Crucial role of interface between layers in thin-film composite membranes for highly efficient CO_2/N_2 separation

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Separation and safe confinement of carbon dioxide (CO_2) from the flue gas at conventional heat-power plants is critically needed to mitigate global climate change. Membrane systems are considered as a potentially effective tool for separation of carbon dioxide (CO_2) from complex gas mixtures. Relative simplicity, potentially lower energy consumption, and lower capital cost as well as smaller environmental footprint are the advantages of membrane systems. However, to succeed in the large-scale industrial application, gas separation membranes should satisfy not only high "separation ability" *i.e.*, selectivity (α) towards CO_2 (e.g.,>40 in post-combustion CO_2/N_2 separation) but also fast "separation speed" *i.e.*, permeance numbers (**Q** >1000 GPU) [1].

Large number of organic polymers have demonstrated high values of CO_2/N_2 selectivity, however at the same time these materials have low CO_2 permeability (**P***)* – trade-off phenomena known as "Robeson upper bound". Straightforward way to achieve high permeances is to reduce thickness of the separating layers (**Q** = **P**/**h**, where **h** - thickness). However, a number of drawbacks such as accelerated physical aging and pronounced defects formation limits the actual thickness in single material membranes at around 100 nm [2]. To overcome these limitations, membranes should have several layers as for example depicted in Fig.1a, when thin selective layer is deposited on the thicker gutter layer and subsequently attached to porous and mechanical supports.

In our latest work we fabricate thin film composite membranes (TFCM) composed of Pebax-1657 block copolymer (*selective layer*), polydimethylsiloxane (*PDMS*, *gutter layer*) on microporous organic polymer supports. Pebax-1657 is highly selective for CO_2 (α_s~60, $\mathbf{P}_s$ ~120 barrer), while PDMS is less selective but highly permeable (α_g~10, $\mathbf{P}_g$ ~3200 barrer), therefore optimized combination of these two materials in in composite membrane enabled us to obtain acceptable values for both selectivity and permeability [3]. To reach the permeances and selectivities required by I^{2}CNER Roadmap, we had to undertake ultimate thinning of the selective layer (down to ~10 nm) as shown in Fig.1b. Careful Pebax-1657/PDMS interface control was necessary to decrease the interfacial gas barrier. As a result, we succeeded to find a reliable approach to design durable, highly selective and ultra-permeable membranes that satisfy economic requirements for post-combustion CO_2 capture (Fig.1c).

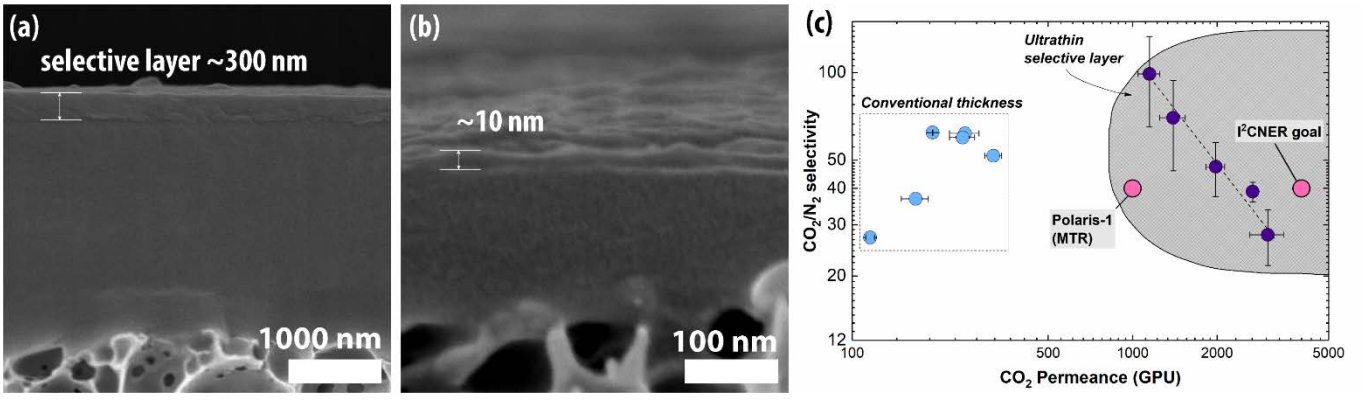

Figure 1. (**a**) SEM image of the conventional tri-layer composite membrane structure with thicknesses commonly used in TFCM; (**b**) Pebax-1657/PDMS TFCM with ultimately thinned selective layer (~10 nm); (**c**) CO_2/N_2 separation performance of series of Pebax-1657/PDMS membranes developed in I^{2}CNER CCU in the context of the economically optimal membrane parameters (grey area) according to [1].

1. Merkel T. C.et.al, *J. Memb. Sci.*, 2013, **359**, 126–139.
2. R. Selyanchyn and S. Fujikawa, *Sci. Technol. Adv. Mater.*, 2017, **18**, 816–827.
3. R. Selyanchyn, M. Ariyoshi and S. Fujikawa, *Membranes.*, 2018, 8**(4)**, 121.