

## **GCEP Annual Scientific Progress Report**

### **Advanced CO<sub>2</sub>/H<sub>2</sub> separation materials incorporating active functional agents**

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### **1. Research Subject**

Advanced CO<sub>2</sub>/H<sub>2</sub> separation materials incorporating active functional agents

### **2. Abstract**

The concept for a novel supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) structure directing method was invented and tried for preparation of an innovative CO<sub>2</sub>/H<sub>2</sub> separation membrane possessing a CO<sub>2</sub> molecular gate function. Poly(amidoamine) (PAMAM) dendrimer was selected as the CO<sub>2</sub> molecular gating material, held within a polymeric matrix of polyethylene glycol dimethacrylate (PEGDMA) and X. SC-CO<sub>2</sub> may work as a structure directing agent for creating the CO<sub>2</sub> molecular gate channel. CO<sub>2</sub> molecules would form carbamate ion pairs with the amino moieties of the PAMAM dendrimer under the SC-CO<sub>2</sub> atmosphere to regulate PAMAM dendrimer morphology for ideal CO<sub>2</sub> molecular gating channels. The resulting membrane had increased CO<sub>2</sub>/H<sub>2</sub> selectivity and CO<sub>2</sub> permeability.

### **3. Introduction**

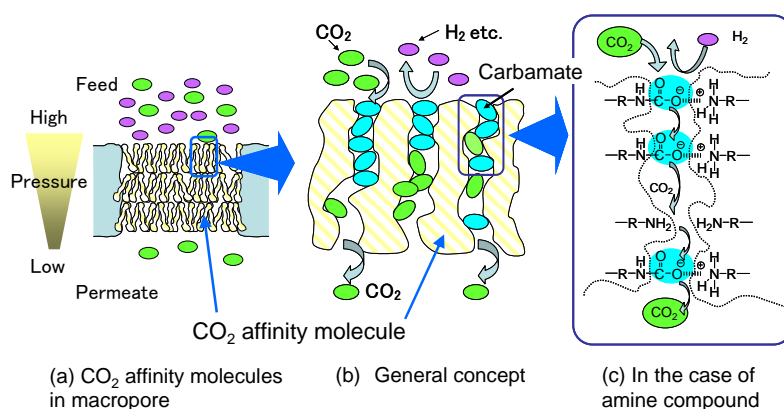
CO<sub>2</sub> capture and storage (CCS) is an important option for mitigating global warming. However, CCS in terms of present-day technology consumes a large amount of energy and is costly, especially in CO<sub>2</sub> capture. Several CO<sub>2</sub> capture technologies such as chemical and physical absorption, adsorption and membranes are under research and development. Among these, membranes are the least energy intensive method.

We have been developing advanced composite materials possessing molecular interaction forces with specific molecules using nanoscale control technologies in polymeric and inorganic materials. For example, such forces can selectively extract CO<sub>2</sub> from CO<sub>2</sub> and H<sub>2</sub> mixed gas. The materials consist of active functional agents in the nanopores of a porous substrate or polymeric matrix. We control the configurations, surface atoms/molecules and the compositions of the pore/matrix and functional compounds to create the desired molecular interaction forces. Our research is expected to provide detailed insight into molecular dynamics in nanoscale structures and result in the future production of superior separation materials.

One objective of this research is to realize the development of an improved CO<sub>2</sub> separation membrane for CCS. Such an innovative material will greatly reduce energy consumption and costs in the separation process.

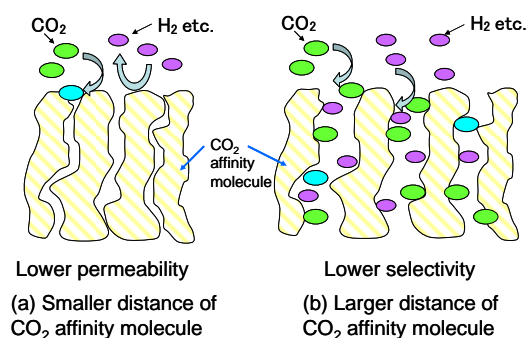
### Basic concept of CO<sub>2</sub> molecular gate membrane

Figure 1 shows the basic outline of the CO<sub>2</sub> molecular gate membrane. In Figure 1 (b), the pathway for gas molecules is occupied solely by CO<sub>2</sub>, which acts as a gate to block the passage of other gases. Consequently, the amount of H<sub>2</sub> permeating to the other side of the membrane is greatly limited and high concentrations of CO<sub>2</sub> can be obtained. The molecular gate membrane can achieve reverse size separation of CO<sub>2</sub> and H<sub>2</sub>. Figure 1 (c) shows further detail of the amine compounds, such as polyamidoamine (PAMAM) dendrimers. In the figure, one CO<sub>2</sub> molecule is shown to form a carbamate ion pair with two amino moieties from the membrane material. The carbamate ion pair works as a quasi cross-linkage that restricts H<sub>2</sub> permeation through the membrane. On the other hand, because carbamate ion pairs are in equilibrium with free CO<sub>2</sub> and amine moieties, CO<sub>2</sub> can release from the original carbamate ion pair and jump down to the next pair of amine moieties via the CO<sub>2</sub> concentration gradient in the membrane. As a result, only CO<sub>2</sub> molecules permeate the membrane.



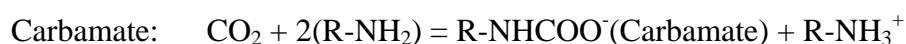
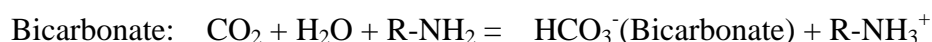
**Figure 1:** Concept of the CO<sub>2</sub> molecular gate membrane

The CO<sub>2</sub> molecular gate requires strict morphological arrangement. In Figure 1 (c), a strict morphological control of the distance between two amine moieties is required for the perfect CO<sub>2</sub> molecular gate. If the distance is too small and allows strong hydrogen bonding of the amine moieties, the membrane will not have sufficient CO<sub>2</sub> permeability (Figure 2(a)). On the other hand, if the distance is too large, there will not be enough carbamate ion pairs for the gate to function. It is critical that this is avoided for better CO<sub>2</sub> selectivity (Figure 2(b)).



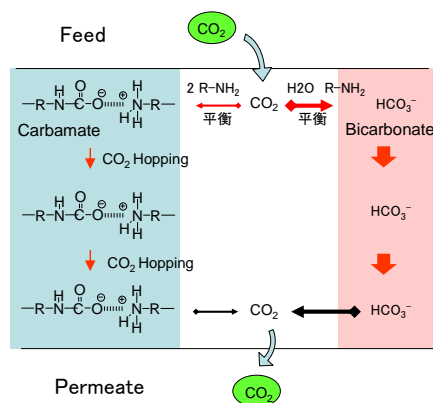
**Figure 2:** Morphological deformation and the molecular gate function

As for CO<sub>2</sub> affinity molecules, amine compounds were preferably selected. Amine compounds react with CO<sub>2</sub> to form both bicarbonate and carbamate ions as follows:



As shown in the equation, bicarbonate was formed with one molar of CO<sub>2</sub>, H<sub>2</sub>O and amine moiety. On the other hand, carbamate was formed with one molar of CO<sub>2</sub> and two molars of amine moieties. Accordingly, a formation of bicarbonate needs a H<sub>2</sub>O, not for carbamate.

Actually, a polyamidoamine (PAMAM) dendrimer was observed to form both bicarbonate and carbamate ions by NMR observation. In the molecular gate membrane using PAMAM dendrimer, CO<sub>2</sub> would exist as bicarbonate and carbamate ions. And those ions could move in the membrane. Figure 3 shows a conceptual diagram of those ions transportation through membrane.



**Figure 3:** Expected CO<sub>2</sub> permeation through membrane via carbamate and bicarbonate.

In the figure, the transportation of bicarbonate essentially requires the existence of an equal mole of H<sub>2</sub>O. On the other hand, the CO<sub>2</sub> transportation via carbamate does not need a water existence.

Existing molecular gate membranes containing PAMAM dendrimer work well under a highly humid feed gas condition. For example, a CO<sub>2</sub>/H<sub>2</sub> selectivity of the membrane shows a maximum value at 80-90 %RH (relative humidity) of a feed gas. Lower relative humidity decreases CO<sub>2</sub>/H<sub>2</sub> selectivity of the membrane drastically. Stable selectivity over a wide range of moisture content in a feed gas would be favorable performance for CO<sub>2</sub> separation from various gas mixtures.

From the strong influence of moisture content in a feed gas on CO<sub>2</sub> permselectivity, bicarbonate ions seem to be dominant species of CO<sub>2</sub> permeation in the conventional PAMAM dendrimer membrane.

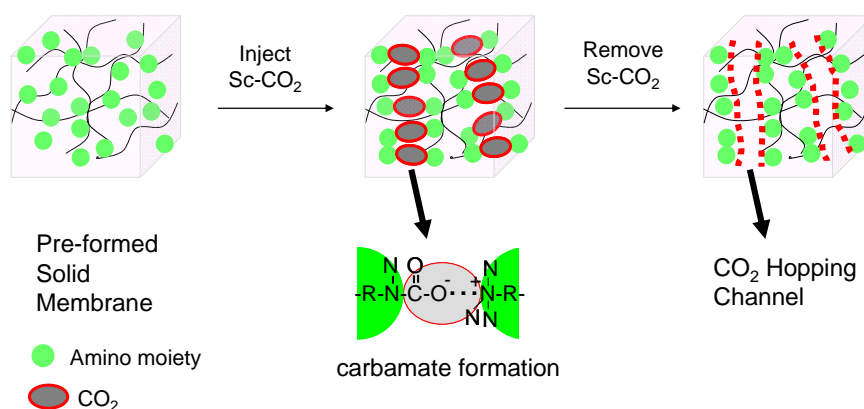
If carbamate ions are dominant species for CO<sub>2</sub> permeation of membranes, no water existence would be required. In addition, smaller moisture influence on CO<sub>2</sub> permeation would be observed. Therefore, dry or less humid gas feed would be acceptable to the membrane separation system. The mechanism of CO<sub>2</sub> permeation via carbamate ions should be preferable to that of bicarbonate ion transportation for CO<sub>2</sub> separation. However, the dominant transportation via carbamate ion was not achieved until now. Actually, bicarbonate ions are the dominant species for CO<sub>2</sub> permeation in various facilitated membranes.

The reason why the CO<sub>2</sub> transportation via carbamate ion was not attained in membrane permeation is the difficulty to precisely conformational control of adjacent amino moieties for the transportation. The suitable conformation of precisely controlled adjacent amino moieties would enable to form carbamate ion easily and accept the rapid hopping movement of CO<sub>2</sub> via carbamate.

#### Our methodology

A promising way of creating the best morphology for the CO<sub>2</sub> hopping via carbamate is the rearrangement of amino moiety to form an ion hopping channel by using a structure directing agent. We select supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) as a structure directing agent for rearranging amino moiety conformation for the CO<sub>2</sub> hopping channel. SC-CO<sub>2</sub> can penetrate easily into a pretreated membrane to act as the structure directing agent to form carbamate ion pairs.

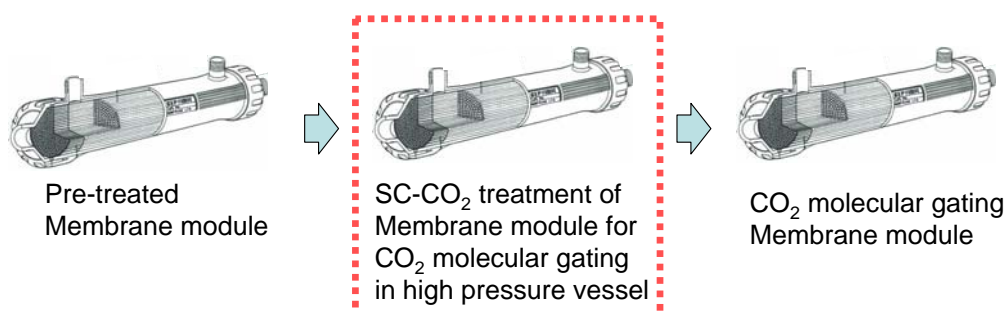
Figure 4 shows conceptual diagram of our methodology. A membrane containing amine compound was treated under SC-CO<sub>2</sub> atmosphere. SC-CO<sub>2</sub> can easily penetrate into the membrane and swell it. And spontaneously SC-CO<sub>2</sub> would form carbamate ion pairs to rearrange the morphology of amino moieties for the CO<sub>2</sub> hopping channel. Because of their having near-zero surface tension, after removing SC-CO<sub>2</sub>, the rearranged morphology would be kept for serving the best channel for CO<sub>2</sub> hopping.



**Figure 4:** Concept of creation of CO<sub>2</sub> hopping channel via carbamate ion

The selection of membrane materials and tuning the SC-CO<sub>2</sub> treatment condition would be critically important to create the best channel of CO<sub>2</sub> hopping.

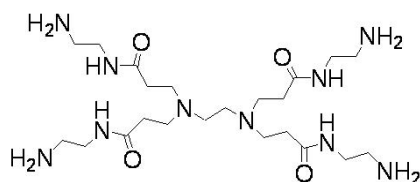
Another strong point of SC-CO<sub>2</sub> treatment is that this method can be applied to membranes in a module formation. It means membranes in a module would gain the molecular gate function by our method. Figure 5 shows a conceptual image of SC-CO<sub>2</sub> treatment of a membrane module for CO<sub>2</sub> molecular gating. A membrane module containing nascent membranes is set in a high pressure vessel, followed by treated by SC-CO<sub>2</sub> to create a CO<sub>2</sub> molecular gating layer.



**Figure 5:** Concept of SC-CO<sub>2</sub> treatment of membrane module

#### 4. Background

Creation of a CO<sub>2</sub>/H<sub>2</sub> separation membrane is a very hot topic in gas separation membrane research. RITE is a leading research institute on CO<sub>2</sub> separation technologies and has studied polyamidoamine (PAMAM) dendrimer membranes for CO<sub>2</sub> separation (Figure 6). A PAMAM dendrimer membrane was first reported by Professor Sirkar's group at the New Jersey Institute of Technology as an immobilized liquid membrane for CO<sub>2</sub>/N<sub>2</sub> separation [1]. A liquid state dendrimer has been successfully and stably fixed in a polymeric matrix as a composite hollow fiber membrane at RITE [2]. RITE's membrane holds the world record for CO<sub>2</sub>/H<sub>2</sub> separation properties (CO<sub>2</sub>/H<sub>2</sub> selectivity: 30) at an elevated CO<sub>2</sub> pressure. In this membrane, PAMAM dendrimer was incorporated into a cross-linked polymeric matrix, whereby a continuous channel of PAMAM dendrimer through membrane was formed. Further improvement of the dendrimer membrane and morphologic regulation of the dendrimer channel is required.



**Figure 6:** Chemical structure of PAMAM dendrimer (conventional).

Professor Freeman's group at the University of Texas at Austin also attains very good CO<sub>2</sub>/H<sub>2</sub> separation membranes of cross-linked poly(ethylene glycol) (PEG) network, which show a selectivity of 10 at 30 °C and an elevated CO<sub>2</sub> pressure, as well as a good CO<sub>2</sub> permeability [3]. Professor Ho's group at Ohio State University has reported a cross-linked poly(vinyl alcohol) membrane containing amine compounds [4]. Professor Matsuyama's group at Kobe University in Japan has also reported a gel membrane, which consists of poly(vinyl alcohol)/poly(acrylic acid) co-polymer and an amine as CO<sub>2</sub> carrier [5]. Both membranes exhibit very good CO<sub>2</sub>/H<sub>2</sub> selectivity at an elevated temperature and a low CO<sub>2</sub> partial pressure.

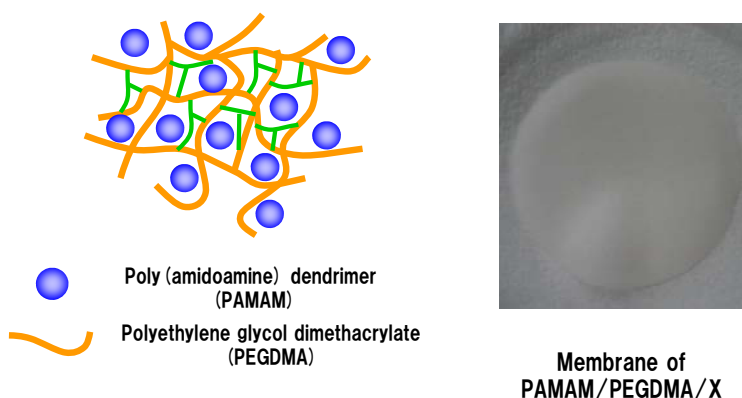
The word "molecular gate" is sometimes used in the field of separation membranes. The term is also used by Sirkar's group but its concept in their paper was not clear [1]. The concept of a CO<sub>2</sub> molecular gate mentioned above was developed at RITE and the concept is now being confirmed. Conventional RITE's molecular gate membranes work well at highly humid condition. Ideal CO<sub>2</sub> molecular gate membrane should also work under a dry or less humid condition.

In this GCEP research, the creation of the ideal CO<sub>2</sub> molecular gate channel using CO<sub>2</sub> hopping via carbamate is studied. SC-CO<sub>2</sub> has been selected, for the first time, as the structure directing agent of the CO<sub>2</sub>/H<sub>2</sub> separation membrane for the reasons given above.

## 5. Results

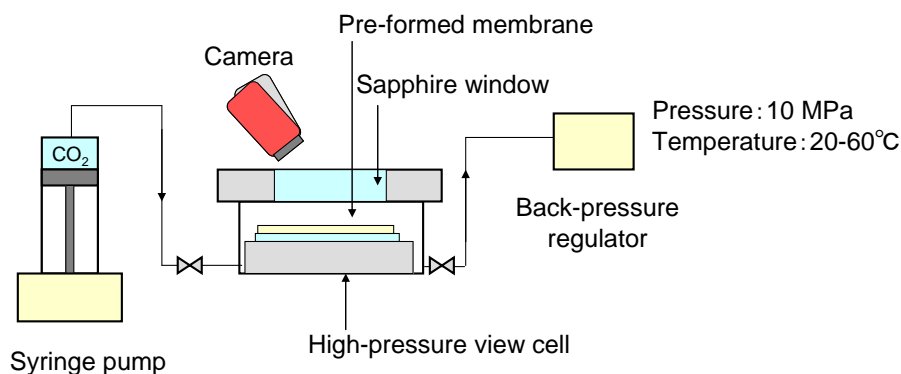
We have developed CO<sub>2</sub> molecular gate membranes using poly(amidoamine) (PAMAM) dendrimer immobilized in a polymer matrix network. Typical dendrimer immobilized membrane was prepared with PAMAM dendrimer and polymer matrix of polyethylene glycol dimethacrylate (PEGDMA) and X.

The ethanol solution containing these three materials was casted on a glass plate. A just casted film containing solvent was photo cured and evaporated the solvent. Figure 7 shows the schematic image of PAMAM dendrimer immobilized membrane in a polymer matrix network of PEGDMA and X. Photo of the membrane is also shown in the Figure.



**Figure 7:** Schematic image and photo of PAMAM dendrimer immobilized membrane.

Figure 8 shows the setup for the SC-CO<sub>2</sub> structure directing method. The setup consists of a syringe pump, high pressure view cell with a sapphire window, a back pressure regulator and a monitoring camera. The resulting solid membrane containing PAMAM dendrimer was placed on a glass plate in a high-pressure cell. CO<sub>2</sub> was injected gradually into the cell with a high pressure pump to produce a supercritical condition at 20-60 °C. Pressure was maintained for four hours at 10 MPa and then decreased at a rate of 0.1 MPa/min to create channels for CO<sub>2</sub> hopping via carbamate ion pairs.



**Figure 8:** Setup for the SC-CO<sub>2</sub> structure directing method.

Structural control on a nanometric scale is critically important to attain the ideal molecular gating channel with specific amine compounds. In our new research in GCEP, CO<sub>2</sub> itself will be used as the structure-directing agent for producing an ideal channel of CO<sub>2</sub> hopping via carbamate ion.

Figure 9 shows a membrane in a high pressure cell for SC-CO<sub>2</sub> treatment. A membrane containing PAMAM dendrimer was placed on a glass plate.

As mentioned above in Figure 4, SC-CO<sub>2</sub> would work as a structure-directing agent for controlling the dimensional accuracy of amino moieties of PAMAM dendrimers for the CO<sub>2</sub> transporting channel, due to the formation of carbamate ion pairs that bridges the amino moieties. SC-CO<sub>2</sub> would cause negligible deformation of the formed structure during the treatment, due to the near-zero surface tension of SC-CO<sub>2</sub>. As a result, the SC-CO<sub>2</sub> directing method will offer an ideal channel structure of CO<sub>2</sub> hopping via carbamate for the CO<sub>2</sub> molecular gate.



**Figure 9:** Membrane in a high pressure cell for SC-CO<sub>2</sub> treatment.

In preliminary experiments, several kinds of membranes were treated under various SC-CO<sub>2</sub> conditions. Cellulose tri-acetate, polyimide and various cross linked polymeric materials containing dendrimers were tested. From these results, some data indicates the effectiveness of SC-CO<sub>2</sub> treatment for improving CO<sub>2</sub> permeance and CO<sub>2</sub>/H<sub>2</sub> selectivity.

Regarding the PAMAM dendrimer immobilized membrane prepared with PAMAM dendrimer, polyethylene glycol dimethacrylate (PEGDMA) and X, SC-CO<sub>2</sub> treatment shows positive effects. The original PAMAM immobilized membrane shows relatively good CO<sub>2</sub>/H<sub>2</sub> separation properties. Table 1 shows CO<sub>2</sub> and H<sub>2</sub> permeance (Q) and CO<sub>2</sub>/H<sub>2</sub> selectivity ( $\alpha$ ) of the pre- (original) and post-treated PAMAM dendrimer immobilized membrane prepared with PAMAM dendrimer, PEGDMA and X. Gas permeation data was taken at atmospheric pressure and 40 °C. A feed gas contains 80 % of CO<sub>2</sub> and 20% of H<sub>2</sub>. Relative humidity in the feed was 80%RH.

**Table 1:** CO<sub>2</sub>/H<sub>2</sub> separation properties of SC-CO<sub>2</sub> treated membrane.

	<b>SC-CO<sub>2</sub> Treatment Temperature</b>	<b>QCO<sub>2</sub></b> m <sup>3</sup> (STP) / (m <sup>2</sup> sPa)	<b>QH<sub>2</sub></b> m <sup>3</sup> (STP) / (m <sup>2</sup> sPa)	<b><math>\alpha</math></b> CO <sub>2</sub> /H <sub>2</sub>
<b>Reference (Pre-treated)</b>		<b>4.38E-12</b>	<b>2.98E-14</b>	<b>144</b>
<b>SC-CO<sub>2</sub> treated</b>	<b>40</b>	<b>8.80E-12</b>	<b>3.62E-14</b>	<b>243</b>
<b>SC-CO<sub>2</sub> treated</b>	<b>60</b>	<b>8.52E-12</b>	<b>4.00E-14</b>	<b>213</b>

SC-CO<sub>2</sub> treatment condition: 10 MPa, 4 hr

In the table, the original membrane containing PAMAM dendrimer showed  $4.38 \times 10^{-12} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$ , and  $2.98 \times 10^{-12} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$  for QCO<sub>2</sub> and QH<sub>2</sub>, respectively. CO<sub>2</sub>/H<sub>2</sub> selectivity ( $\alpha$ ) was 144. On the other hand, the membrane treated by SC-CO<sub>2</sub> at 40 °C shows  $8.80 \times 10^{-12} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$ , and  $3.62 \times 10^{-14} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$  for QCO<sub>2</sub> and QH<sub>2</sub>, respectively. And CO<sub>2</sub>/H<sub>2</sub> selectivity ( $\alpha$ ) was 243. Compared with those of the pre-treated membrane, both of QCO<sub>2</sub> and QH<sub>2</sub> were increased, however, increment of QCO<sub>2</sub> was larger than that of QH<sub>2</sub>. As a result, CO<sub>2</sub>/H<sub>2</sub> selectivity was increased. A similar result was obtained by SC-CO<sub>2</sub> treatment at 60 °C. For the treatment at 60 °C, QCO<sub>2</sub> and QH<sub>2</sub> were  $8.52 \times 10^{-12} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$ , and  $4.00 \times 10^{-14} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$ , respectively.

## **6. Progress**

Basic concept of SC-CO<sub>2</sub> treatment was invented, tested and modified. As a result, possibility of SC-CO<sub>2</sub> treatment was found. And also, the direction of attaining the ideal molecular gating with CO<sub>2</sub> hopping via carbamate ion pairs was obtained.

CO<sub>2</sub> separation membranes of the moment will be preferably employed for CO<sub>2</sub> capture from a pressurized gas stream such as Integrated Coal Gasification Combined Cycle (IGCC) as a means of CO<sub>2</sub> capture and storage (CCS). And CO<sub>2</sub> separation membranes will be also one of strong candidates of CO<sub>2</sub> removal from high CO<sub>2</sub> content natural gases. In addition, CO<sub>2</sub> separation membranes are considered as a measure of CO<sub>2</sub> capture from a flue gas of a coal power plant.

An IGCC power plant of 300 MW would emit roughly one million metric tons of CO<sub>2</sub> a year. Assuming 90% CO<sub>2</sub> recovery in the membrane system, the GCEP outcome will potentially contribute to a CO<sub>2</sub> reduction of 0.9 million metric tons per 300 MW power plant. When 100 IGCC plants employ the membrane system, the contribution to CO<sub>2</sub> reduction is counted as 90 million metric tons per year. Additionally, the GCEP outcomes in CO<sub>2</sub> membrane research might be applicable to natural gas plants and existing power plants such as coal-fired thermal power plants. Our final goal is the creation of a game-changing CO<sub>2</sub> separation membrane, which is applicable to existing power plants and steel works, as well as new plants such as IGCC.

## **7. Future Plans**

The following research will be conducted into an ideal CO<sub>2</sub> molecular gate membrane with carbamate ion hopping in a succeeding research period.

- Improvement of the SC-CO<sub>2</sub> structure directing method.
- Investigating the structure of the SC-CO<sub>2</sub> treated membrane.
- Investigating the mechanism of the SC-CO<sub>2</sub> directing method.

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