

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

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2. Objective:

Separating CO₂ from other gases present in flue or synthesis gas, in conjunction with a suitable means of storing the CO₂, could allow the utilization of abundant fossil fuel reserves with significantly decreased emissions of CO₂ to the atmosphere. This project intends to develop a variety of efficient, low-cost polymeric and inorganic membranes that separate CO₂. Material structure engineering at the scale of gas molecules will be used to increase permeability and selectivity.

3. Background:

Membrane separation of CO₂ from other gases is an active field, but the best membranes today are likely too energy intensive and expensive to be implemented on a large scale. Gas separation in membranes is driven by a pressure difference on either side of the membrane. Decreasing the required pressure difference by increasing the permeability of the membrane would reduce energy cost and membrane area. However, in order to obtain a sufficiently pure stream of CO₂, the selectivity for CO₂ must also be high. Many current systems require cascading the permeate through multiple membrane stages to achieve the desired purity.

Two areas of gas separation membrane research are polymer and inorganic membranes. Polymer membranes are relatively easy to manufacture and are suited for low temperature applications. The polymer morphology and mobility determine the gas permeability and selectivity. Figure 1 shows an asymmetric hollow fiber membrane. A thin layer of functional cardo polyimide material supported by a porous structure allows high permeability.

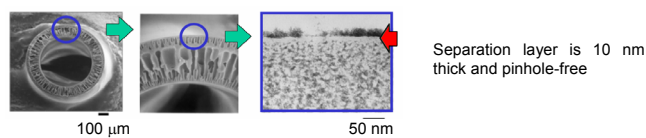


Figure 1: Cardo polyimide hollow fiber membrane with a thin, functional outer layer.

Inorganic membranes have much greater thermal and chemical stability. Appropriate sized pores in materials including zeolites and silicas can act as molecular sieves that separate gas molecules by effective size. Surface adsorption and diffusion inside the pores can also play a role. Figure 2 illustrates gas separation using an ordered array of pores in an inorganic material. Defects in the pore structure can have a large negative effect on selectivity.

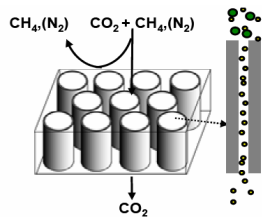


Figure 2: Porous inorganic membranes act as molecular sieves, differentiating gas molecules by effective size.

4. Approach.

Since the effective size of CO₂, N₂, H₂, and other gases present in fossil fuel conversion systems are very similar, membrane pore spaces must be controlled on a scale comparable to the size differences among these gas molecules. This will be achieved for a variety of membrane types using several different techniques.

Cardo polymer membranes will be optimized for CO₂ permeability and selectivity, for example, by carbonizing the outer surface of the membrane. Thermal motion of organic polymers can cause variations in the morphology and effective pore size of the membrane. Carbonization by heat, UV, plasma, or ion beam treatment could serve to restrict the thermal motion of the polymer chain and enhance the molecular gate function of the polymer. Functionalizing the polymer may change its morphology at the sub-nanoscale, allowing for fine tuning of the pore space. As illustrated in Figure 3, channel surface of carbon membrane will be modified to achieve high CO₂ affinity.

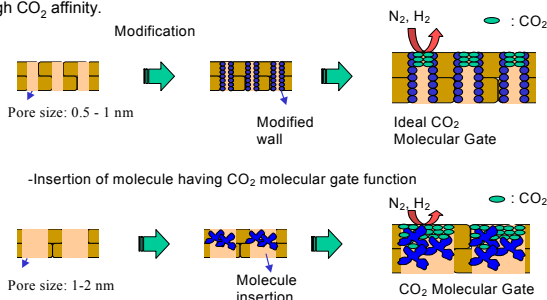


Figure 3: Modification of channel surface for high CO₂ affinity.

While most zeolite membranes consist of randomly oriented crystals, a thin, mono-layer crystal with an ordered lattice of pores would demonstrate superior permeability and freedom from defects. As illustrated in Figure 4, this will be achieved by applying a coating of seed crystals on a substrate with perpendicularly oriented channels. After secondary crystal growth, the properties of the resulting pore structure reflect the morphology of the seed crystal.

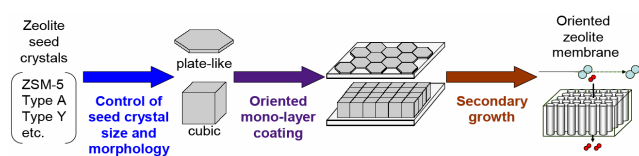


Figure 4: Functionalization process for a mono-layer crystalline zeolite pore structure.

5. Major Results:

5.1. Cardo polymer based carbon membranes:

RITE is developing novel cardo polymer based carbon membranes using cardo-type polyimide. As shown in Figure 5, thin carbon layer was formed on porous alumina support by dip-coating of precursor solution and carbonization. Asymmetric carbon membranes could be prepared by phase inversion process (Figure 6). Nanoporous carbon membranes could be prepared by blending polyimide with poly(ethylene glycol) (Figure 7). Pore size of carbon membrane was controlled to ca. 3nm by optimizing preparation conditions (Figure 8). In the future, RITE will modify the channel surface for high CO₂ affinity, as well as to improve the pore-size control technique.

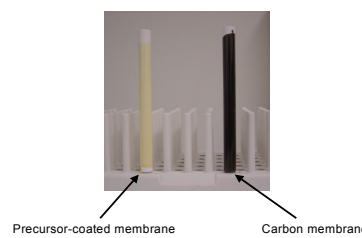


Figure 5: Photograph of precursor-coated membrane and carbon membrane.

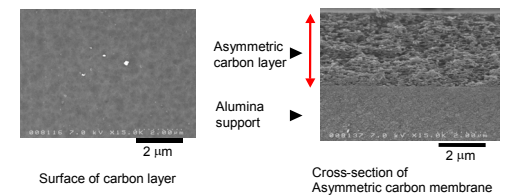


Figure 6: SEM image of asymmetric carbon membrane.

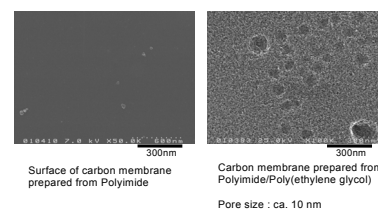


Figure 7: SEM image of carbon membranes prepared from (a) polyimide and (b) polyimide/poly(ethylene glycol).

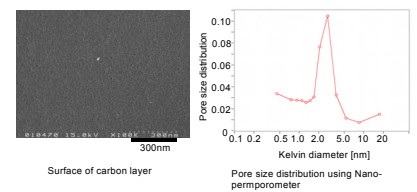


Figure 8: SEM image of pore size distribution of nanoporous carbon membrane.

5.2. Ceramic membranes:

Preparation of ultra thin zeolite membranes having high permeation rate and high selectivity of CO₂ was studied using ultrasonication-coating method and rubbing-seeding method. As shown in Figure 9, highly oriented thin zeolite membranes (1 ~ 2 μm) were obtained by ultrasonication-coating method. The denseness of membrane prepared by rubbing-seeding method was higher than ultrasonication-coating method (Figure 10). The separation factor of zeolite Y membrane synthesized by rubbing-seeding method was 69.3, and the permeability of this membrane was close to the upper bound performance of zeolite membranes reported up to now (Figure 11). To improve the permeation performance of the zeolite membrane, the preparation of defect free and perfect membrane by new preparation method is now in progress.

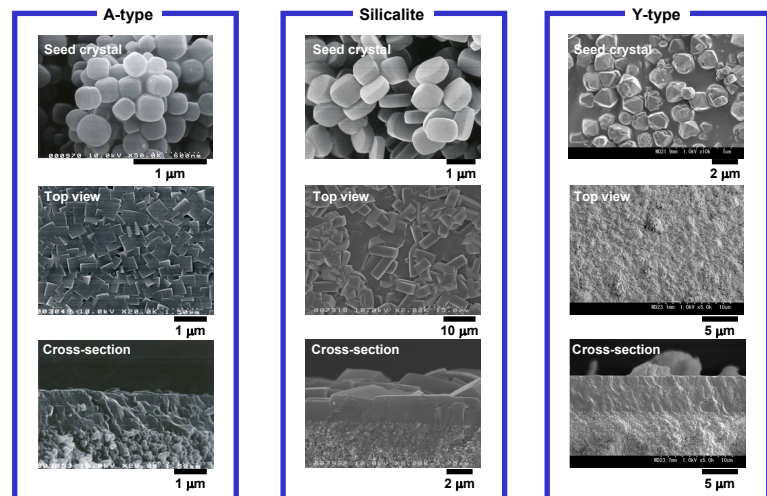


Figure 9: SEM images of zeolite membranes prepared by ultrasonication-coating method.

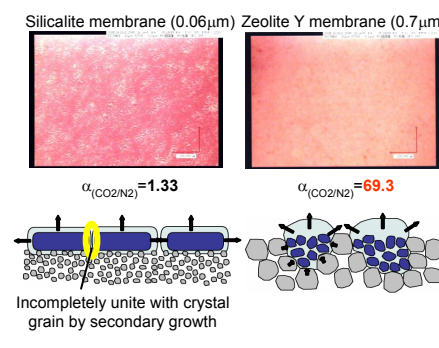


Figure 10: Evaluation of defect in zeolite membranes prepared by ultrasonication-coating method and rubbing-seeding method.

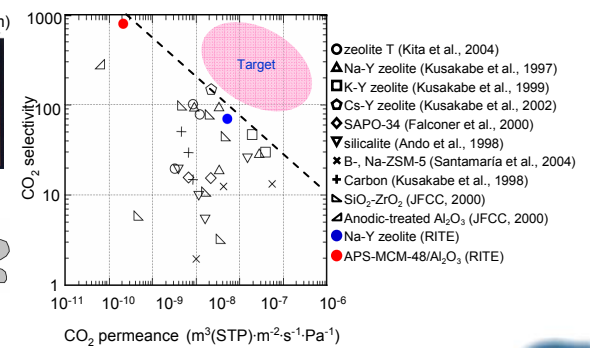


Figure 11: Comparison of CO₂ separation performances of zeolite membranes.

