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GCEP Research Symposium

Research Pathways to Low GHG-Emitting Energy Systems

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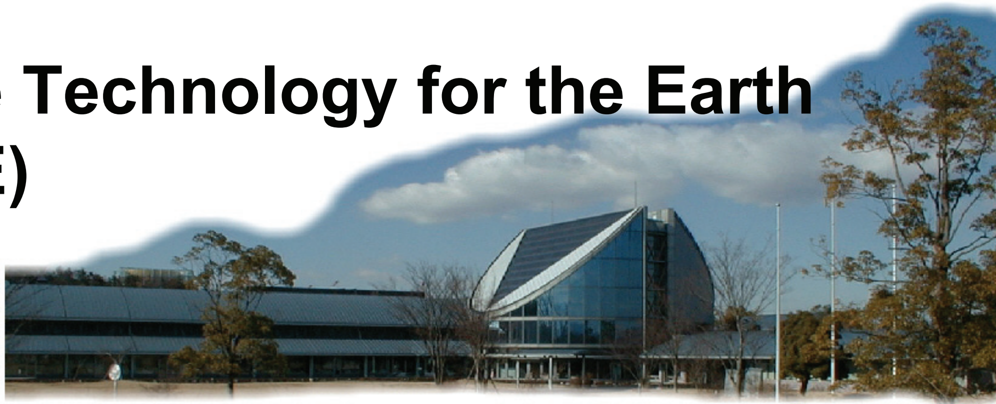
Development of Innovative Gas Separation Membranes through Sub-Nanoscale Materials Control -Development of Novel Carbon Membranes

Teruhiko Kai, Shingo Kazama and Yuichi Fujioka

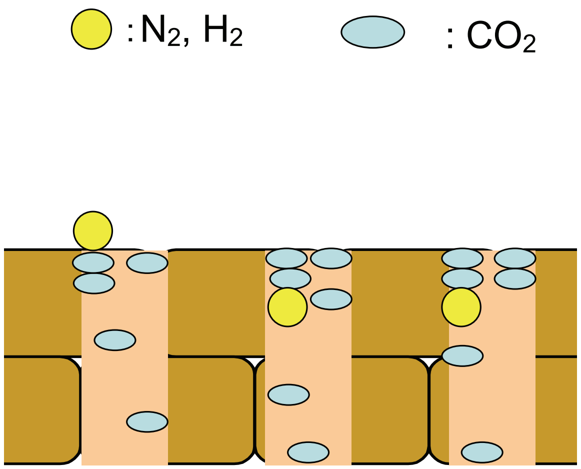
Research Institute of Innovative Technology for the Earth (RITE)



Background

CO_2/N_2, CO_2/H_2 Separation performance of carbon membrane

CO_2/N_2: Separation factor: 6.8-101 [1)]
High CO_2/N_2 separation performance



CO_2/H_2: Separation factor: 5.5 [2)]

CO_2 selective permeation due to

selective adsorption on the pore surface

Affinity to CO_2 ↑ ⟶ Separation performance ↑

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

2) M. B. Rao and S. Sircar, Gas Separation & Purification, 7 (1993) 279-284.

Problem: Decline of separation performance under humidified conditions

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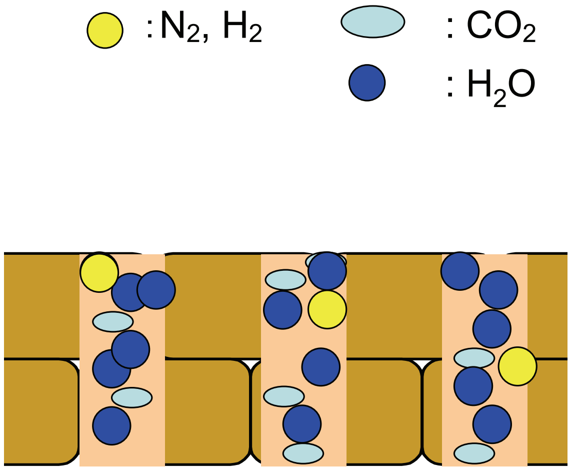
Separation target: Humidified gas

(WGS gas, flue gas)



H_2O blocks CO_2 permeation

Humidity ↑ ⟶ Permeance ↓

Separation factor ↓

Cause: H_2O adsorption and blockage

Previous approach: Hydrophobic layer coating [3)]

<u>Our approach</u>

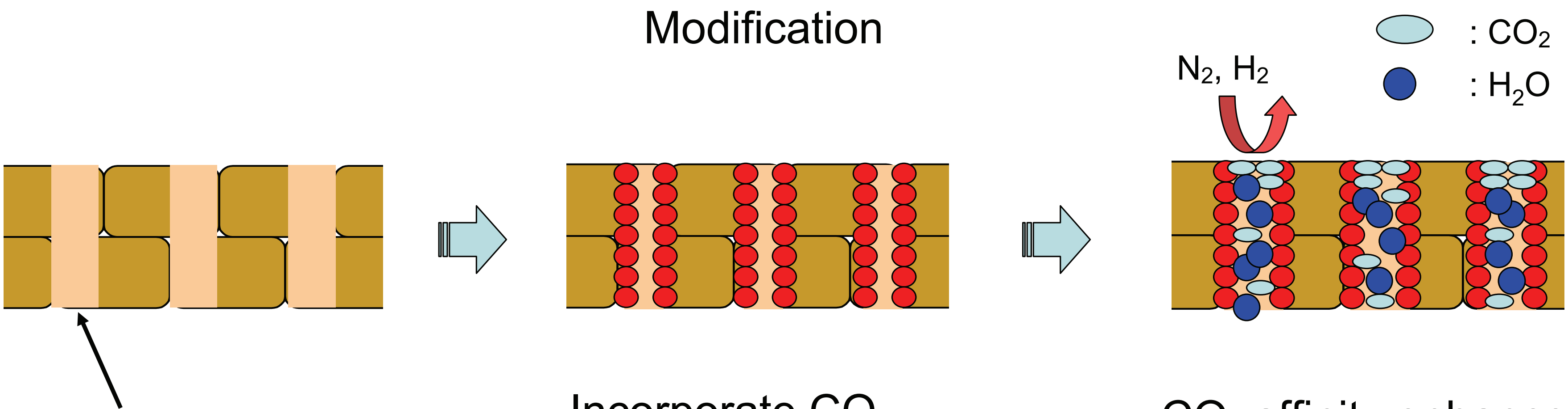
Incorporate CO_2 affinity materials in the pores

→Enhanced CO_2 permeation using adsorbed H_2O in the pores

3) C.W. Jones and W. J. Koros, *Ind. Eng. Chem. Res.,* 1995, 34 (1995) 158-163, 164-167.

Approach

Novel Carbon Membranes with enhanced CO_2 affinity



Pore size: 0.5-5 nm

Incorporate CO_2 affinity materials
・Alkali metal carbonate
・Amine containing organic materials

CO_2 affinity enhanced Carbon membranes

Incorporate CO_2 affinity materials in the pores
→ Enhanced CO_2 permeation under humidified conditions

Materials

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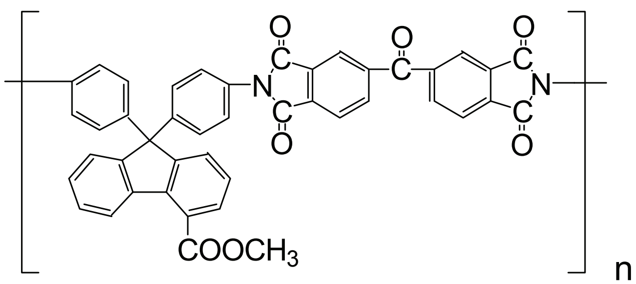
Porous support: tubular porous α-alumina membrane

(Noritake Co., Japan,
pore diameter: 150nm (symmetric),
Outer-diameter: 10mm)

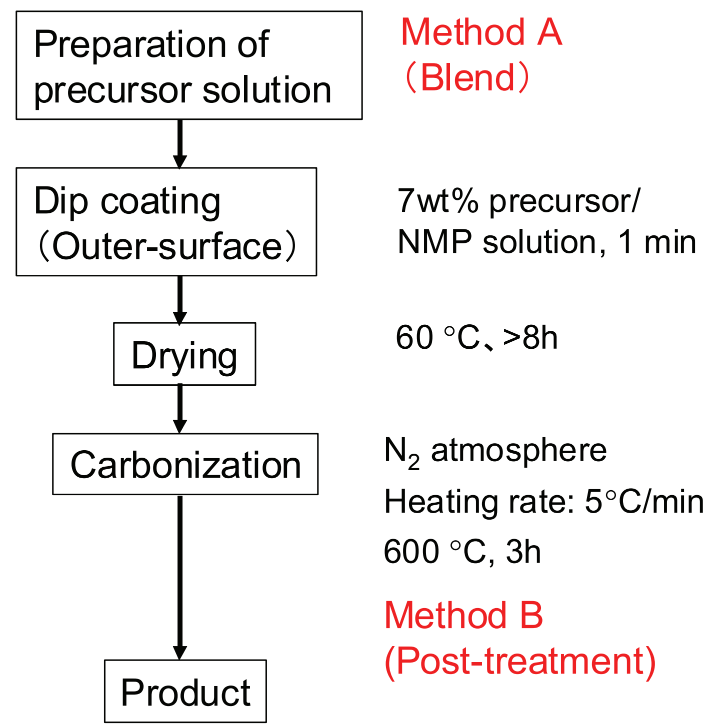
Precursor: Cardo polyimide
(PI-BTCOOMe)



PI-BT-COOMe

Solvent: 1-Methyl-2-pyrrolidinone (NMP)

Membrane preparation procedure



CO_2 affinity materials:

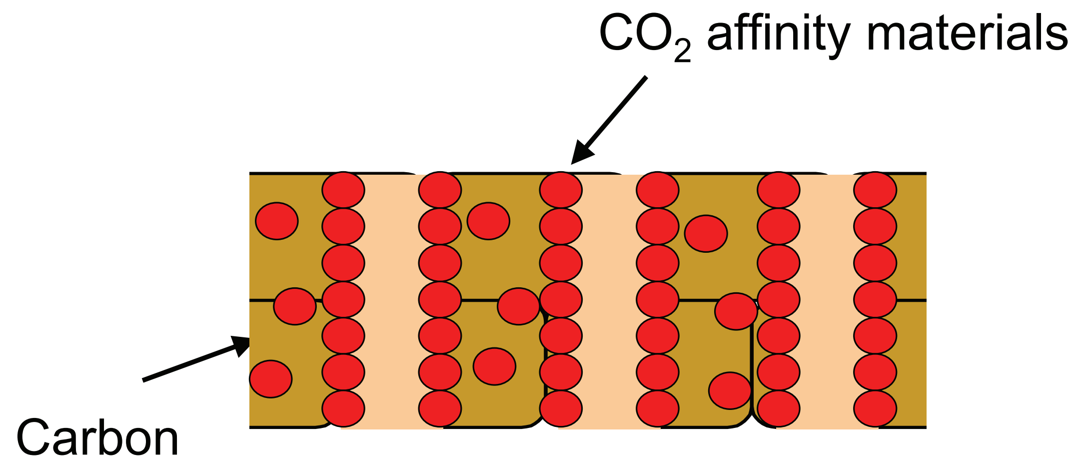
(1) Alkali metal carbonate

(2) (2) DL-2,3-Diaminopropionic acid hydrochloride (DAPA)

Method to incorporate CO_2 affinity materials

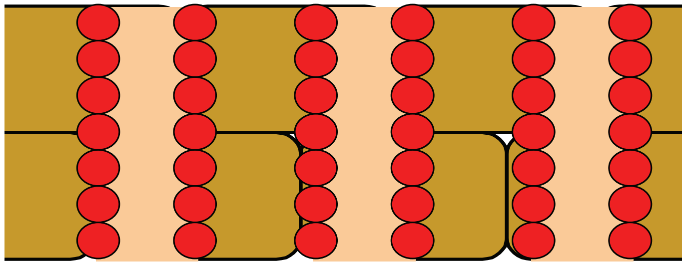
Method A:

Blend CO_2 affinity materials in precursor solution

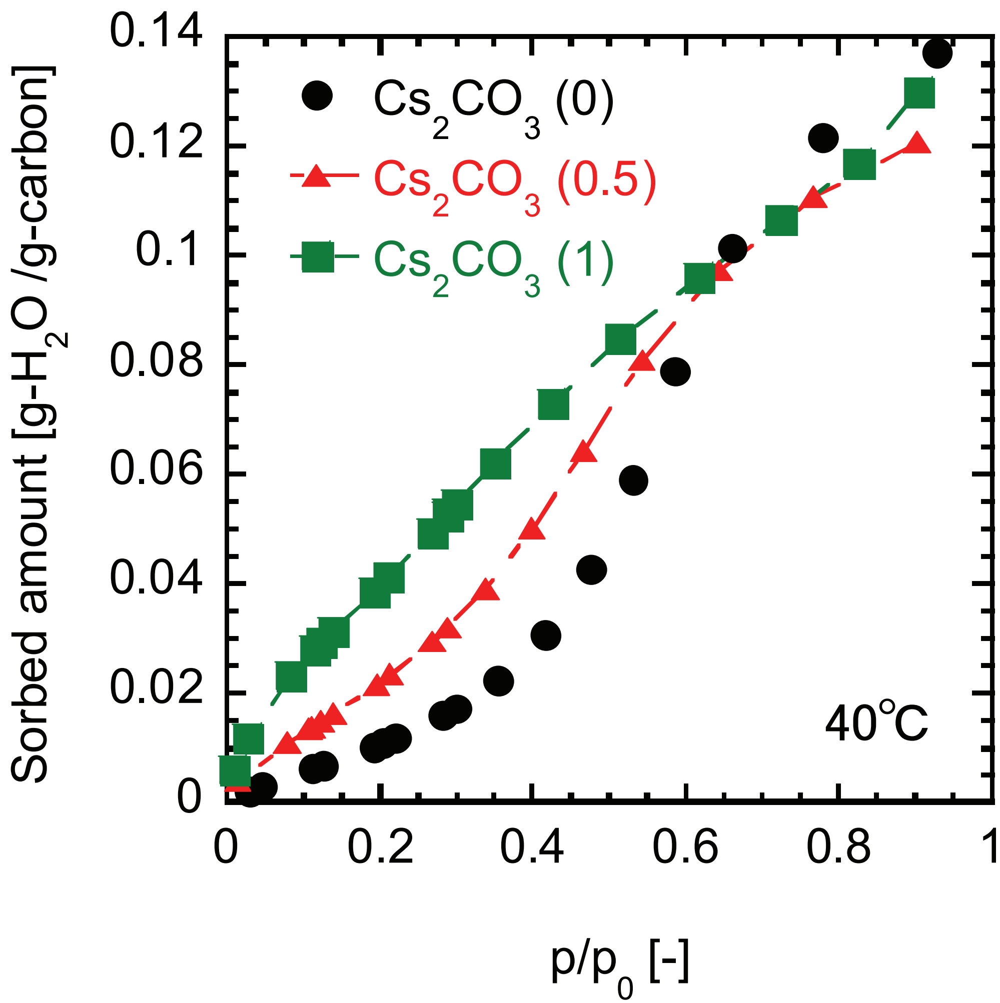


Method B:

Post-treatment of CO_2 affinity materials after preparation of carbon membranes



Water vapor sorption using carbon films with/without Cs_2CO_3 (Method A)



Cs_2CO_3 (x):
Precursor solution:
PI-BTCOOMe/(Cs_2CO_3/H_2O/NMP = x/(10-x)/90wt%) (7/93 wt%)

→ Increase in H_2O adsorption at low humidity

More hydrophilic pores

Effect of Cs_2CO_3 post-treatment on separation performance

With/without Cs_2CO_3	Method	Relative humidity [RH%]	Q_{CO2} [$m^3 m^{-2} s^{-1} Pa^{-1}$]	Q_{N2} [$m^3 m^{-2} s^{-1} Pa^{-1}$]	Separation factor
Without Cs_2CO_3	N/A	0	8.9×10^{-10}	4.0×10^{-11}	19
	N/A	100	3.6×10^{-10}	3.0×10^{-11}	12
Cs_2CO_3	**Method A**	100	3.0×10^{-10}	2.8×10^{-10}	1
Cs_2CO_3	**Method B**	100	1.2×10^{-9}	2.6×10^{-11}	46

Gas separation conditions:
Temp.: 40 °C, Feed gas: CO_2/N_2 (5/95 vol/vol),
Feed pressure: 0.1 MPa, Permeate pressure: ca. 0 MPa

Separation performance was enhanced by Method B.

Effect of alkali metal carbonate post-treatment on separation performance (Method B)

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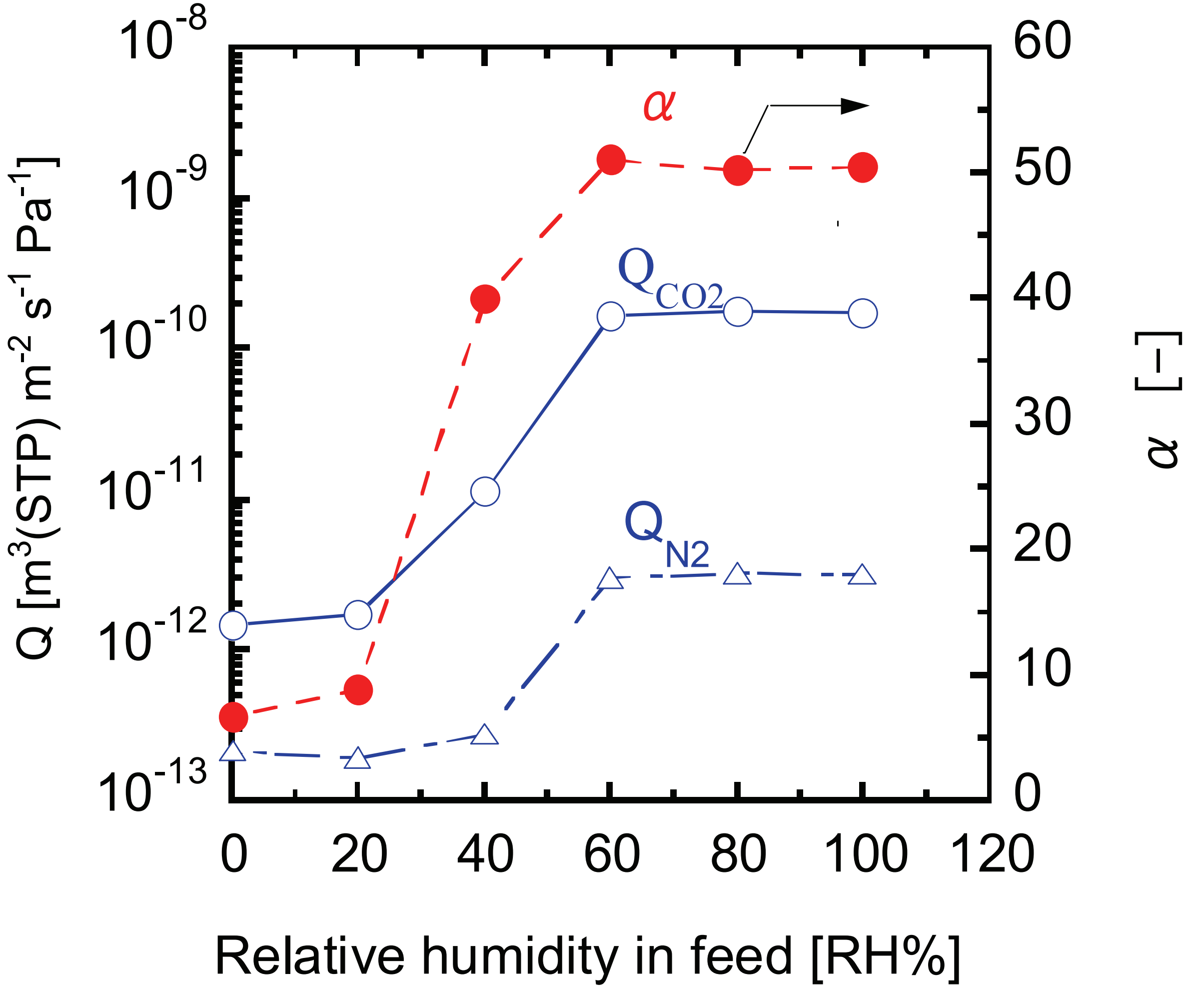
Alkali metal carbonate	Q_{CO2} [$m^3m^{-2}s^{-1}Pa^{-1}$]	Q_{N2} [$m^3m^{-2}s^{-1}Pa^{-1}$]	Separation factor
Na_2CO_3	7.2×10^{-10}	1.7×10^{-11}	42
K_2CO_3	4.5×10^{-10}	1.0×10^{-11}	43
Rb_2CO_3	1.5×10^{-9}	2.9×10^{-11}	48
Cs_2CO_3	1.2×10^{-9}	2.6×10^{-11}	46
Cs_2CO_3 +DAPA	1.6×10^{-9}	2.6×10^{-11}	57

Gas separation conditions: Temp.: 40 °C, Feed gas: CO_2/N_2 (5/95 vol/vol), Humidity: ca. 100RH%. Feed pressure：0.1 MPa, Permeate pressure: ca. 0 MPa

Effect of humidity on separation performance



Carbon membrane with Cs_2CO_3+ DAPA post-treatment

Gas separation conditions: Temp.: 40 °C, Feed gas: CO_2/N_2 (5/95 vol/vol), Feed pressure: 0.1 MPa, Permeate pressure: ca. 0 MPa

Constant separation performance at 60-100RH%

Summary of carbon membrane

Novel carbon membranes with enhanced CO_2 affinity for CO_2 separation under humidified conditions were developed.

Method A (Blend CO_2 affinity materials with precursor solution)

・Sorbed H_2O increased as the amount of alkali metal carbonate increased at low relative humidity.

・Prepared membrane did not show good separation performance, probably due to defect formation.

Method B (Post-treatment)

・Separation performance was enhanced. Effect of CO_2 affinity materials were confirmed.

・Treated membrane showed constant separation performances at 60-100RH%.

Future plan

(1)Improve separation performance
(Increase Q_{CO2} and α)

-Control membrane thickness
-Optimize carbonization condition
-Screen CO_2 affinity materials

(2) Separation performance under high pressure

-Control membrane structure for high pressure

Goal: $Q_{CO2} > 1 \times 10^{-9}$ [m^3(STP) m^{-2} s^{-1} Pa^{-1}]
$\alpha > 100$ at 4 MPa.