frontiers in Membrane Science and Technology

SPECIALTY GRAND CHALLENGE
published: 10 February 2022
doi: 10.3389/frmst.2022.853402

Grand Challenges in Membrane Applications—Gas and Vapor

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Keywords: membrane science and technology, vapor separation of membranes, membranes for gas separation, hollow fiber membrane, polymer membrane applications, separation technology

OPEN ACCESS

Edited and reviewed by:
Michael D. Guiver, Tianjin University, China

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Specialty section:
This article was submitted to Membrane Applications - Gas and Vapor, a section of the journal Frontiers in Membrane Science and Technology

Received: *12 January 2022*
Accepted: *28 January 2022*
Published: *10 February 2022*

Citation:
Kim JH (2022) Grand Challenges in Membrane Applications—Gas and Vapor. Front. Membr. Sci. Technol. 1:853402. doi: 10.3389/frmst.2022.853402

INTRODUCTION

Membranes for Gas and Vapor Separation

Membrane-based gas separation is a well-established, energy-saving, and evolving technology. Gas separation technology using polysulfone hollow fiber membranes (with the tradename Prism) for H_2 recovery was first introduced and successfully commercialized as early as 1979 by Permea Inc. (now a subsidiary of Air Products) (Lonsdale, 1982; Air Products Advanced Pri). Since then, the market for gas separation membranes has been growing rapidly and is expected to grow even further as technology advances.

Over the last few decades, various polymer membranes such as polysulfone, polyimides, cellulose acetates, and poly(dimethyl siloxane) silicone rubber have been used for gas or vapor separation (Galizia et al., 2017). The specific applications include 1) hydrogen recovery from nitrogen, methane and etc.; 2) nitrogen production from oxygen; 3) methane production from natural gas; 4) vapor recovery (such as that of olefins) from nitrogen; 5) volatile organic compound (VOC) removal; 6) air and natural gas dehydration; 7) olefin/paraffin (e.g. ethylene/ethane, propylene/propane) separation; 8) hydrocarbon (methane, ethane, propane and etc.) separation; and 9) carbon dioxide capture from flue gas (mostly nitrogen). These applications have received significant attention and account for the majority of current membrane-based gas separation industries. Advances in separation technologies and materials design will aid growth and development in the field of membranes.

Inorganic membranes based on dense ceramic membranes, dense metallic membranes, and microporous membranes have also been investigated extensively (Lin, 2019). Microporous inorganic membranes can be effectively utilized in applications such as catalytic reactors and coal gasification. The materials commonly used to fabricate microporous inorganic membranes include alumina (Al_2O_3), silica (SiO_2), zirconia (ZrO_2), zeolite, and carbon. Recently, mixed-matrix membranes (MMMs), in which porous inorganic fillers are dispersed in a dense polymer matrix, have received significant attention because of the synergetic effects of organic and inorganic materials. Various porous inorganic nanomaterials such as graphene oxide (GO) and metal-organic frameworks (MOFs) have been utilized as fillers in MMMs, resulting in improved permeation and separation properties (Qiao et al., 2020).

Materials Challenges

Over the last few decades, materials research has enabled significant advances in membrane technology and expanded the viability of membranes. For the design of membrane materials, it is important to consider the separation factors of permeability and selectivity (Park et al., 2017). A variety of high-performance polymer membranes with excellent separation properties have been developed, such as thermally rearranged (TR) polymers, polymers of intrinsic microporosity (PIMs), and perfluoropolymers (Sanders et al., 2013). These membrane materials surpass the performances of existing polymer materials, and through a new approach, they have been in the spotlight as next-generation membrane materials (Koros and Zhang, 2017). Nevertheless, for polymer membranes, an upper limit exists based on the trade-off between permeability and selectivity; polymers with high selectivity possess low permeability and vice versa. Furthermore, despite the excellent separation properties of novel membrane materials, disadvantages such as plasticization and physical aging are still observed, hampering their industrial applications. Presently, the major challenge regarding membrane materials is to develop advanced materials with high permeability and selectivity as well as high tolerance to plasticization and physical aging. Thus, it is important to understand and elucidate the structure—property relationships and permeation/separation mechanisms. Advances in experimental characterization techniques, corresponding theoretical simulations, and artificial intelligence may be helpful and efficient in expediting this process. The improvement and optimization of membrane materials are also pivotal factors for the industrial applications of gas/vapor separation technology. The rational design approach with improved interfacial properties serves as an efficient toolbox for improving the selective permeability properties of MMMs with molecular sieve fillers (Liu et al., 2018).

Membranes Challenges

The properties of the membrane material are characterized by the permeability, which is normalized by the membrane thickness, while the properties of the membrane itself are characterized by permeance, which represents the actual flux. Several materials reported over the past decades exhibit excellent permeability but low permeance. This can be attributed to the challenges in the preparation of defect-free, low-thickness membranes with great separation properties. To achieve a high permeance, thin-film composite (TFC) membranes are prepared consisting of a thin, dense and selective layer on relatively inexpensive, mechanically strong, and porous supports. In many cases, additional gutter layers are also introduced between the thin selective layer at the top and the porous support at the bottom. This effectively helps in the formation of a thin selective layer without significant infiltration into the support pores.

The design of novel membrane materials without considering the support properties often leads to deteriorated performance in TFC membranes compared to the performance of free-standing dense membranes. Despite several reports on high-performance membranes, polymers that dissolve in environmentally friendly, inexpensive, and mild solvents (e.g., alcohol or water) are uncommon, which is an important consideration for TFC membrane processing (Kim et al., 2019; Lee et al., 2022); this is because many organic solvents that are used to dissolve the thin selective layer at the top also dissolve the porous supports at the bottom, resulting in defect formation or dense structures. The development of membrane preparation processes without solvents or with mild solvents is important. Furthermore, it can lead to disruptive and sustainable changes in current membrane preparation processes.

Another challenging issue in MMMs is that they are difficult to prepare as TFC membranes (Chuah et al., 2018). When the thickness of the selective layer at the top is reduced (e.g., ~100 nm), interfacial defects/voids often arise, resulting in a loss of selectivity. Thus, it is necessary to optimize the membrane design to achieve optimal separation properties and permeance efficiency by controlling the morphology, structure, and interactions of MMMs. A well-designed TFC membrane not only improves the efficiency (flux), but also reduces the waste of energy, improving the economic benefit.

The design and synthesis of high-performance membrane materials is only the first step in the membrane process to be commercially successful. Beuscher et al. described four major obstacles that must be overcome before applying a membrane material to a membrane process (Beuscher et al., 2022). These obstacles arise in the following order; 1) from material to membrane, 2) from membrane to membrane module, 3) from membrane module to membrane process, and 4) from membrane process to overall process. Additionally, these obstacles are strongly interconnected and should be fed back to the early development stage when problems arise from later obstacles.

A recent paper by Sholl and Lively (2022) suggested that well-defined exemplar mixtures should be developed to close the gap between basic research and practical application. Membrane materials and processes for gas and vapor separation need to be utilized in complex environments as they have varying effects in many real-world applications. To better reflect real-world conditions such as temperature and humidity, for example, membrane performance testing should be extended from single gases to mixed gases and multi-component gas mixtures.

CONCLUDING REMARKS

Significant progress in membrane materials science and membrane fabrication engineering is now driving several changes in the field of gas and vapor separation technologies, but there is still considerable scope for further development. Careful design and control of the morphology, structure, and interactions of membranes offer a high level of performance based on a deep understanding of the material properties and membrane performance. This aspect accounts for the hundreds of articles and registered patents published each year on membranes for gas and vapor separation. The aim of the section *Membrane Applications - Gas and Vapor* of the journal *Frontiers in Membrane Science and Technology* is to present high-quality original research articles and review articles in this field by committing to play a pivotal role in addressing this developmental challenge.

AUTHOR CONTRIBUTIONS

The author confirms that he is the sole contributor to this work and has approved it for publication.

REFERENCES

Air Products Advanced Prism® Membrane Systems for Cost Effective Gas Separations. Available at: http://www.airproducts.co.kr/~/media/Files/PDF/industries/membranes-supply-options-brochure-advanced-prism-membrane-systems.pdf.

Beuscher, U., Kappert, E. J., and Wijmans, J. G. (2022). Membrane Research beyond Materials Science. *J. Membr. Sci.* 643, 119902. doi:10.1016/j.memsci.2021.119902

Chuah, C. Y., Goh, K., Yang, Y., Gong, H., Li, W., Karahan, H. E., et al. (2018). Harnessing Filler Materials for Enhancing Biogas Separation Membranes. *Chem. Rev.* 118, 8655–8769. doi:10.1021/acs.chemrev.8b00091

Galizia, M., Chi, W. S., Smith, Z. P., Merkel, T. C., Baker, R. W., and Freeman, B. D. (2017). 50th Anniversary Perspective: Polymers and Mixed Matrix Membranes for Gas and Vapor Separation: a Review and Prospective Opportunities. *Macromolecules* 50, 7809–7843. doi:10.1021/acs.macromol.7b01718

Kim, N. U., Park, B. J., Lee, J. H., and Kim, J. H. (2019). High-performance Ultrathin Mixed-Matrix Membranes Based on an Adhesive PGMA-Co-POEM Comb-like Copolymer for CO2 Capture. *J. Mater. Chem. A.* 7, 14723–14731. doi:10.1039/c9ta02962a

Koros, W. J., and Zhang, C. (2017). Materials for Next-Generation Molecularly Selective Synthetic Membranes. *Nat. Mater* 16, 289–297. doi:10.1038/nmat4805

Lee, C. S., Kang, M., Kim, K. C., and Kim, J. H. (2022). *In-situ* Formation of Asymmetric Thin-Film, Mixed-Matrix Membranes with ZIF-8 in Dual-Functional Imidazole-Based Comb Copolymer for High-Performance CO_2 Capture. *J. Membr. Sci.* 642, 119913. doi:10.1016/j.memsci.2021.119913

Lin, Y. S. (2019). Inorganic Membranes for Process Intensification: Challenges and Perspective. *Ind. Eng. Chem. Res.* 58 (15), 5787–5796. doi:10.1021/acs.iecr.8b04539

Liu, G., Chernikova, V., Liu, Y., Zhang, K., Belmabkhout, Y., Shekhah, O., et al. (2018). Mixed Matrix Formulations with MOF Molecular Sieving for Key Energy-Intensive Separations. *Nat. Mater* 17, 283–289. doi:10.1038/s41563-017-0013-1

Lonsdale, H. K. (1982). The Growth of Membrane Technology. *J. Membr. Sci.* 10, 81–181. doi:10.1016/s0376-7388(00)81408-8

Park, H. B., Kamcev, J., Robeson, L. M., Elimelech, M., and Freeman, B. D. (2017). Maximizing the Right Stuff: The Trade-Off between Membrane Permeability and Selectivity. *Science* 356, 356 1137. doi:10.1126/science.aab0530

Qiao, Z., Liang, Y., Zhang, Z., Mei, D., Wang, Z., Guiver, M. D., et al. (2020). Ultrathin Low-Crystallinity MOF Membranes Fabricated by Interface Layer Polarization Induction. *Adv. Mater.* 32, 2002165. doi:10.1002/adma.202002165

Sanders, D. F., Smith, Z. P., Guo, R., Robeson, L. M., McGrath, J. E., Paul, D. R., et al. (2013). Energy-efficient Polymeric Gas Separation Membranes for a Sustainable Future: A Review. *Polymer* 54, 4729–4761. doi:10.1016/j.polymer.2013.05.075

Sholl, D. S., and Lively, R. P. (2022). Exemplar Mixtures for Studying Complex Mixture Effects in Practical Chemical Separations. *JACS Au*. doi:10.1021/jacsau.1c00490

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The handling editor declared a past co-authorship with the author.

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