A Critical Role of the Molecular Interface in Double-Layered Nanomembranes on Highly Efficient CO_2/N_2 Gas Separation

Roman Selyanchyn
Platform for International Collaborations and Partnerships
WPI International Institute for Carbon-Neutral Energy Research (WPI-I^{2}CNER), Kyushu University

Gas separation membranes have potential to deliver economically feasible CO_2 capture in the post-combustion process at fossil-fueled facilities. However, to handle this challenging task membranes should possess the CO_2/N_2 selectivity of 20-60 with substantial values of CO_2 permeances (>1000 GPU). Thin-film composite membranes (TFCM) composed of several functional layers: porous support, gutter, selective, and protective layers are generally used to achieve the membranes with desired performance which can be enhanced by tuning the properties of each layer separately. Design of the selective layer is a major research issue to achieve high membrane selectivity to CO_2 over nitrogen.

In this work, we have studied ultra-thin selective layers (2-20 nm) made of hydrophilic and CO_2-selective block-copolymer (Pebax MH-1657) which was deposited on the O_2-plasma activated surface of much thicker (~400 nm) gutter layer composed of polydimethylsiloxane (PDMS). The structure assembled with polyacrylonitrile (PAN) microporous support completed the TFCM (Fig.1a). We have found that contrary to the theoretical predictions (resistance in series model) [1] for the layered membrane, highly selective CO_2/N_2 separation membrane was achieved in the TFCM with ultra-thin selective layer (Fig.1b). Critical role to achieve this selectivity was attributed to the molecular interface formed between selective and gutter layers which was controlled by the duration of oxygen plasma treatment (PDMS activation).

Permeances of CO_2 in the developed TFCM were between 1000-3000 GPU and CO_2/N_2 selectivities between 30-100, providing the gas separation parameters that are within optimal range for cost-efficient CO_2 capture in post-combustion processes. Detailed characterization of the interface revealed the chemical structure of the outermost membrane surface suggesting the blending of the ultra-thin Pebax-1657 layer with activated surface of PDMS. This nano-thick blend layer contributed to the overall selectivity of the membrane significantly exceeding the selectivity expected from polymer intrinsic properties. Formed interface demonstrated stable gas separation with only moderate change of performance over one-year time.

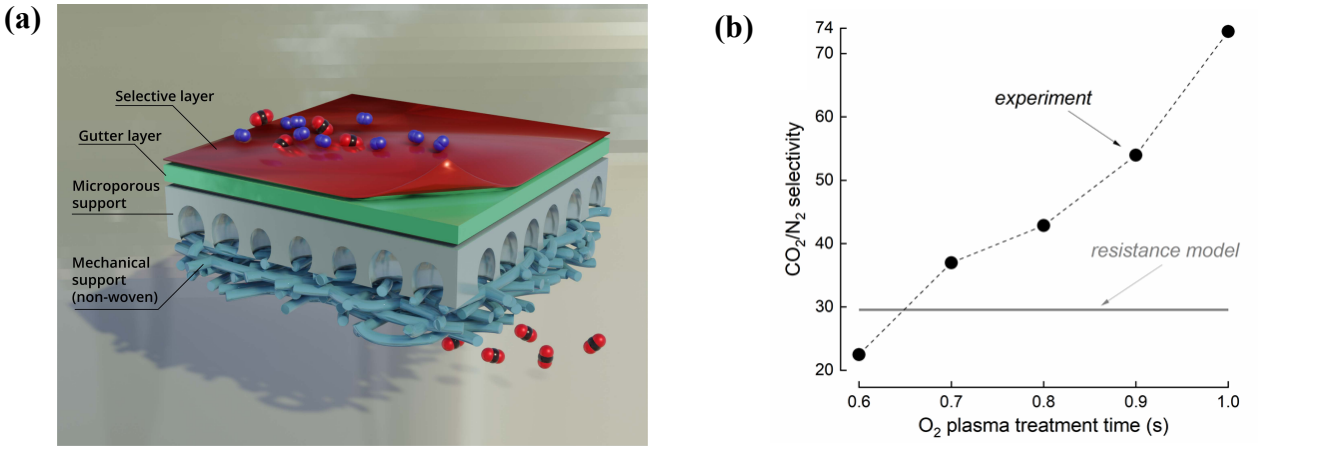

Figure 1. (a) Schematic illustration of the tri-layer TFCM fabricated in this work; **(b)** CO_2/N_2 separation selectivity of series of *interface-active* Pebax-1657/PDMS membranes depending on the duration of O_2-plasma treatment deviates strongly form the theoretical predictions based on bult polymer properties (resistance model), manifesting the importance of the molecular interface between polymer layers.

1. Selyanchyn, R.; Fujikawa, S. Membrane Thinning for Efficient CO_2 capture. *Sci. Technol. Adv. Mater.* **2017**, *18* (1), 816–827.
2. Selyanchyn, R.; Ariyoshi, M.; Fujikawa, S. Thickness Effect on CO_2/N_2 Separation in Double Layer Pebax-1657®/PDMS Membranes. *Membranes*. **2018**, 8 (4), 121.