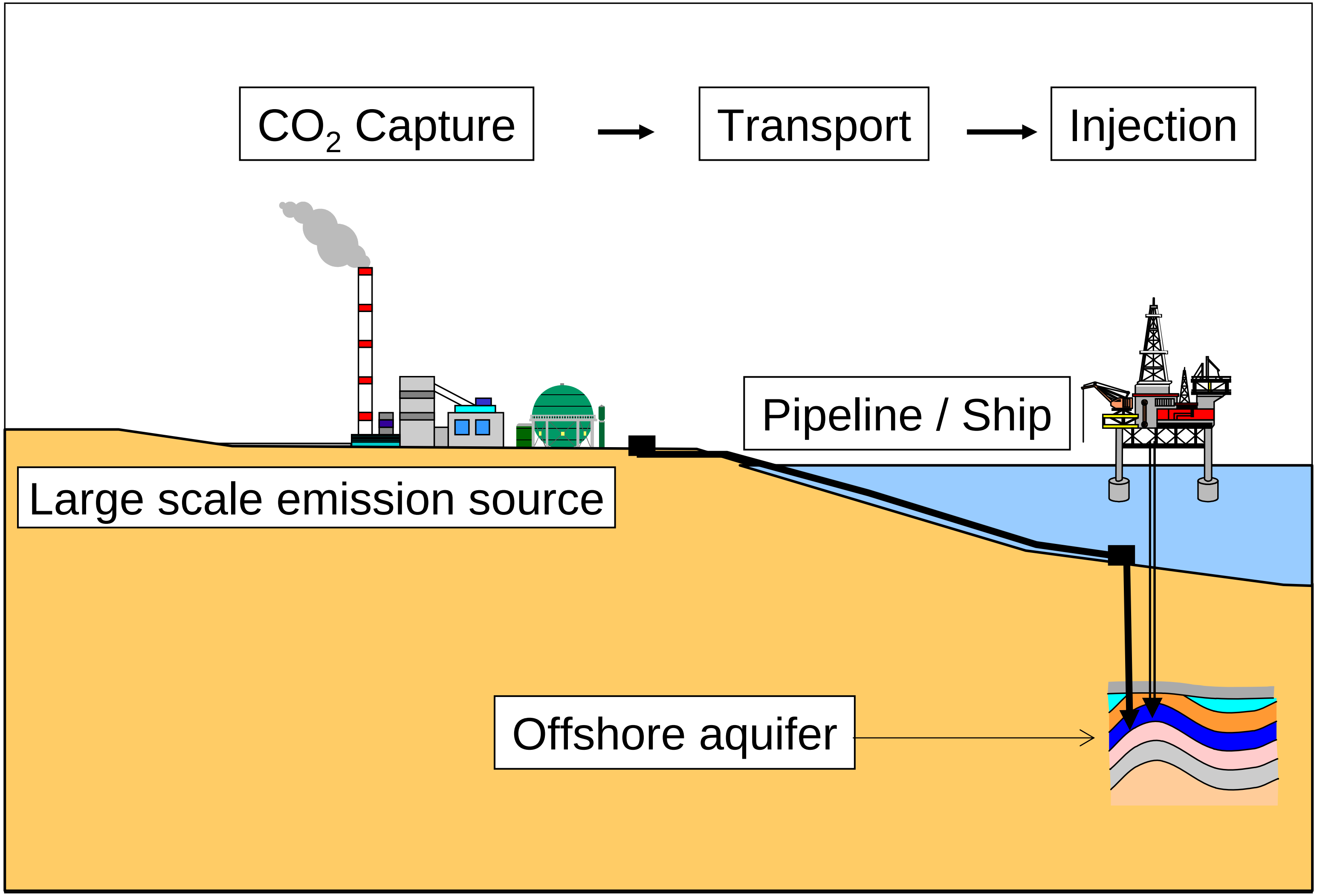
2. Our previous researches

3. Researches in this year
   - Carbon membrane
   - PAMAM dendrimer / mesoporous silica membrane

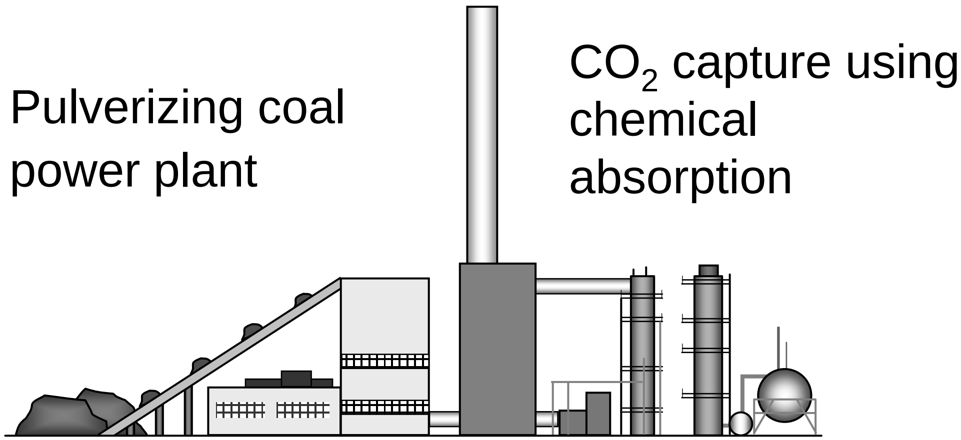
Technological Options for 550 ppmv Stabilization



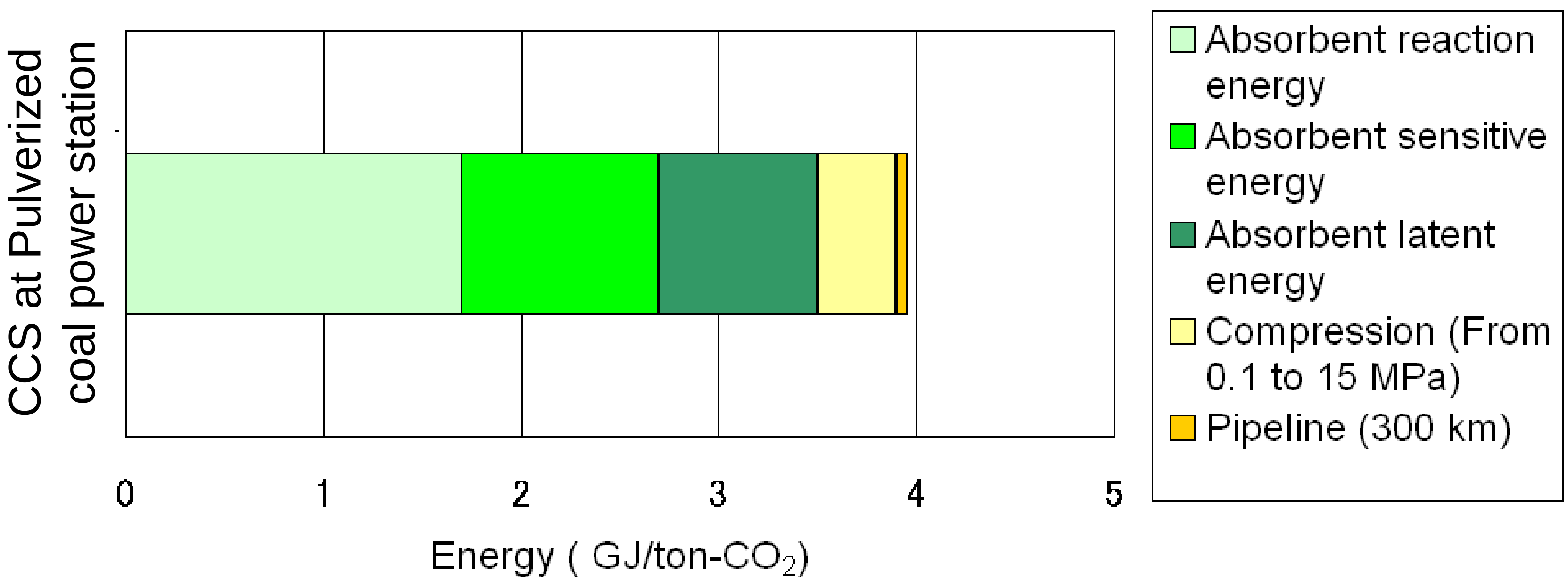
Carbon Capture and Storage (CCS)



Estimation of CO_2 capture energy



A chemical absorption consumes 80% of total energy in CCS system.



Application membrane for CO_2 separation

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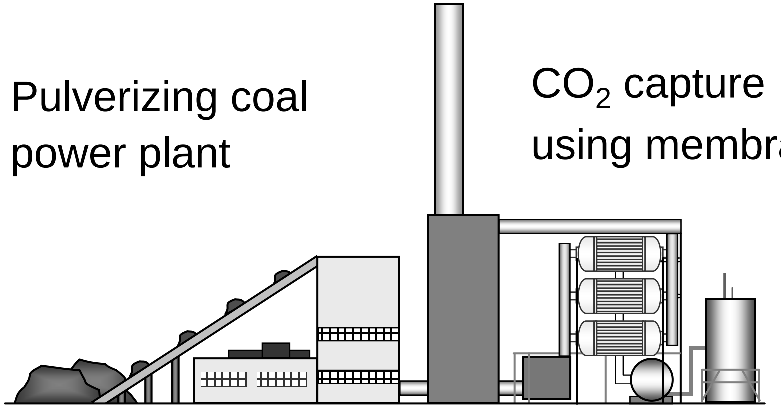
Pulverizing coal power plant

CO_2 capture using membrane



Target: Less than 1 GJ / ton-CO_2

Separation factor > 100

Less than 20$ / ton-CO_2

CO_2 Permeance > 1 x 10^{-8}

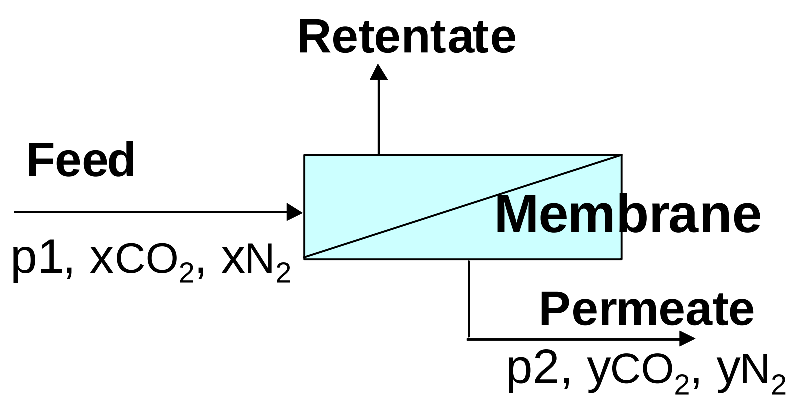
Definition of Permeance & Separation factor

CO_2 permeance(Q_{CO_2}): $Ft \cdot y_{CO_2} / (p1 \cdot x_{CO_2} - p2 \cdot y_{CO_2}) / A$

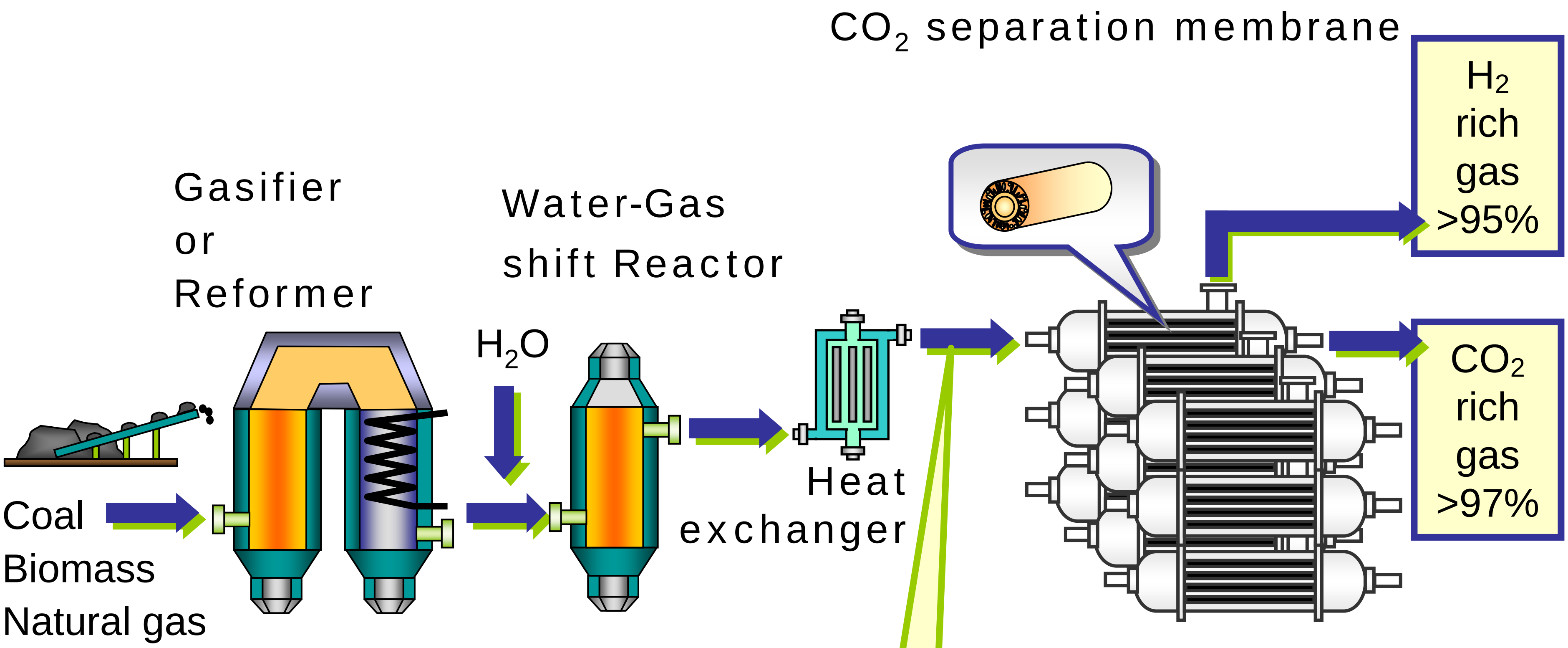
N_2 permeance(Q_{N_2}): $Ft \cdot y_{N_2} / (p1 \cdot x_{N_2} - p2 \cdot y_{N_2}) / A$

CO_2/N_2 separation factor(α_{CO_2/N_2}) : $(y_{CO2}/y_{N2})/(x_{CO2}/x_{N2}) \approx Q_{CO_2}/Q_{N_2}$

x (-): molar fraction in feed
y (-): molar fraction in permeate
p1 (Pa): total pressure in feed
p2 (Pa): total pressure in permeate
Ft ($m^3 s^{-1}$): total gas flow of permeate
A (m^2): membrane area



Application of membrane for pressurized gases



Composition: CO_2 40 vol%/ H_2 balance
Temperature: <150 °C for carbon membrane, 200 °C> for zeolite membrane
Pressure: < 4 MPa

Membrane performances in previous works

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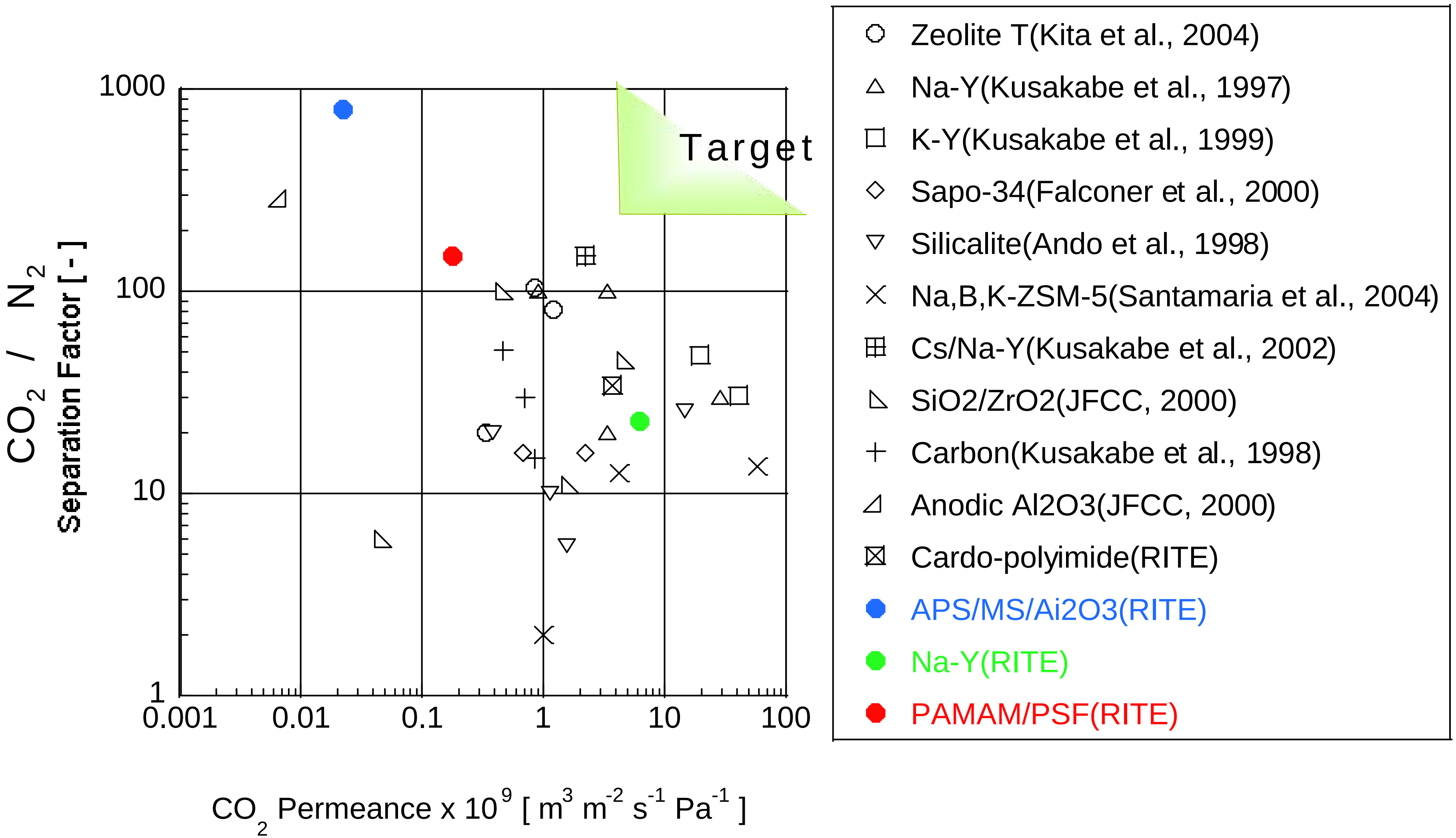
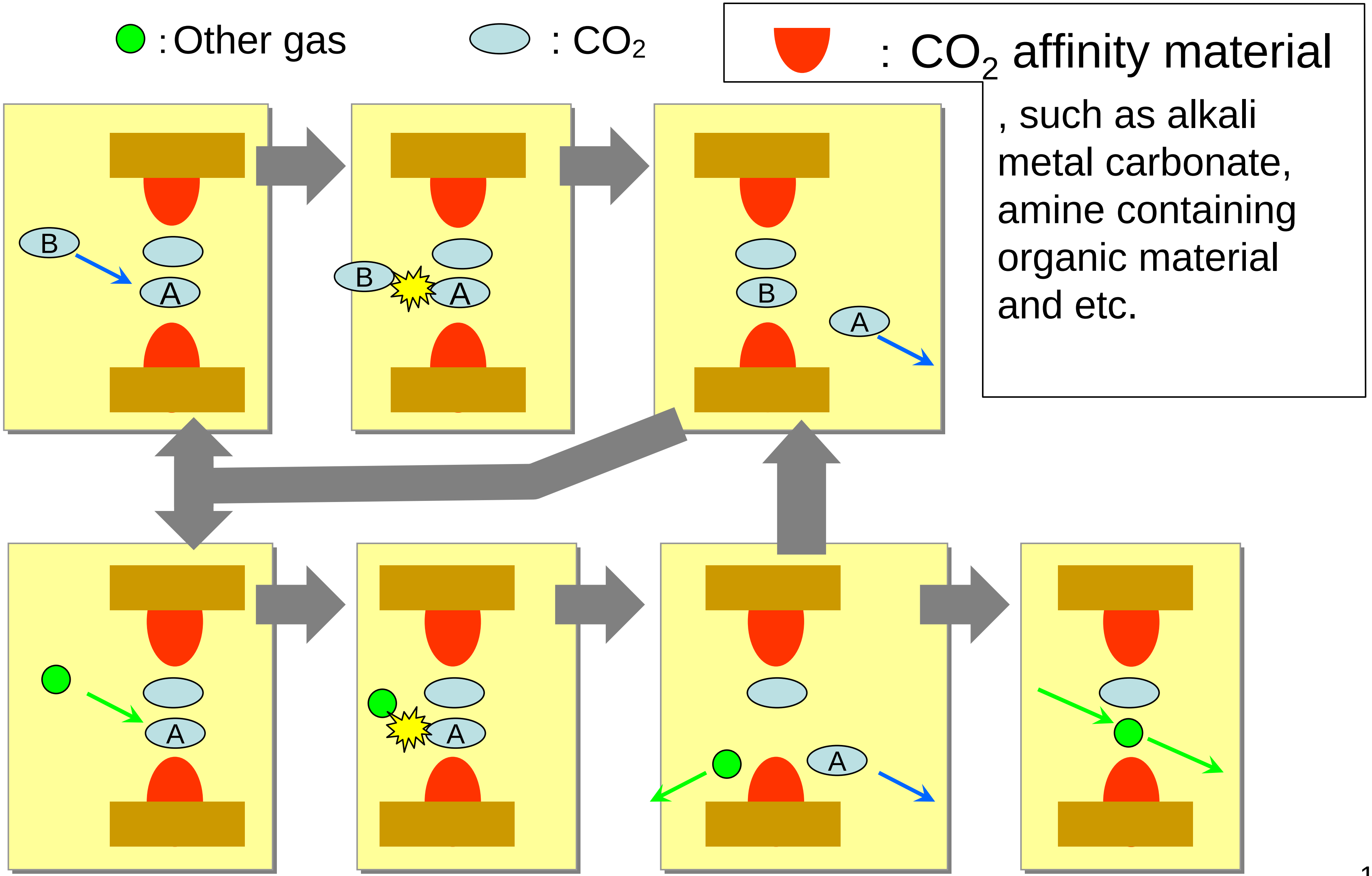


2. Our previous researches including GCEP

Concept of "Molecular Gate" membrane



CO_2/H_2 Separation by PAMAM dendrimer

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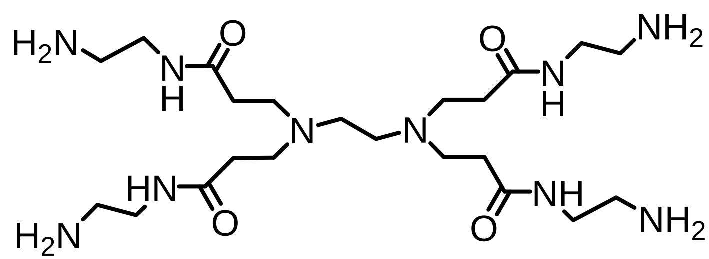
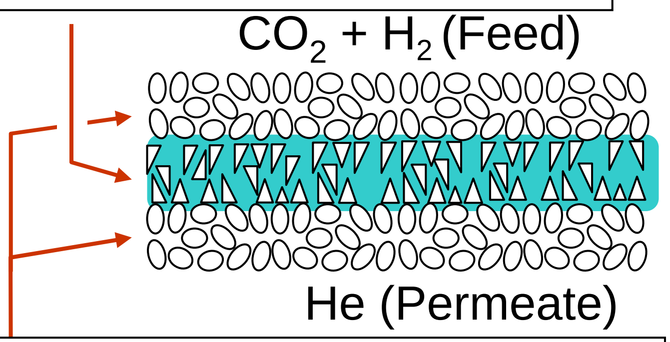
Cross section diagram of Membrane



PAMAM Dendrimer*

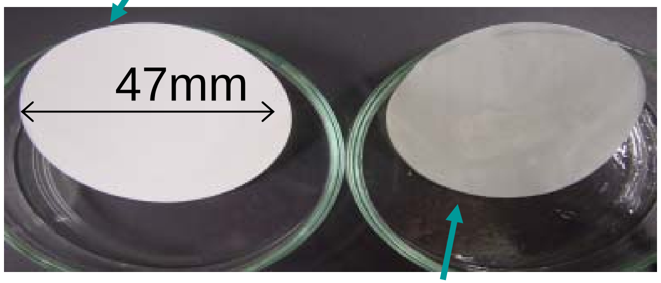
1) Selective Layer
PAMAM Dendrimer
+ Hydrophilic porous substrate



2) Hydrophobic porous substrate

Photo of Membrane

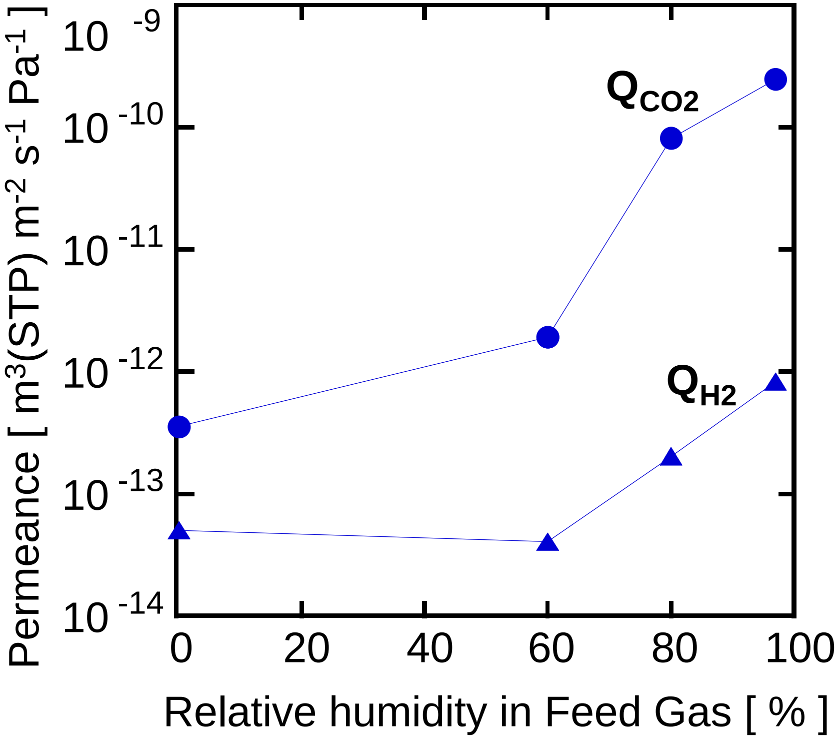
Hydrophilic porous substrate



After supporting PAMAM dendrimer in Hydrophilic porous substrate

* A. S. Kovvali, H. Chen, and K. K. Sirkar, J. Am. Chem. Soc. 2000, 122, 7594-7595

CO_2/H_2 Separation by PAMAM dendrimer



Feed: 100 kPa, CO_2 / H_2 = 5% / 95%, 298 K (25 °C)
Permeate: 1 kPa

RH → increase
CO_2 permeance → increase
H_2 permeance → increase

Duan, S., et al, J. Membr. Sci., 283, 2 (2006)

Suggestive mechanism of CO_2 and N_2 separation with PAMAM dendrimer membrane

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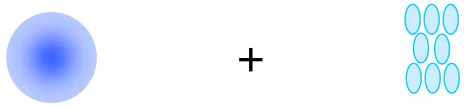
RH → increase
CO_2 permeance → increase
H_2 permeance → increase

Before humidification

PAMAM H_2O

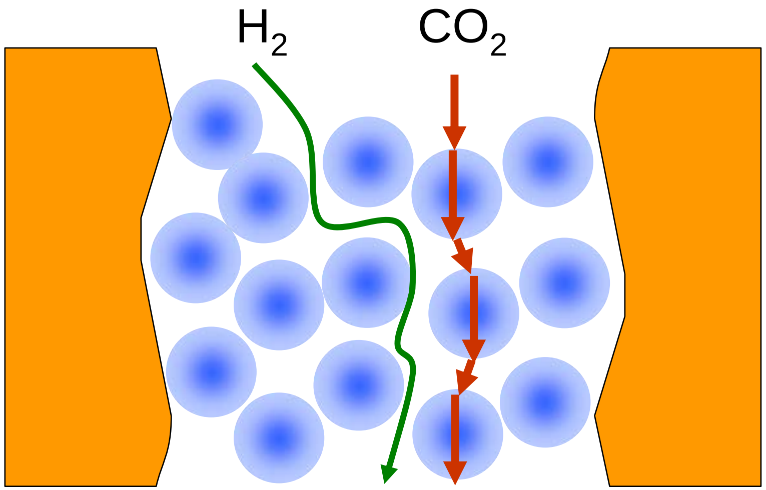


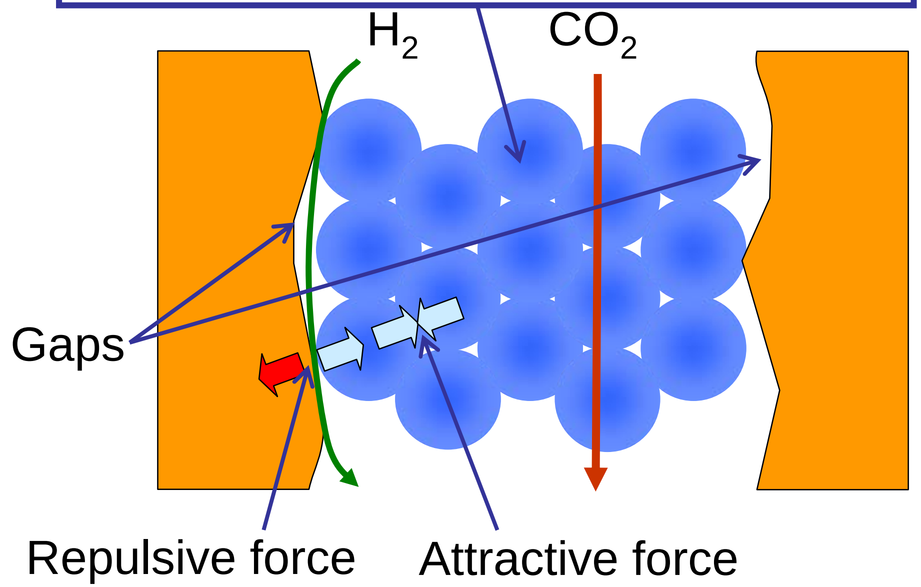
After humidification

RH > 60 % → Hydrate PAMAM

swelling →

Swelling and Hydrophilic force makes agglomeration Hydrate PAMAM





Fixation PAMAM dendrimer on inside hollow fiber

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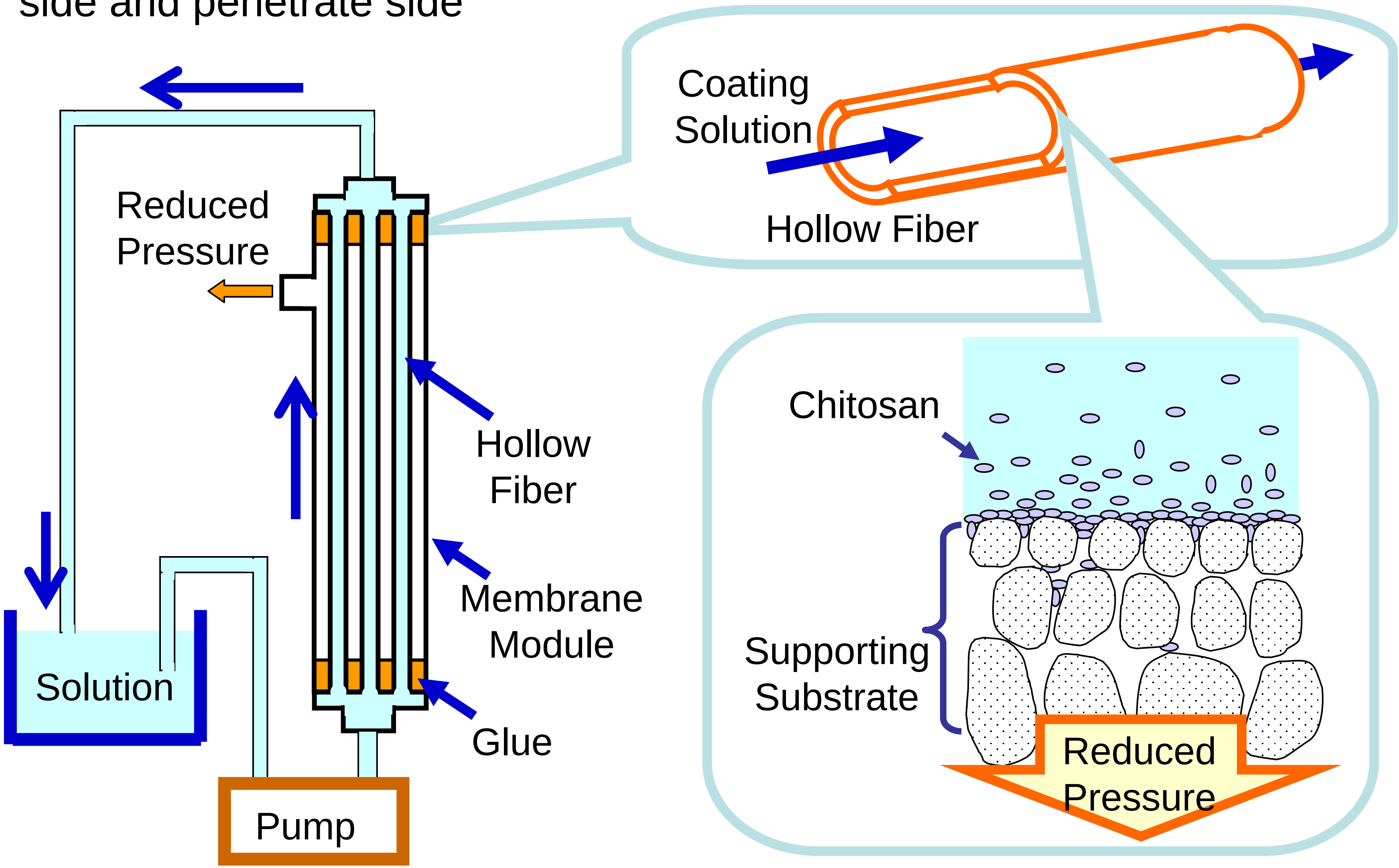
- Procedure for separating CO_2 in difference pressures between feed side and penetrate side



Performances of PAMAM dendrimer / Chitosan composite membrane

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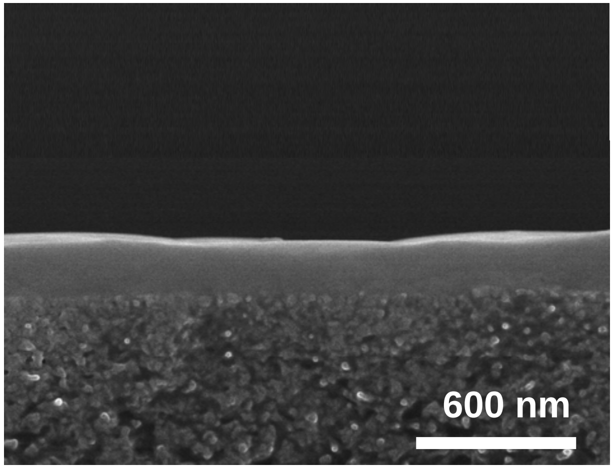

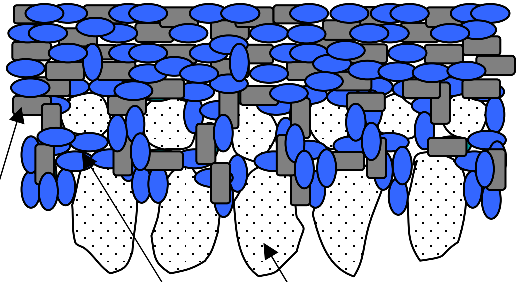

Membrane	Q_{CO2} [$m^3(STP)m^{-2}\ s^{-1}\ Pa^{-1}$]	$\alpha_{CO2/N2}$
PSF-substrate(a)	2.3×10^{-7}	1
Chi-substrate(b)	1.8×10^{-8}	1
PAMAM dendrimer / polymer composite	4.6×10^{-10}	230

(a): PSF hollow fiber membrane as dried
(b): PSF-substrate with chitosan gutter layer
Feed : water saturated, CO_2 /N_2 = 5% / 95% of at 101 kPa
Permeate: evacuated at 4 kPa.
Temperature: 313 K

This PAMAM fixation method can apply PAMAM membrane to gas separation at large pressure difference, such as between 100 kPa and 1 kPa.

Kouketsu, T., et al, J. Membr. Sci., 287, 51 (2007)

PAMAM Dendrimer density and Performances

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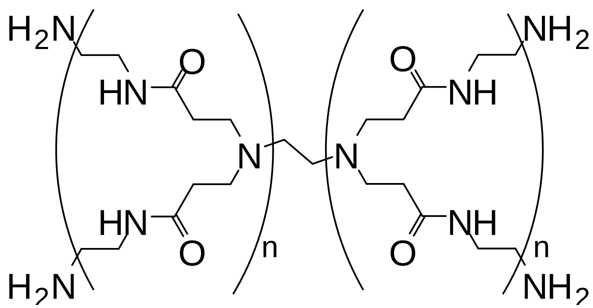
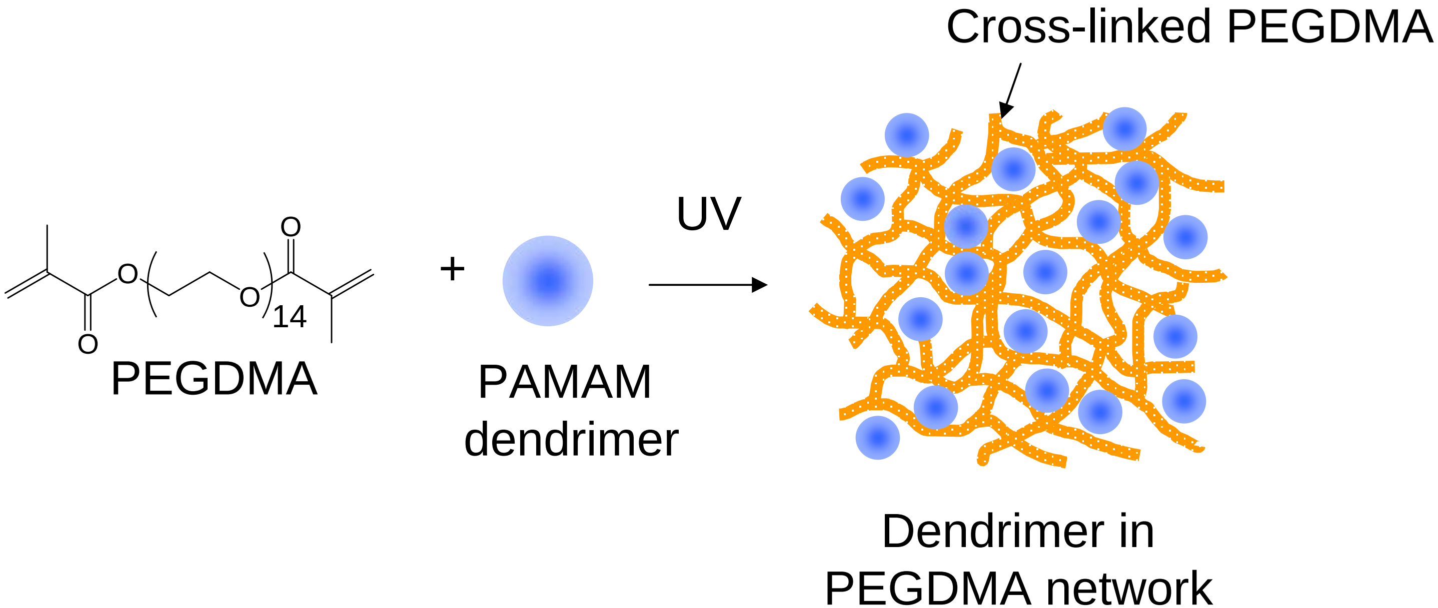


PAMAM dendrimer

Generation	n
0	1
1	2
3	4
5	6



Taniguchi, I., et al, J. Membr. Sci., 322, 277-288 (2008)

PAMAM dendrimer effects

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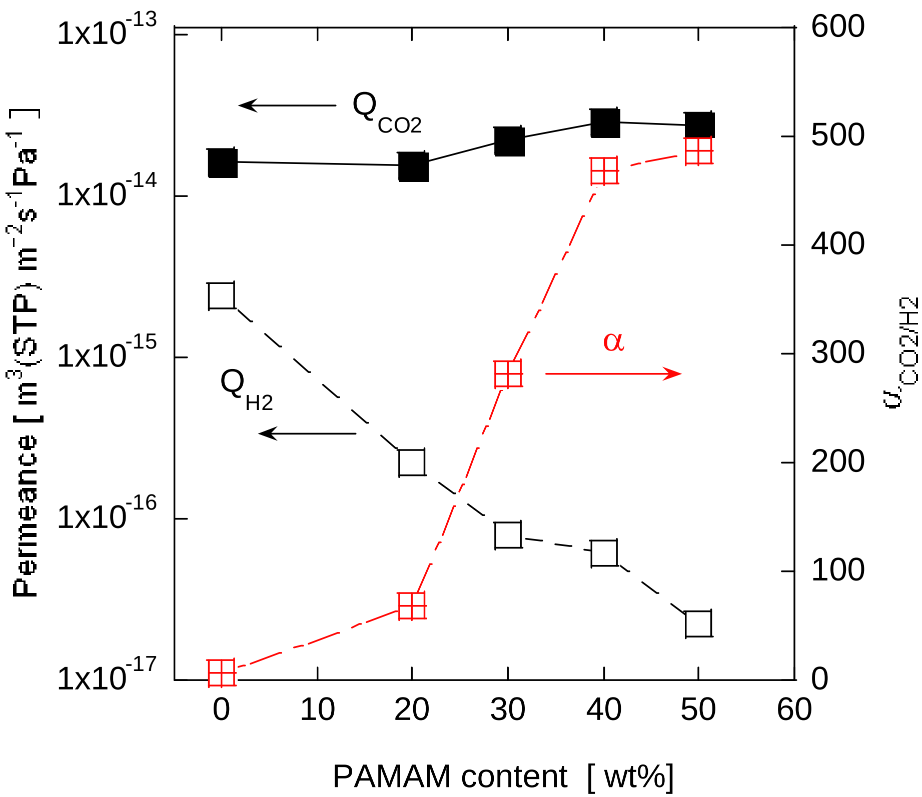


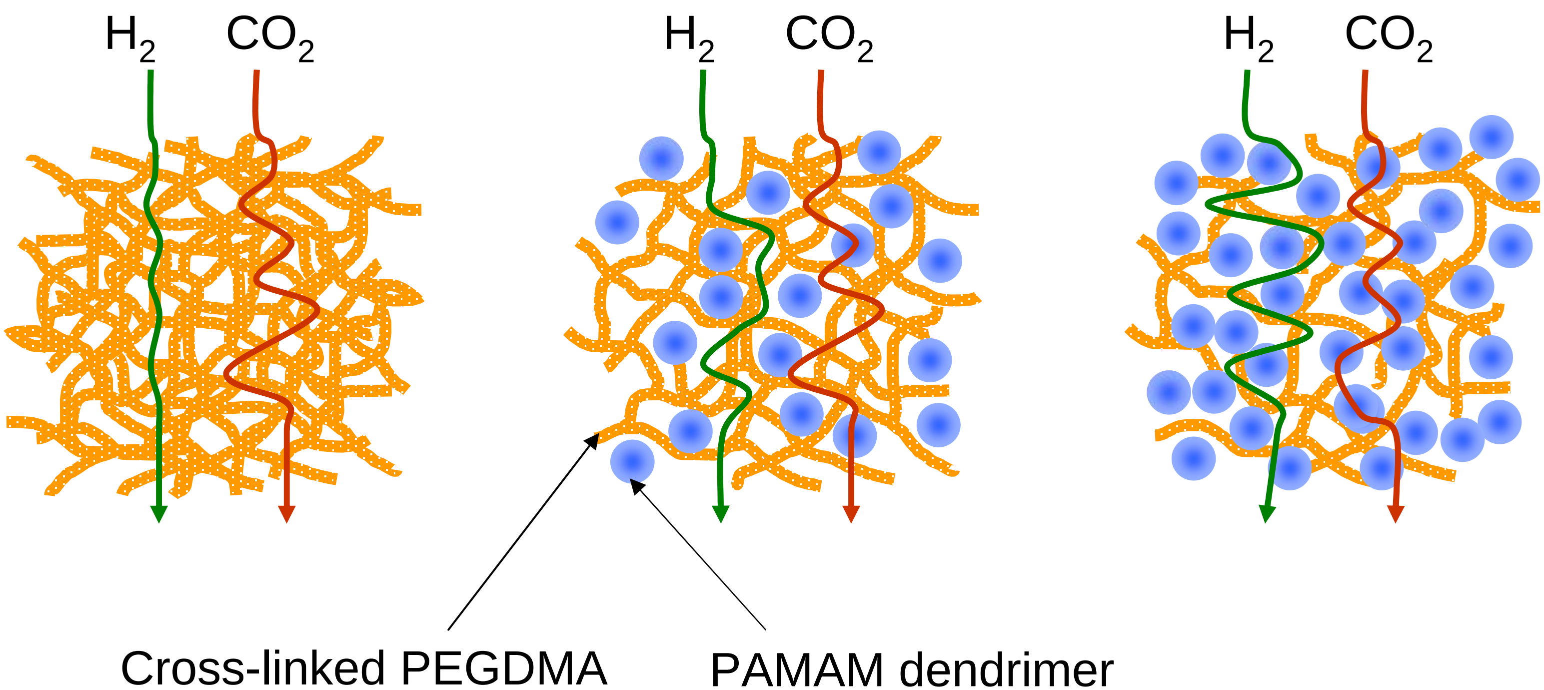
298 K 80% RH, Feed gas CO_2/H_2 5/95

PAMAM content [%]	Permeance $[m^3(STP)\ sec^{-1}\ m^{-2}\ Pa^{-1}]$	
	CO_2	H_2
0	1.63×10^{-14}	2.39×10^{-15}
	1.7	1/100
50	2.74×10^{-14}	2.22×10^{-17}

PAMAM enhanced CO_2 permeation rate

Suggestive mechanism of CO_2 and H_2 separation with PAMAM / PEGDMA membrane

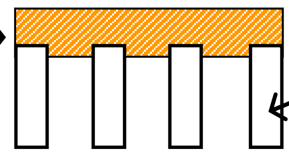
Content of PAMAM dendrimer:	0	→	20	→	50
H_2 permeation rate :	1		1/10		1/100
CO_2 permeation rate :	1		1		1.7



Amino-modified mesoporous silica membrane

- **Structure of membrane**

Mesoporous silica layer →

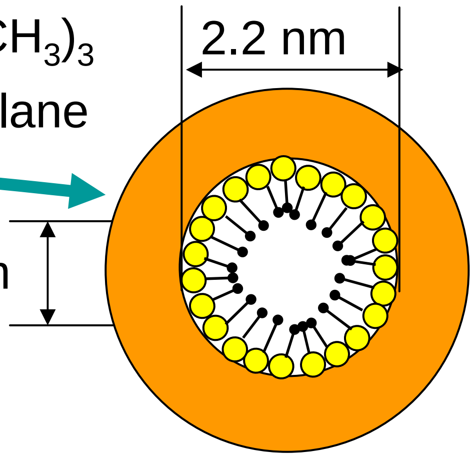


Alumina substrate

MCM - 48

APS: H_2N~~~$Si(OCH_2CH_3)_3$

3-aminopropyltrietoxysilane



CO_2 = 0.33 nm
APS = 0.7 nm

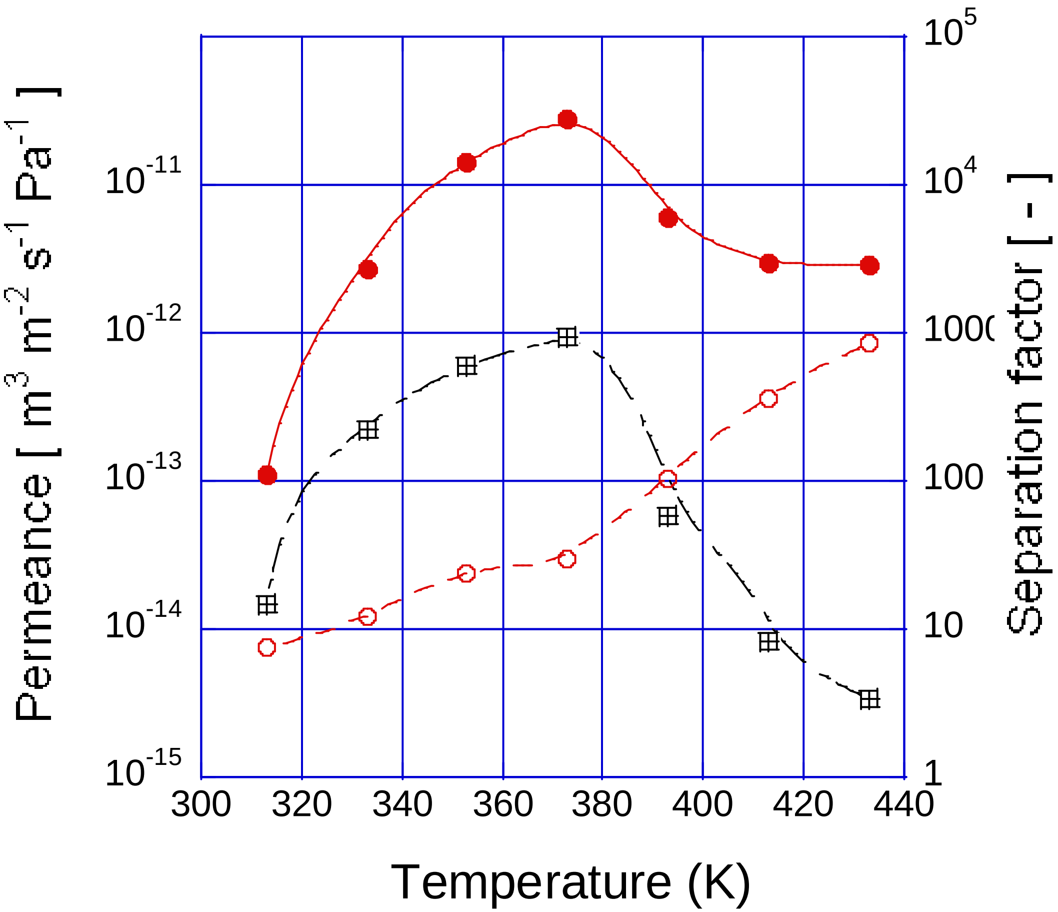
→ MCM-48 (2.2 nm pore) is promising

APS / MCM - 48

Sakamoto, Y., et al, Microporous and Mesoporous Materials, 101, 303-311 (2007)

Result of amino-modified mesoporous silica membrane

- High CO_2/N_2 separation factor without H_2O
- Amino-modified mesoporous silica membrane



Attractive force by amino-function and CO_2 separation

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- Increasing temperature made CO_2 and N_2 permeance. CO_2 permeance increased 100 times larger from 313 K to 353K.
  - It is supposes that decreasing CO_2 attractive force by amino-function enhances CO_2 movement inside pores.
  - CO_2 molecules near amino function block out N_2 molecules.

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3. This year researches

- Carbon membrane
- PAMAM dendrimer / mesoporous silica membrane

CO_2/N_2 Separation performance of carbon membrane

CO_2/N_2: Separation factor: 7 - 101 [1)]

CO_2/N_2 separation factors are in a wide range

1) S. M. Saufi, A.F. Ismail, Carbon, 42 (2004) 241-259.

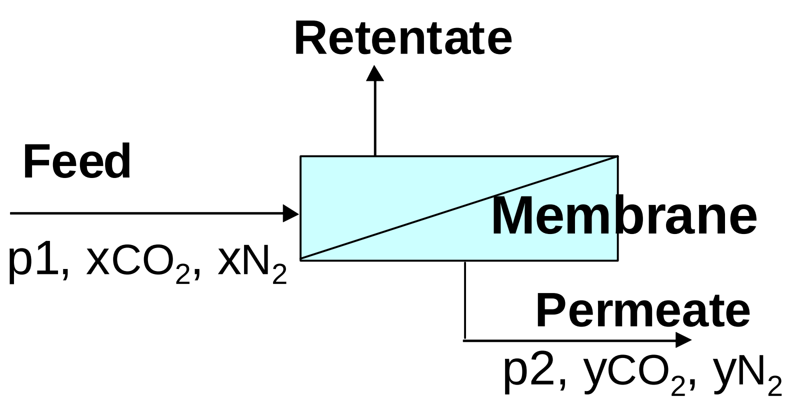
Definition of Permeance & Separation factor

CO_2 permeance(Q_{CO_2}): $Ft \cdot y_{CO_2} / (p1 \cdot x_{CO_2} - p2 \cdot y_{CO_2}) / A$

N_2 permeance(Q_{N_2}): $Ft \cdot y_{N_2} / (p1 \cdot x_{N_2} - p2 \cdot y_{N_2}) / A$

CO_2/N_2 separation factor(α_{CO_2/N_2}) : $(y_{CO2}/y_{N2})/(x_{CO2}/x_{N2}) \approx Q_{CO_2}/Q_{N_2}$

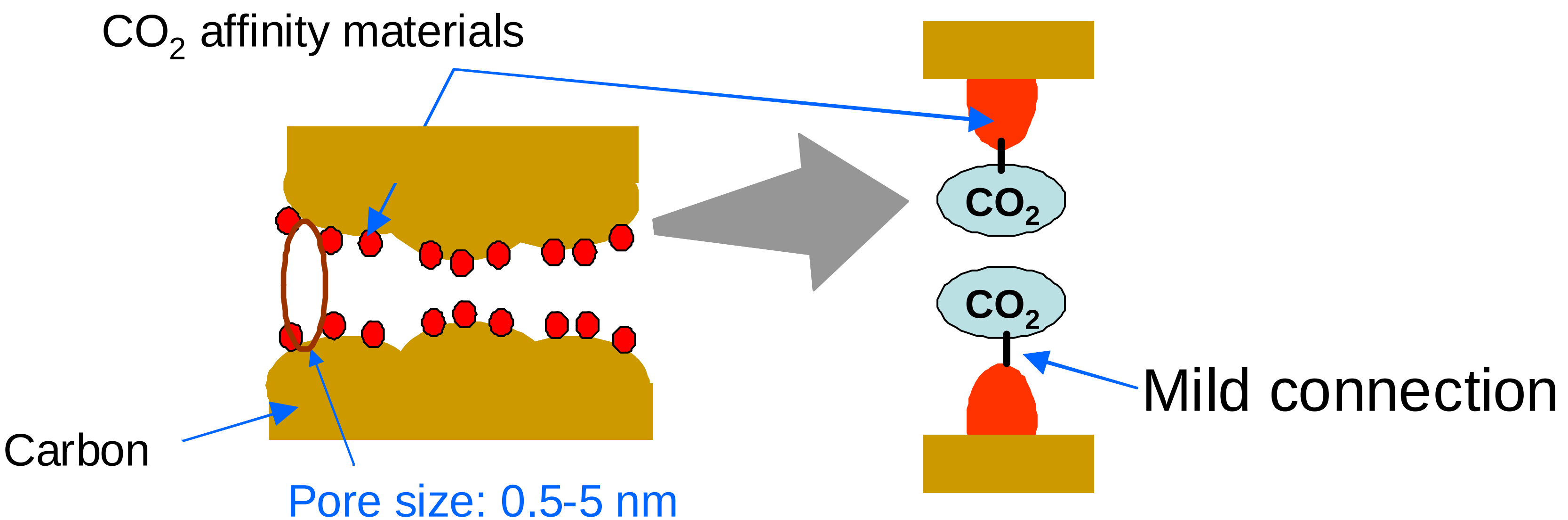
- x (-): molar fraction in feed
- y (-): molar fraction in permeate
- p1 (Pa): total pressure in feed
- p2 (Pa): total pressure in permeate
- Ft ($m^3\ s^{-1}$): total gas flow of permeate
- A (m^2): membrane area



Our approach to carbon membrane

Incorporate CO_2 affinity materials in the pores

→Enhanced CO_2 permeation using adsorbed CO_2 in the pores



Concept

- Building adequate bond between CO_2 and CO_2 affinity material for CO_2 separation

Membrane preparation procedure

Preparation of precursor solution ← Blending $CeCO_3$ with polymer

↓

Dipping to coat (Outer-surface) — NMP solution with precursor

↓

Drying — 60 °C, >8h

↓

Carbonization — 600 °C, 3h; Heating rate: 5°C/min

↓

Product

Photo of precursor & carbon membrane

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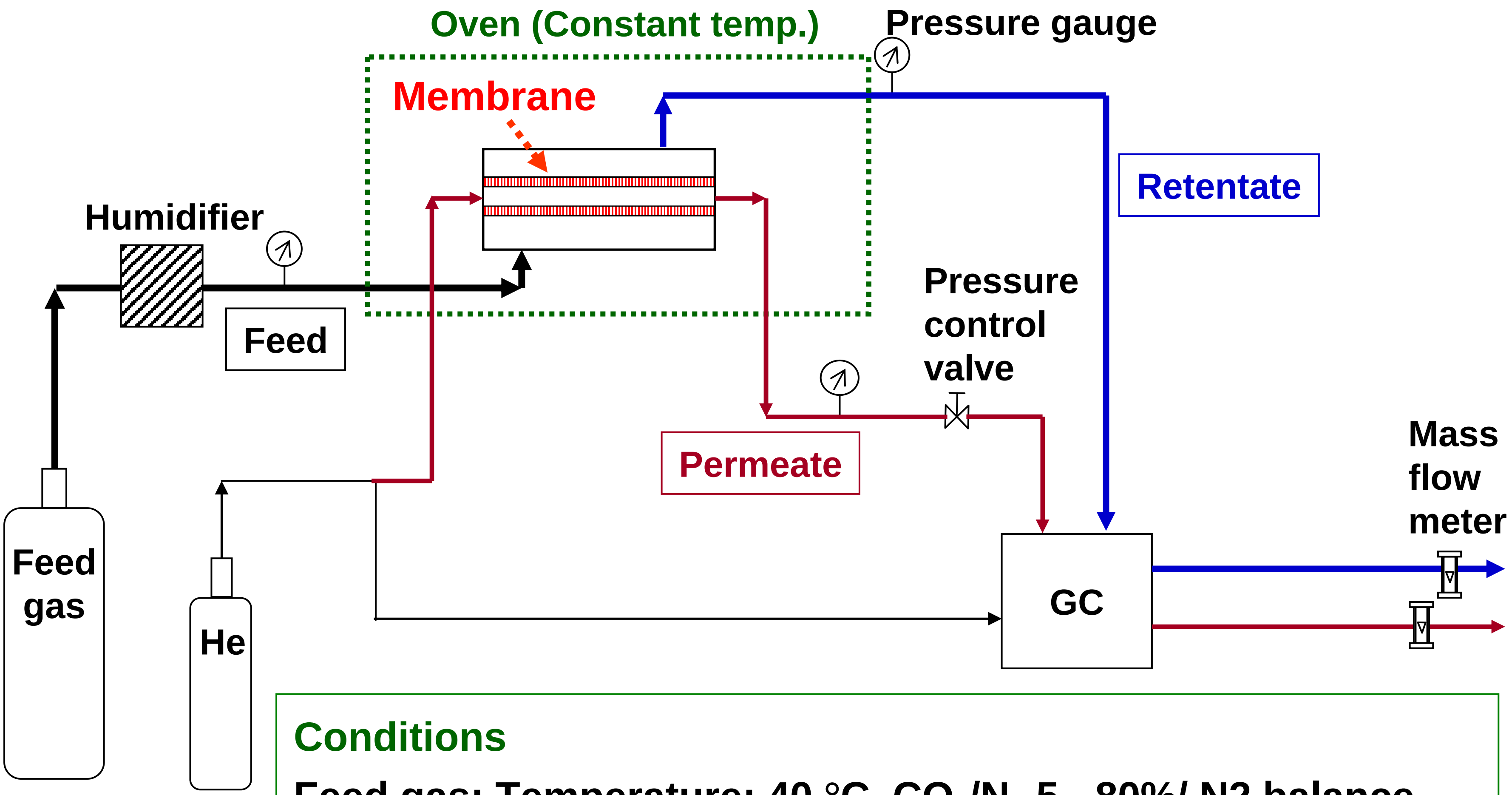
Precursor-coated membrane

Carbon membrane

Substrate: porous alumina

CO_2/N_2 gas separation measurement



Conditions

Feed gas: Temperature: 40 °C, CO_2/N_2 5 - 80%/ N2 balance,

Humidity in feed gas: 0-100RH%

Pressure of feed：0.1 MPa

Pressure of permeate: 0.1 MPa (He sweep)

Separation performance as a function of relative humidity in feed gas

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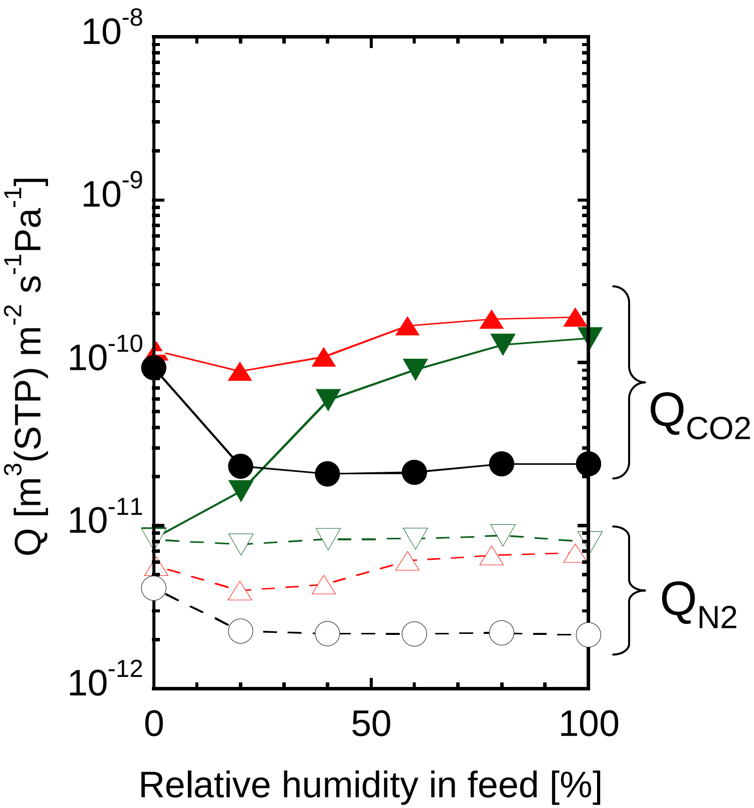
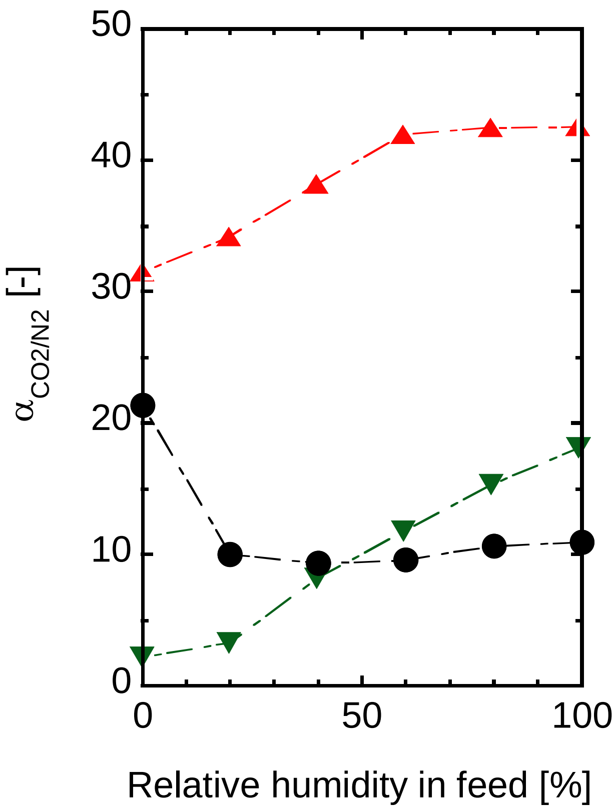
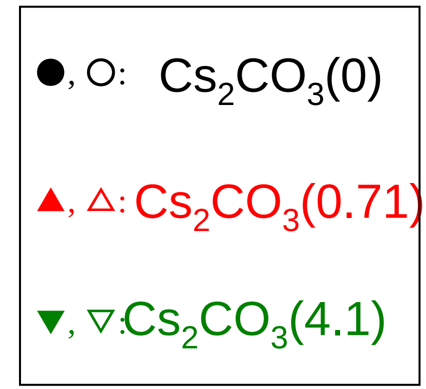


(a) Q_{CO2}, Q_{N2}



(b) $\alpha_{CO2/N2}$



Gas separation conditions: Temp.: 40 °C, Feed gas: CO_2/N_2 gas mixture (5/95 vol/vol), Feed pressure : 0.1 MPa, Permeate pressure: 0.1 MPa (He sweep method).

- Higher separation performance under the humidified conditions.
- Higher separation performance than the original carbon membranes at high relative humidity.

Relative permeance in carbon membrane

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Relative N_2 Permeance (as a basis of N_2 permeance at RH = 0 %)

N_2 Permeance	Cs_2CO_3 content [%] in carbon membrane		
	0	0.71	4.1
RH = 0 %	1.0	0.7	1.7
RH = 80 %	0.5	0.9	1.8

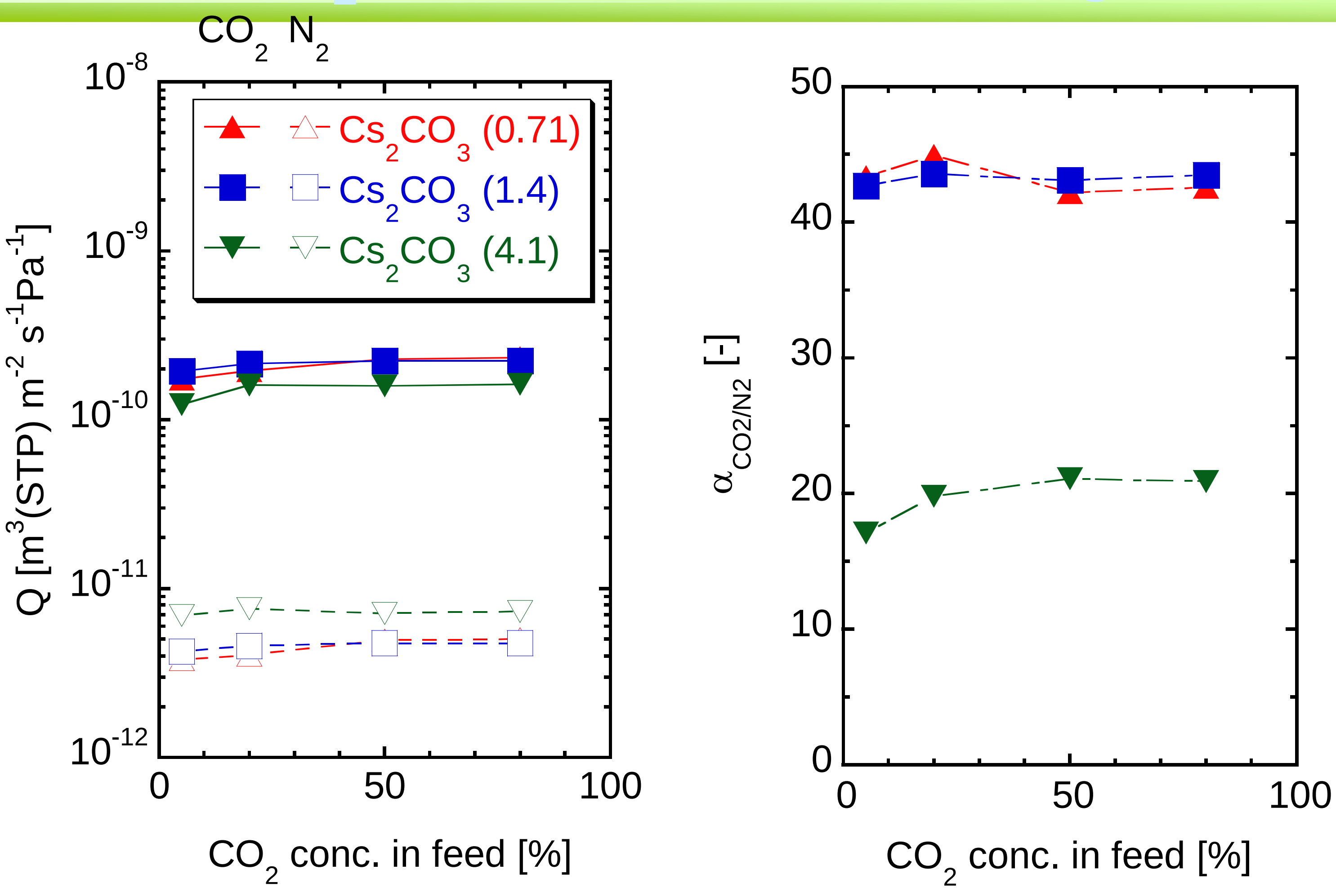
- N_2 permeance at Cs(4.1%) is large. → Cs enlarges the pore diameter.
- RH only decreased N_2 permeance at Cs(0 %).

Relative CO_2 Permeance (as a basis of N_2 permeance at RH = 0 %)

CO_2 Permeance	Cs_2CO_3 content [%] in carbon membrane		
	0	0.71	4.1
RH = 0 %	22.5	24.3	1.8
RH = 80 %	5.8	40.5	27.0

- CO_2 permeance at Cs(4.1%), RH(0) is small. → Excess Cs reduced CO_2 permeance.
- RH differently effected on CO_2 permeance at Cs(0 %).

Separation performance as a function of CO_2 concentration in feed gas



(a) Q_{CO2}, Q_{N2} (b) α

Gas separation conditions:
Temp.: 40 °C,
Humidity in feed gas: 100RH%
Feed pressure：0.1 MPa, Permeate pressure: 0.1 MPa
(He sweep method).

Constant separation performance at CO_2/N_2=5/95-80/20 %

Analysis method for Characterization

Thermogravimetric analysis (TGA)

- Thermal decomposition behavior of precursor.

Atomic absorption spectrometry (AAS)

- Cs concentration in carbon free-standing films

Inductively coupled plasma mass spectrometry (ICP-MS)

- Cs concentration in carbon layer of carbon-coated membranes

Electron probe microanalysis (EPMA)

- Cs distribution in the cross-section of carbon free-standing films

X-ray Photoelectron Spectroscopy (XPS) depth profile

- Cs distribution in the cross-section of carbon membrane

Nano-Permporometer:

-Pore size distribution of carbon-coated membranes by He

Distribution of Cs in the cross-section of carbon free-standing films

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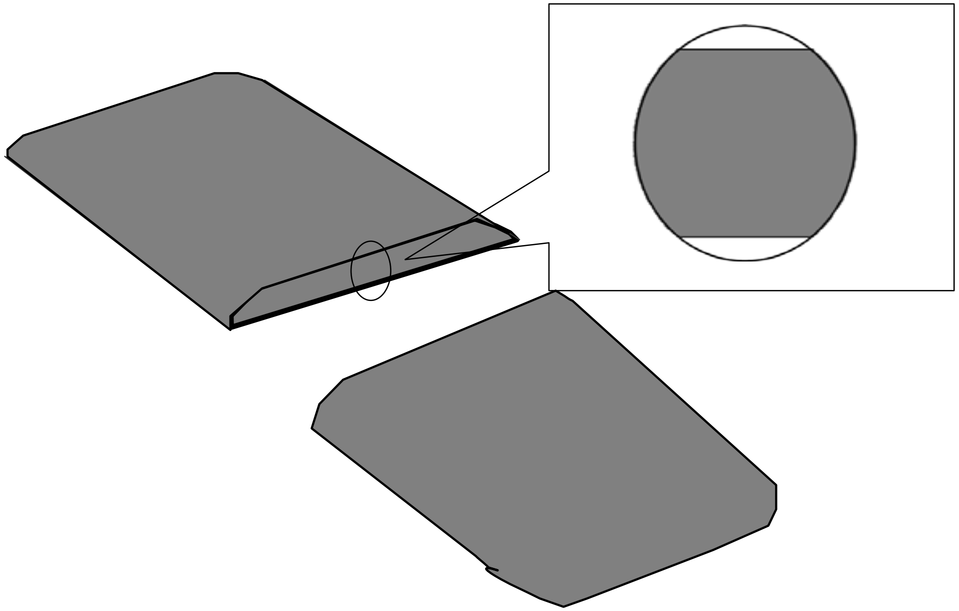
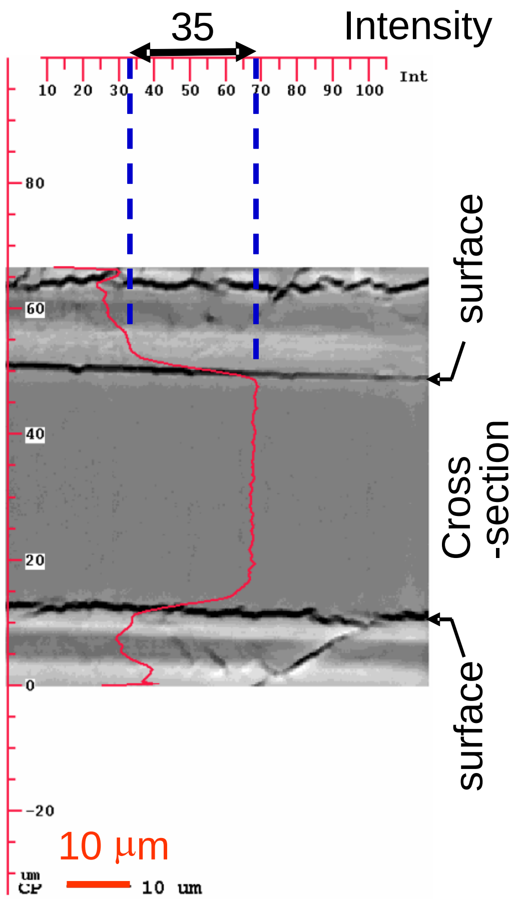
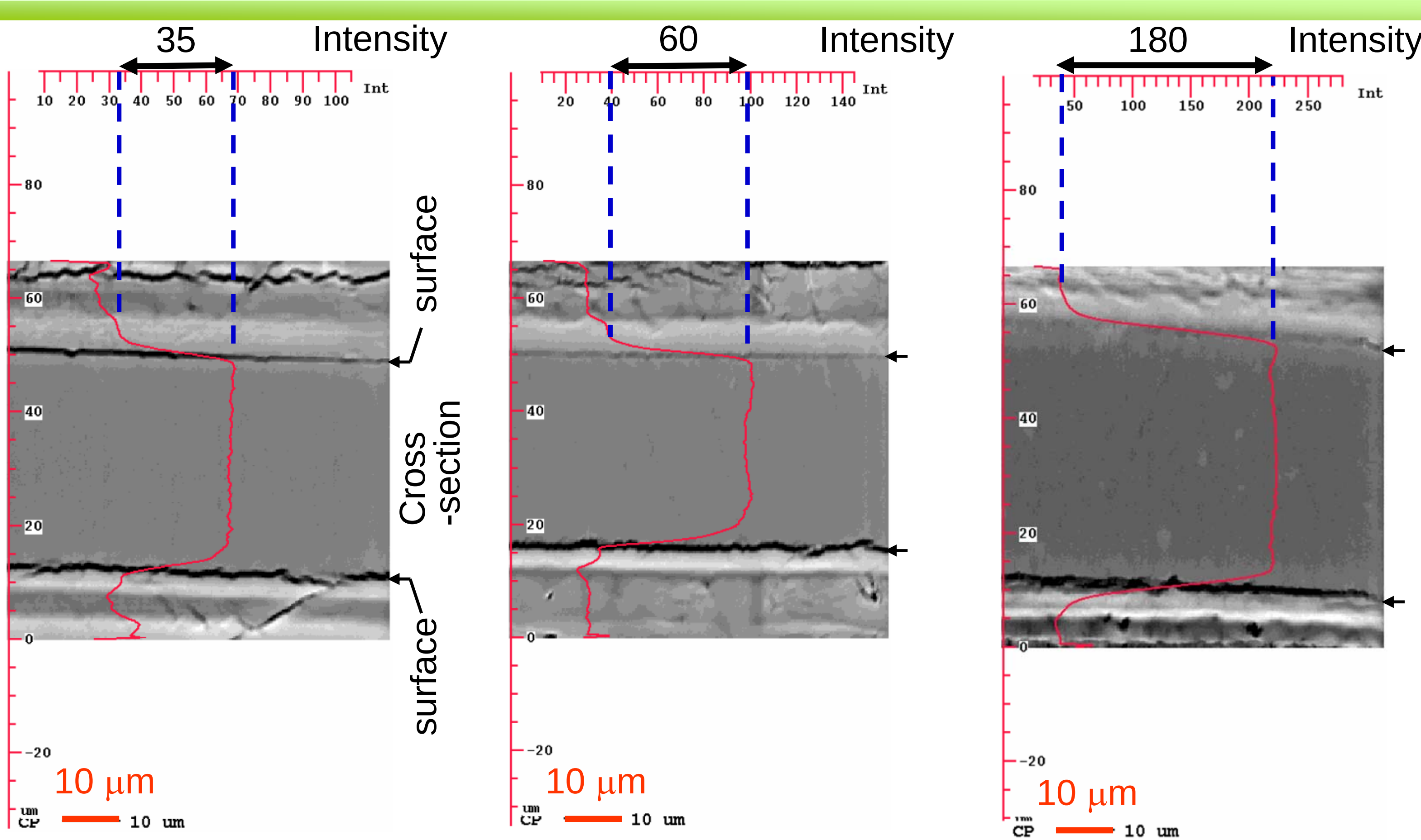


Carbon free-standing film



EPMA line-mapping

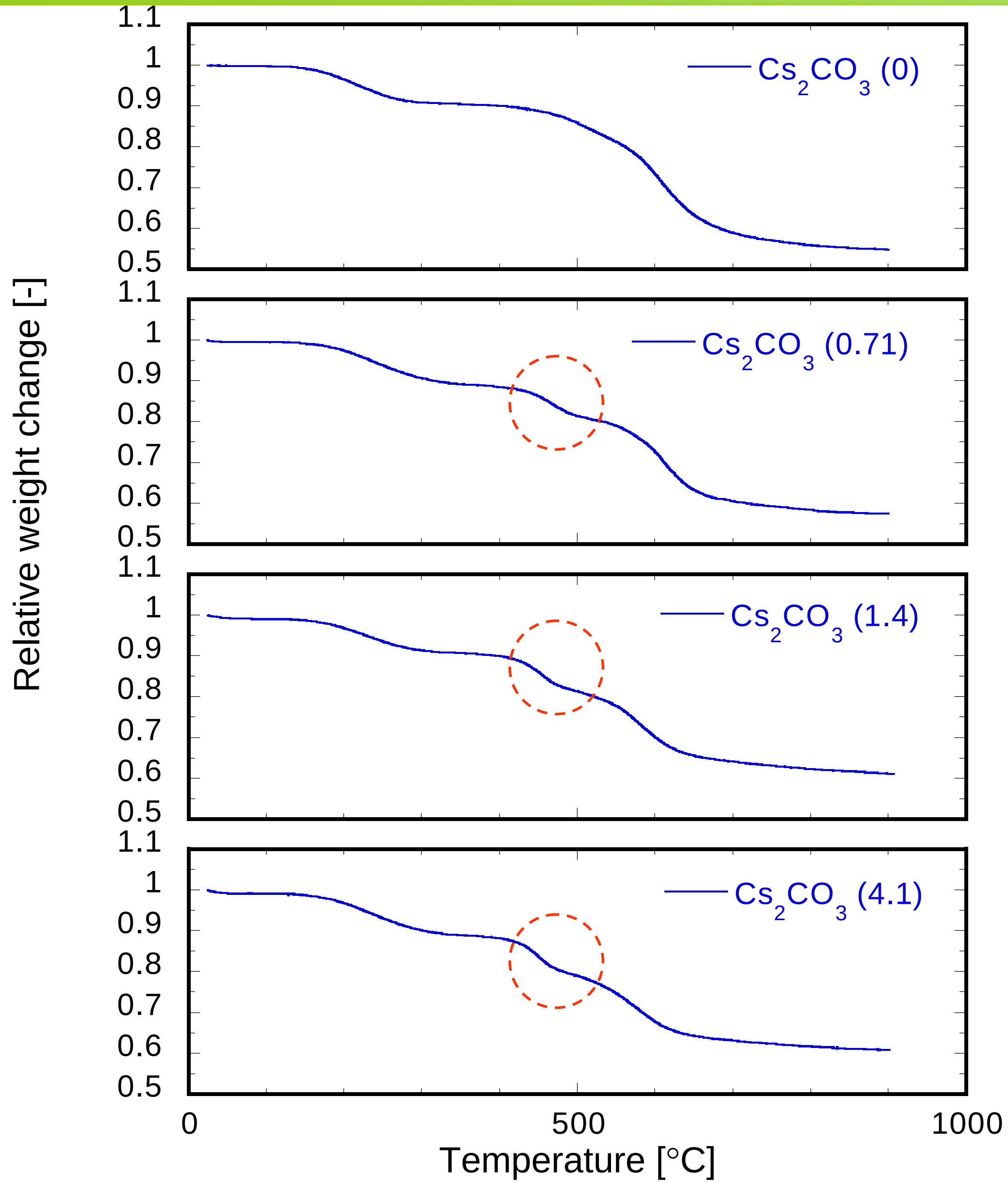
Distribution of Cs in the cross-section of carbon free-standing films (EPMA line-mapping)



(1) Cs_2CO_3 (0.71)　(2) Cs_2CO_3 (1.4)　(3) Cs_2CO_3 (4.1)

(1) Uniform Cs distribution over the cross-section
(2) Cs conc. increased as Cs_2CO_3 conc. in precursor increased.

TGA curve of polyimide precursors with/without Cs_2CO_3



Additional weight loss at 400-500 °C for Cs_2CO_3-containig precursors

Relative permeance in carbon membrane

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Relative N_2 Permeance (as a basis of N_2 permeance at RH = 0 %)

N_2 Permeance	Cs_2CO_3 content [%] in carbon membrane		
	0	0.71	4.1
RH = 0 %	1.0	0.7	1.7
RH = 80 %	0.5	0.9	1.8

- RH only decreased N_2 permeance at Cs(0 %).

Relative CO_2 Permeance (as a basis of N_2 permeance at RH = 0 %)

CO_2 Permeance	Cs_2CO_3 content [%] in carbon membrane		
	0	0.71	4.1
RH = 0 %	22.5	24.3	Up 1.8
RH = 80 %	Down 5.8	40.5	27.0

- RH differently affected CO_2 permeance.

Relative permeance in carbon membrane

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- RH differently affected CO_2 permeance depending on Cs content.
  - There are two pathways of CO_2 permeation.
    1) Dry carbon on surface without H_2O
    2) Cs + water on surface

Relative CO_2 Permeance (as a basis of N_2 permeance at RH = 0 %)

CO_2 Permeance	Cs_2CO_3 content [%] in carbon membrane		
	0	0.71	4.1
RH = 0 %	22.5	24.3	1.8
RH = 80 %	5.8	40.5	27.0
Increment	-16.7	16.2	25.2

(a) Decrease value; -16.7 → Disappearance of dry carbon
(b) Increase value; 25.2 → Appearance of Cs + Water
(c) Increase value 16.2 → Appearance of Cs + water - Disappearance of dry carbon
-16.7 + 25.2 = 8.6

Observed value 16.2 and estimated value 8.6 → OK or no?

Summary of carbon membrane mechanism

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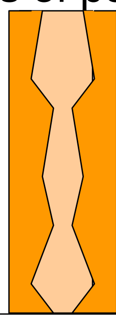
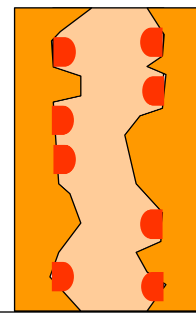
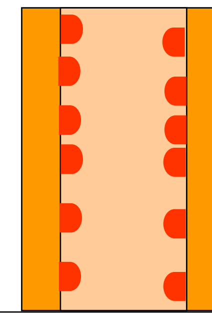
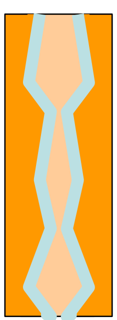
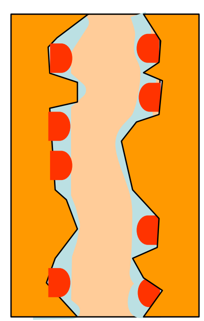
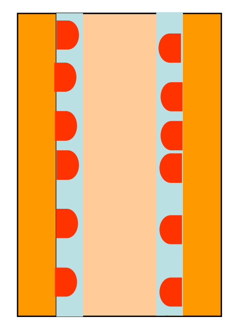
Pore diameter, both CO_2 attractive force by carbon and Cs + water on pore surface effect on CO_2 and N_2 permeance.

Low RH	CO_2 and N_2 permeance is low, because diameters of pores are small. 	Surface has CO_2 attractive force by carbon and Cs +water. 	Surface has CO_2 attractive force by carbon. 
High RH	Water on pore surface block out N_2 and CO_2. 	Surface has CO_2 both attractive forces by carbon and Cs +water. 	It is too large attractive force for CO_2 to move inside pores. 

PAMAM / Mesoporous silica / Al_2O_3 membrane

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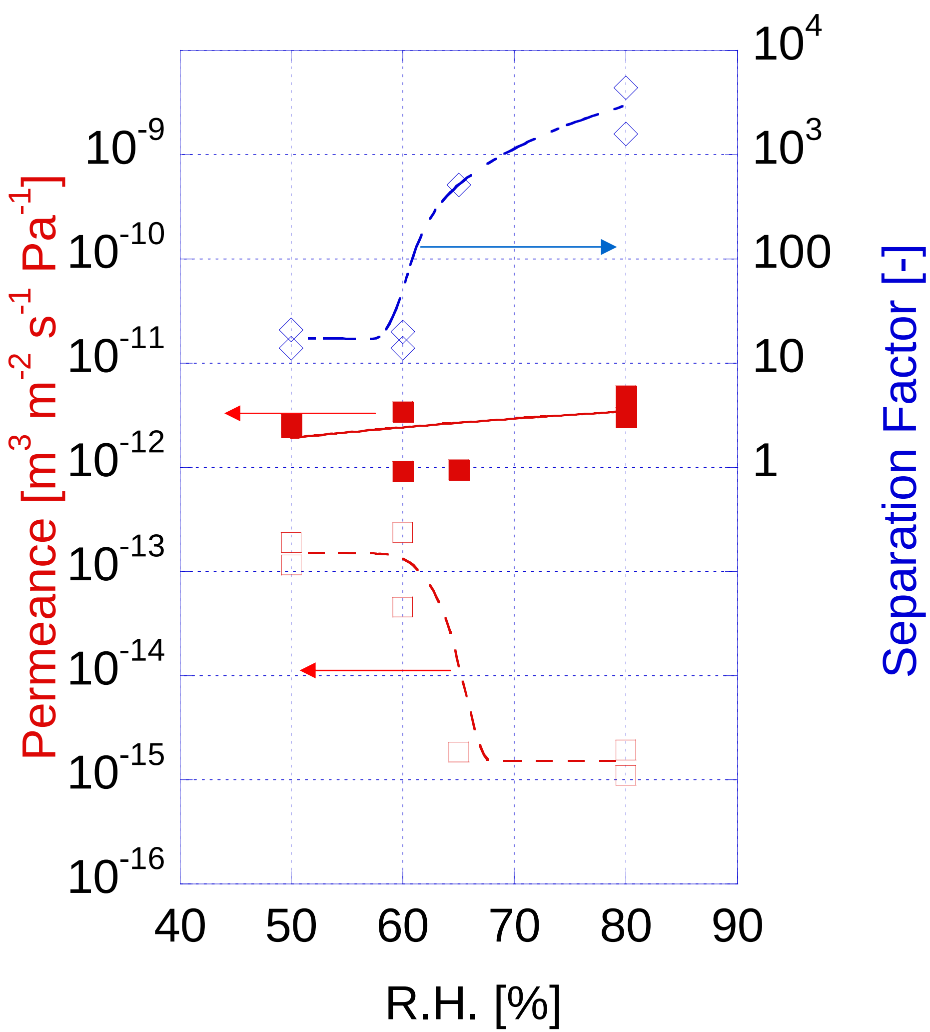
- Conceptual figure of PAMAM / MS / Al_2O_3 membrane

Performances of PAMAM / MS / Al_2O_3 Membrane



CO_2 / N_2=50% / 50%, Temperature: 313 K

- Separation factor is more than 1000.
- But, CO_2 permeance is small.
- Now, studying on structure of selective layer.

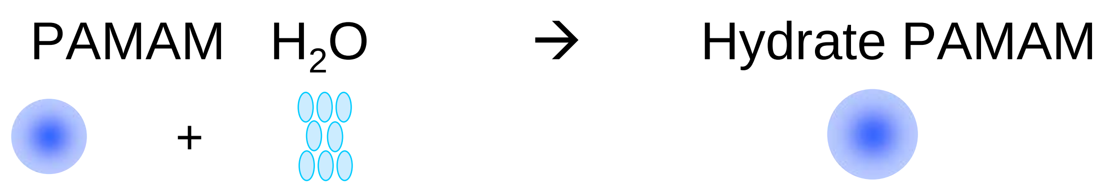
Effect of PAMAM on permeance

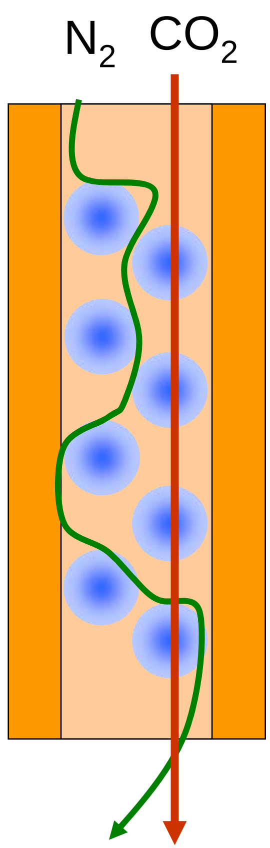
	Temp (K)	R.H. (%)	Permeance [m^3(STP) sec^{-1} m^2 Pa^{-1}]		CO_2/N_2 Separation factor	
			CO_2	N_2		
Al_2O_3 substrate	298	-	2.5×10^{-8}	2.5×10^{-8}	1.0[1)]	Non selective
			↓	Down		
MS / Al_2O_3	298	-	7.6×10^{-10}	8.4×10^{-10}	0.8[1)]	Knudsen diffusion
			c.a. 1 / 300 ↓	c.a. 1 / 7000 ↓		
PAMAM / MS / Al_2O_3	313	50	2.4×10^{-12}	1.2×10^{-13}	21	CO_2 selective
			Slightly up ↓	c.a. 1 / 60 ↓		
PAMAM / MS / Al_2O_3	313	80	3.1×10^{-12}	1.9×10^{-15}	1581	

Suggestive mechanism of CO_2 and N_2 separation with PAMAM / MS / Al_2O_3

Before humidification After humidification

RH = 80 %



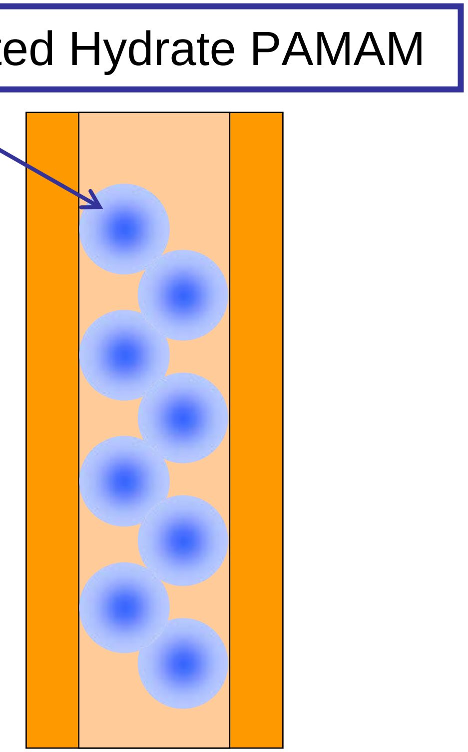


CO_2 permeate rate → decrease 1/300

Other gases → enormously decrease 1/7000

Surface of mesoporous silica has enough hydrophilic property to adhere hydrate PAMAM at RH = 80 %, so PAMAM can interrupt N_2 movement.

Swelling and agglomerated Hydrate PAMAM



Conclusions

- CO_2 attractive force on pore inner-surface and distribution of pore diameter affect membrane performances.
- Carbon membrane needs ten times larger CO_2 permeance and twice larger separation factor than those of our result.
- PAMAM / MS / Al_2O_3 membrane has very high separation factor, but it needs thousand times larger CO_2 permeance.

Future Work

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- It is possible that PAMAM dendrimer with rigid support and with hydrophilic material, such as mesoporous silica, highly block gases without CO_2.
- It is not precisely unknown how to enhance PAMAM dendrimer CO_2 permeation rate.
- We are focusing on
  - the interruptions between PAMAM dendrimer, pore figure and function of pore surface to increase CO_2 permeation rate,
  - temperature effect, and
  - thickness of selective layer of a membrane.

Acknowledgement

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Thank you for your attention!

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