Development of Molecular Gate Membrane for CO_2 Capture

CSLF Project: CO_2 Separation from Pressurized Gas Stream

Research Institute of Innovative Technology for the Earth

1. Project Coordinator: Japan: Research Institute of Innovative Technology for the Earth (RITE)

2. Project Partner: USA: Department of Energy, National Energy Technology Laboratory (U.S. DOE/NETL)

3. Background:

Carbon dioxide (CO_2)capture with existing technology consumes 70-80% of the total cost of carbon dioxide capture and storage. Cost reduction of CO_2 capture is the urgent subject of the implementation of CCS. CO_2 capture with separation membrane from a pressurized gas steam such as products of water-gas shift reaction (Figure 1) is a great concern for CO_2 cost reduction, because of no additional energy requirement for CO_2 separation. As shown in figure 2, CO_2 separation membrane which has CO_2/H_2 selectivity of 500 is estimated to achieve one third of CO_2 separation cost of conventional MEA solution. RITE is currently involved in developing a CO_2 molecular gate membrane with the goal of producing a new, high-performance CO_2 separation membrane.

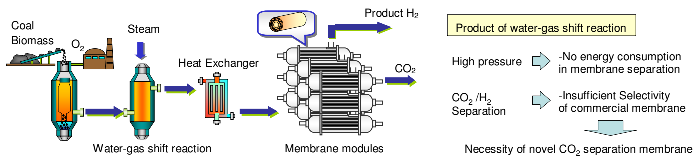
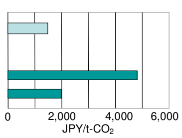


Figure 1. CO_2 separation from pressurized gas stream with membrane

CO_2 Source	Gas Pressure	Gas Composition	Membrane Performance (Target)
Product of Water-gas Shift reaction	4MPa	CO_2:40% H_2, H_2O	CO_2 permeance:1×10^{-9} ($m^3\ m^{-2}\ s^{-1}\ Pa^{-1}$) CO_2/H_2 selectivity: 500
Ref.	Chemical Absorption	Current(MEA)	
		2013 Target (New Solvent)	



Membrane Cost: 50,000JPY/m^2

Duration period
Facility:15 years
Membrane:5 years

Figure 2. Cost estimates of CO_2 capture with promising CO_2 molecular gate membrane

4. Primary Project Goal:

The purpose of this project is to develop a molecular gate membrane module that can greatly reduce the costs and energy requirements of CO_2 separation.

5. Objectives:

The major objectives of this project are as follows:
1. Development of membrane material for molecular gate function and composite membrane of excellent CO_2 selectivity
2. Development of membrane module
3. Testing of the module (with NETL, USA)

6. Mechanism of CO_2 Molecular Gate:

Figure 3 shows the basic outline of the CO_2 molecular gate function. The separation membrane (separation function layer) has a pathway through which gas molecules pass. In previous polymeric 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 CO_2 molecular gate membrane, on the other hand, 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 leaking to the other side of the membrane is greatly limited and high concentrations of CO_2 can be obtained.

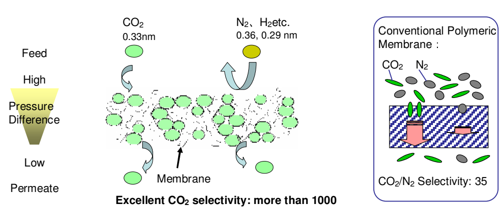


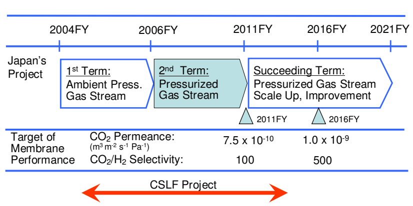
Figure 3. Concept of CO_2 molecular gate membrane.

7. Framework and Schedule:

Cooperation in the sharing of knowledge and information across international borders is the key to the development and implementation of new, innovative technologies. In developing this CO_2 molecular gate membrane, RITE conducted joint research with the US Department of Energy's National Energy Technology Laboratory (NETL). NETL will offer a testing information and apparatus. Meiji University in Japan partly contributes to developing the composite membrane.

RITE:
Development of membrane material
Development of composite membrane (Meiji Univ.)
Development of membrane module

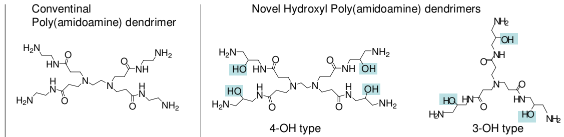
RITE and NETL:
Test of membrane module



9. Major Results:

9.1. Novel materials of CO_2 molecular gate function for CO_2 separation from H_2: (Result of 2nd term)

RITE has been developing novel modified poly(amidoamine) PAMAM dendrimers as CO_2 molecular gate functionalized material. The hydroxyl modified PAMAM dendrimers show CO_2 selectivity over N_2 of more than 4000 at practical usage condition. The excellent CO_2 selectivity enables to produce a 99 % CO_2 concentration stream comparable to that of amine solution. The novel PAMAM dendrimer, 3-OH type, also shows the world largest CO_2/H_2 selectivity of 1000, which encourages a great reduction of the energy requirements and costs of CO_2 separation from a pressurized gas stream such as products of water-gas shift reaction.



	Conventinal Poly(amidoamine) dendrimer	Novel Hydroxyl Poly(amidoamine) dendrimers: 4-OH type	3-OH type
CO_2 Permeability Coefficient [$m^3\ m\ m^{-2}\ s^{-1}\ Pa^{-1}$]	8.8×10^{-15}	8.7×10^{-15}	8.7×10^{-15}
CO_2/N_2 Selectivity	2400	4300	4300
CO_2/H_2 Selectivity	400	730	1000

Improved CO_2 selectivity over H_2

Figure 4. Chemical structure and CO_2 separation properties of poly(amidoamine) PAMAM dendrimers

9.2. Dendrimer composite membrane for CO_2 separation at ambient pressure: (Result of 1st term)

RITE has developed dendrimer composite membrane by using an In-situ module modification method [1]. The method is applicable to surface modification of membranes in a commercial module to invest excellent CO_2 separation performance. Figure 5 shows cross sectional SEM photos of a dendrimer composite membrane. In the right, selective layer of dendrimer hybrid is about 300 nm in thickness. Figure 6 shows CO_2 separation performance of PAMAM dendrimer composite membranes at ambient pressure. The dendrimer composite membranes had good CO_2 separation performance.

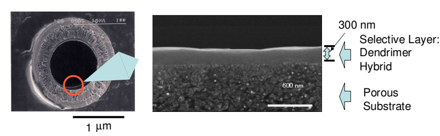


Figure 5. SEM image of cross section of dendrimer composite membrane

Pencil Module  200 mm in length, 3/8 inch in diameter

CO_2 Permeance $m^3/(m^2\ s\ Pa)$	CO_2/N_2 Selectivity -	Dendrimer
8×10^{-10}	400	Conventional PAMAM
1×10^{-9}	1200	Novel Hydroxyl PAMAM (4-OH)

Temperature: 40 °C, Pressure difference: 101 kPa

1 meter Module 

1100 mm in length, 1 inch in diameter

CO_2 Permeance $m^3/(m^2\ s\ Pa)$	CO_2/N_2 Selectivity -	Dendrimer
3×10^{-10}	150	Conventional PAMAM

Temperature: 25 °C, Pressure difference: 101 kPa

Figure 6. Membrane modules and CO_2 separation properties at ambient pressure

9.3. Membrane module test at U.S. DOE/ NETL: (Result of 1st term)

Commercial scale dendrimer membrane modules (1 meter module in figure 6) produced by RITE were tested at U.S. DOE/NETL in March of 2006. The test was operated under the condition of various CO_2 concentration at ambient pressure. The results of the test were reported at Pittsburgh Coal Conference, Pittsburgh, USA (2006) as "Experimental Investigation of a Molecular Gate Membrane for Separation of Carbon Dioxide from Flue Gas, Shingo Kazama, Teruhiko Kai, Takayuki Kouketsu, Shigetoshi Matsui, Koichi Yamada, James S. Hoffman, Henry W. Pennline".

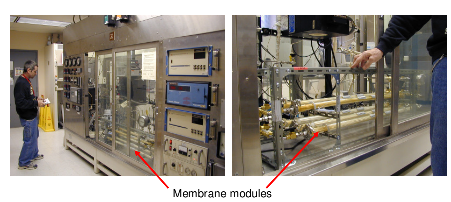


Figure 7. Membrane module test at U.S. DOE/ NETL

10. Acknowledgement:

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11. Reference:

[1] Takayuki Kouketsu, Shuhong Duan, Teruhiko Kai, Shingo Kazama*, and Koichi Yamada, PAMAM Dendrimer Composite Membrane for CO_2 separation: Formation of a Chitosan Gutter Layer, J. Membrane Sci. 287 (2007) 51-59

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