



Unexpected H₂ solubility of polyimide/polyphthalonitrile H₂-selective membranes with tailorable microstructure and performance

Chun-Po Hu^{1,2,3}, Jacob Song Kiat Lim³, Xiao Matthew Hu^{1,3*}

¹*Nanyang Technological University, Environmental Chemistry & Materials Centre, Nanyang Environment & Water Research Institute, SINGAPORE*

²*Nanyang Technological University, Interdisciplinary Graduate Programme, Collage of Engineering, SINGAPORE*

³*Nanyang Technological University, School of Materials Science and Engineering, SINGAPORE*

Membrane separation technologies are emerging as energy-efficient alternatives to traditional distillation processes. The growing demand for clean energy on “hydrogen economy” has highlighted the need for high-performance H₂-selective gas separation membranes. Polyimides (PIs) show promise in these applications due to their excellent thermal stability, good hydrogen permeability, and processability. However, PIs often have insufficient selectivity, mainly because they have a poor affinity H₂ over other gases. Despite the rigid molecular structure of polyimides provides excellent size-sieving property for hydrogen, the low H₂ solubility of PIs limits the H₂ selectivity, which is crucial for hydrogen purification. To address this issue, this study demonstrated a simple blending method to fabricate polyimide/polyphthalonitrile blend membranes with adjustable microstructure.

The study found that the blend membranes exhibited remarkable H₂ separation performance that the H₂/CO₂ and H₂/N₂ selectivity over 60 and 1600, respectively, exceeding the Roberson's upper bound (2008). The improved gas separation performance was attributed to enhanced H₂ solubility, resulting in superior H₂ solubility selectivity. The addition of polyphthalonitrile benefits the blend membranes toward a more narrowed distribution of fractional free volume, promoting the sorption of H₂ over 8 times higher than both polyimide or polyphthalonitrile. Additionally, gas separation performance of the blend membranes can be further adjust through thermal crosslinking of the blend membranes into a semi-interpenetrating network (semi-IPN). Overall, this study presents a novel approach to tailoring the polymer matrix of polyimide-based membranes, opening up possibilities for the development of advanced gas separation membranes.

Keywords: polyimides, polyphthalonitrile, polymer blend, hydrogen purification, gas separation membranes