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Annotated Bibliography on

Membrane Gas Separation: Recent Technologies

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Table of Contents:

Introduction:

Membrane science and technology is a multi-disciplinary field that has been considerably developing in the last decades. Membrane technology refers to the process of separating elements or materials such as gas or liquids by the use of membrane that functions as a selective semitransparent barrier allowing specific materials to pass across. The applications of membrane technology are wide and various. This annotated bibliography is concerned with membrane gas separation. The process of gas separation using membrane technology has gained more focus than other gas-separation processes due to its various advantages, such as the uncomplicated installation with little space needed. In addition, it is a clean technology that contributes in reducing the environmental issues. Moreover, it reduces the cost of industrial processes as well as producing high-quality products. This annotated bibliography contains 27 articles that covers different aspects regarding membrane gas separation, such as mixed matrix membrane (MMM), hollow fiber membrane and thin-film composite (TFC).

This annotated bibliography contains article abstracts from 2021-2023.

This benefits PRC/RCEF researchers.

E-resources used: Scopus and American Chemical Society (ACS).

Contact NSTIC to request full-text articles.

Articles Abstract:

1. Lee, T. H., Balçık, M., Lee, B. K., Ghanem, B. S., Pinnau, I., & Park, H. B. (2023). Hyperaging-induced H2-selective Thin-film Composite Membranes with Enhanced Submicroporosity toward Green Hydrogen Supply. *Journal of Membrane Science*, 672

Abstract: Repurposing the existing natural gas infrastructure by blending hydrogen with methane (i.e., Hythane) is one feasible option to develop a low-carbon hydrogen supply chain, although this process requires extraction of the hydrogen from Hythane after distribution. Membrane technology is a potential solution to tackle this application given its many advantages over other separation methods. However, industrial use of developed membrane materials has been challenging due to several practical concerns; for example, insufficient separation abilities and accelerated physical aging of thin membranes in high-free-volume glassy polymers. Herein, we propose an integrated strategy to develop highly H2-selective thin-film composite (TFC) membranes by tuning the aging behavior of polymers of intrinsic microporosity (PIM) thin films. Detailed gas permeation and two-dimensional (2D) grazing incidence wide-angle x-ray scattering (GIWAXS) studies reveal that triptycene-based PIM TFC membranes can exploit beneficial aging effects resulting from aging-induced enhancement in submicroporosity. To directly deploy TFC membranes, a simple post-treatment step was introduced to increase the aging rate, termed "hyperaging." The hyperaged TFC membranes exhibited high H2/CH4 mixed-gas selectivity (>100), moderate H2 permeance (∼100 GPU), and good long-term stability when tested using a binary mixture with dilute H2 concentration (20 mol%), demonstrating promise for downstream hydrogen extraction toward green hydrogen supply. © 2023 Elsevier B.V.

2. Xin, K., Zhou, P., & van Sint Annaland, M. (2023). Experimental Study on CO2 Separation Using Hydrophobic Deep Eutectic Solvent based Supported Liquid Membranes. *Separation and Purification Technology, 310*

Abstract: Deep eutectic solvents (DESs) have been proposed as a viable and more sustainable solvent for CO2 capture, owing to their low volatility and tunable properties. In this work, polymer membranes were combined with hydrophobic DESs to prepare supported liquid membranes (DES-

SLMs), and the potential of using SLMs for CO2/N2 separation was investigated. COSMO-RS model simulations, bond energy analysis as well as stability tests were used to select the polymeric porous support. Hydrophobic polyvinylidene fluoride (PVDF) with a nominal pore size of 0.1 μm was chosen to support three selected hydrophobic DESs. The gas permeabilities through three selected DES-SLMs were experimentally determined, where the thymol-coumarin (1:1) based SLM showed the best performance with a CO2 permeability of 175.0 Barrer and selectivity of 30.2 at room temperature. The separation capability was further improved by mixing the DES with traditional physical absorbents. In addition, the effects of water presence in the gas phase on the DES-SLM were investigated. The membrane was physically stable, but the ideal selectivity of CO2/N2 through the membrane deteriorated with time on steam. By predicting the permeabilities of CO2 and N2 through traditional organic liquid based SLMs, the prospects of developing DESs for SLM applications were demonstrated. Finally, an advanced membrane capture process for a natural gas-fired combined cycle (NGCC) power plant was studied with process simulation and economic analysis, where the SLMs are used to purify the CO2 product.

3. Jheng, L. -., Park, J., Wook Yoon, H., & Chang, F. -. (2023). Mixed Matrix Membranes Comprising 6FDA-based Polyimide Blends and UiO-66 with Co-continuous Structures for Gas Separations. *Separation and Purification Technology, 310*

Abstract: Membrane gas separation is considered a highly promising alternative to conventional gas separation. Recently, mixed matrix membranes containing UiO-66 metal–organic frameworks (MOFs) have been demonstrated to achieve high gas separation performance, especially in CO2-related separation. To date, few studies have used morphological control strategies to enhance the gas transport properties of mixed matrix membranes. In this study, we fabricated mixed matrix membranes comprising porous UiO-66 nanoparticles and immiscible 6FDA-based polyimide blends with co-continuous structures. The selective location of UiO-66 nanoparticles within one polymer phase of the co-continuous polymer blend was observed. However, this co-continuous structure cannot be referred to as a double-percolative morphology since the percolative UiO-66 networks did not successfully form. The gas permeability and gas sorption properties of pure gases (H2, CO2, N2, O2, and CH4) in the dense membranes and mixed matrix membranes were measured using the constant-volume variable-pressure method and the dual-volume pressure

decay method, respectively. On the basis of the solution–diffusion mechanism, the contributions of gas sorption and gas transport to the overall gas permeation properties were determined and examined. When the UiO-66 content reached 35 wt%, the CO2 permeability of the mixed matrix membranes was significantly increased from 16.5 Barrer to 104.7 Barrer (by 635 %) without scarifying the permeability selectivities of CO2/N2 (16.5 ± 1.5) and CO2/CH4 (31.7 ± 5.8). The results suggest that both the addition of porous UiO-66 nanoparticles and the co-continuous structures contributed to the strongly enhanced gas separation performance of the mixed matrix membranes. © 2023 Elsevier B.V.

4. Ingole, P. G. (2023). Inner-coated Highly Selective Thin Film Nanocomposite Hollow Fiber Membranes for the Mixture Gas Separation. *Journal of Applied Polymer Science, 140*(9)

Abstract: Polyamide-based thin film nanocomposite (TFN) membranes were prepared by incorporating nanoparticles in an aqueous phase containing m-phenylenediamine (MPD) and an organic phase containing trimesoyl chloride (TMC) by interfacial polymerization (IP) method. The 3-aminopropyltrimethoxy silane grafted mesoporous synthetic hectorite (APTMSH) was synthesized and added in an aqueous monomer solution while the IP. In this work, the TFN layer interfacial compatibility has been enhanced by building the covalent bond between APTMSH and other two monomers by IP method. The coating of the TFN selective layer was done on the inner surface of polysulfone hollow fiber membranes. The interesting results were obtained for the binary mixture gas separation containing water vapor/N2 and CO2/CH4. Improved gas permeance and selectivity have been obtained using APTMSH-incorporated TFN membranes. The developed TFN membranes have been characterized using several physicochemical methods. The results show that with the addition of APTMSH in MPD solution up to 0.5 w/w% the best water vapor permeance 2485 GPU and CO2 permeance 22.3 GPU were obtained along with water vapor/N2 selectivity 725.5 and CO2/CH4 selectivity 26.68 respectively through APTMSH@TFN-3 membrane. © 2022 Wiley Periodicals LLC.

5. Ye, C., Bai, L., Weng, Y., Xu, Z., Huang, L., Huang, J., Li, J., Wang, Y., & Ma, X. (2023). Fine Tune Gas Separation Property of Intrinsic Microporous Polyimides and their Carbon Molecular Sieve Membranes by Gradient Bromine Substitution/removal. *Journal of Membrane Science, 669*

Abstract: Membrane technology is attracting more and more attention in hydrogen energy and natural gas sweetening applications. One challenge remaining is advanced membranes with both high separation performance and robust. Herein, remarkable gas separation properties of carbon molecular sieve membranes (CMSMs) are obtained by debromination assisted carbonization for a series of brominated intrinsic microporous polyimides (PIM-PIs). The di-bromine substituted 6FDBPI shows over 10 times higher permeability of CO2 (2147 vs 184 Barrer) and similar CO2/N2 selectivity (19.7 vs 22.7) than the non-bromine substituted 6FNBPI. This is due to the bromine introduction creates a large number of ultra-micropore channels. After carbonization and debromination at 550 °C, the CMSM-550s exhibit a smaller (4.20–4.62 vs 4.77–8.49 Å), more intensive (75–90% vs 5–35%) and higher percentage (~80% vs 10–55%) of ultra-micropores than their pristine PIM-PIs. Consequently, the CMSM-550s show both higher permeability and selectivity than their precursors, the larger permeability originates from the higher diffusion and solubility coefficient, the higher selectivity is purely contributed by diffusion selectivity. Notably, the 6FDBPI-550 shows an unprecedented H2 permeability of 30,943 Barrer and H2/N2, H2/CH4 selectivity of 47.5 and 46.6 that by far exceed the latest trade-off lines, coupled with excellent anti-plasticization and mixed-gas separation properties. This high performance together with the bromine facilitate carbonization method provide great potential in H2 enrichment and natural gas sweetening applications. © 2022 Elsevier B.V.

6. Min, H. J., Kang, M., Bae, Y. -., Blom, R., Grande, C. A., & Kim, J. H. (2023). Thin-film Composite Mixed-Matrix Membrane with Irregular Micron-sized UTSA-16 for Outstanding Gas Separation Performance. *Journal of Membrane Science, 669*

Abstract: Low-cost, micron-sized particles still pose a barrier to their use in thin-film composite mixed-matrix membranes (TFC-MMMs) owing to their poor interfacial contact with the polymer matrix. Also, the particles are too large to be fabricated into the submicron-thick membranes. Herein, we report high-performing, TFC-MMMs based on a CO2-philic comb copolymer, poly (tetrahydrofurfuryl methacrylate)–co–poly (poly (oxyethylene methacrylate)) (PTO), and an irregular, micron-sized, CO2-selective metal-organic framework (MOF), UTSA-16. The PTO comb copolymer matrix exhibited excellent film-forming ability, adhesion properties and showed a good gas separating performance. The PTO comb copolymer also enhanced the dispersibility of

UTSA-16 in an environment-friendly solvent mixture (i.e., ethanol/water), which did not adversely damage the underlying porous polymeric support. Despite the micron-scale particle size of UTSA-16, PTO copolymer completely covered the surface of UTSA-16 via strong interactions without any deep pore infiltration and exhibited excellent interfacial contact properties. Consequently, defect-free TFC-MMMs with a polymer thickness of 300 nm were successfully prepared on the porous support. The TFC-MMM with 10% filler loading exhibited excellent CO2 permeance and selectivity, i.e., CO2 permeance of 1070 GPU, CO2/N2 selectivity of 41.0, CO2/CH4 selectivity of 17.2, outperforming the TFC-MMMs prepared with commercially available Pebax. All PTO-based MMMs, with the exception of the low content of UTSA-16 (5%), exceeded the gas separation performance required for post-combustion CO2 capture process.

7. Ji, G., Yin, X., Fu, W., Kou, X., Hotza, D., Wang, Y., Li, A., Olguin, G., & Wang, W. (2023). Enhancement of Hydrogen Clean Energy Production from Greenhouse Gas by In-situ Hydrogen Separation with a Cobalt-silica Membrane. *Journal of Cleaner Production, 388*

Abstract: Methane steam reforming is a representative reaction to convert carbon-rich fuel to carbon-free fuel. However, the thermodynamic equilibrium limits the conversion from methane to hydrogen. Separating hydrogen in-situ from hydrocarbon reforming reactions by inorganic membranes is an effective way to overcome the thermodynamic equilibrium, which improves the conversion of the reforming reactions and the efficiency of hydrogen production. Silica-based membrane, due to its size sieving effect, could separate hydrogen molecules from other larger gases at high temperatures, but the poor hydrothermal stability of silica in steam conditions remains a challenge for the application in hydrogen production. In this study, to improve the hydrothermal stability cobalt was doped in silica membrane precursors with varying ratios. After a series of characterizations by dynamic light scattering, Fourier Transform Infrared spectroscopy, X-ray diffraction, nitrogen adsorption and Scanning Electron Microscope, a cobalt-silica membrane with a cobalt/silicon ratio of 1/4 was fabricated by dip-coating technique. At 500 °C the membrane delivered helium permeance of 9.37 × 10−8 mol m−2 s−1 Pa−1, helium/nitrogen perm-selectivity of 258.48, and helium/carbon dioxide perm-selectivity of 242.19. The membrane was then employed in methane steam reforming for in-situ hydrogen separation to enhance methane conversion and hydrogen production. Raising the reaction temperature favors the

performance of the membrane reactor, but temperature over 550 °C was still challenging due to hydrothermal stability issue. Increasing reaction pressure from 0 to 0.3 MPa favored methane conversion, but pressure over 0.4 MPa led to concentration polarization. Steam to carbon (S/C) ratio of 3 was suitable to avoid nickel/alumina catalyst coking and methane dilution. Reducing the gas hourly space velocity (GHSV) ensured sufficient residence time for methane and favored methane conversion. At T = 500 °C, Δp = 0.3 MPa, S/C = 3 and GHSV = 30 ml g−1 h−1, the membrane elevated the methane conversion from 45.36% (without membrane) to 83.71%. With a cobalt-silica membrane 4.32 ml min−1 of hydrogen was continuously produced with a purity of 82.12 vol% compared to 2.34 ml min−1 of hydrogen with a purity of 65.0 vol% in the case without a membrane. As expected, the micro-morphology of the cobalt-doped membrane after the 20-day steam reforming test showed little visible change in scanning electron microscope. The reduction of pore volume was only 15% as compared to 25% for pure silica material. This membrane demonstrated promising potential in the efficient production of hydrogen. © 2023 Elsevier Ltd

8. Huang, J., Tang, H., Huang, X., Feng, Z., Su, P., & Li, W. (2023). Hansen Solubility Parameters-guided Mixed Matrix Membranes with Linker-exchanged Metal-organic Framework Fillers Showing Enhanced Gas Separation Performance. *Journal of Membrane Science, 668*

Abstract: Membrane processes are more efficient for sustainable separations than traditional energy-intensive technologies, but they suffer from the trade-off limitation about permeability and selectivity. Construction of mixed matrix membranes (MMMs) is effective for improving molecular permselectivity. However, like all hybrid materials that are vitally affected by phase compatibility, production of MMMs with uniform filler dispersion and strong filler-matrix interaction remains extremely challenging. Moreover, there is a lack of generally available guideline for MMM construction. In this study, a versatile Hansen solubility parameters (HSPs)-guided concept, inspired by “like seeks like” principle, is developed to design high-performance MMMs. Based on HSP analysis of porous polymer matrix, metal-organic framework (MOF) filler, and casting solvent, it is found that filler phenylation can shorten HSP “distance” between different components of MMMs. Through surface linker exchange of MOFs by daughter linker that contains HSP-similar phenyls to perform phenylation, the filler-polymer compatibility and the filler

dispersity in solvent and matrix are substantially improved, thereby facilitating the construction of MMMs with ultrahigh filler loading. For carbon capture and hydrogen purification, the HSP-guided MMMs exhibit remarkably enhanced permeability and selectivity, which can easily surpass the latest permeability-selectivity trade-off limitations. © 2022 Elsevier B.V.

9. Araújo, T., Parnell, A. J., Bernardo, G., & Mendes, A. (2023). Cellulose-based Carbon Membranes for Gas Separations - Unraveling Structural Parameters and Surface Chemistry for Superior Separation Performance. *Carbon, 204*, 398-410.

Abstract: Carbon molecular sieve membranes were prepared from the carbonization of a cellulose-based polymeric precursor doped with urea. The addition of urea to the cellulose precursor induces an increase in structural disorder and an increase in pore volume inside the structure of prepared membranes. This unique preparation procedure proved to be an extremely effective method for tuning the pore size of carbon membranes to the desired separations. Urea acts as a pore-forming agent that allows the fabrication of carbon membranes with high porosity. The addition of 2.8 wt% of urea doubled the permeability of the prepared carbon membrane to hydrogen. In addition, a permeability to oxygen of 333 barrer was obtained, without impairing the selectivity. The proposed preparation procedure is compatible with industrial production and scaling, hopefully making carbon membranes a viable solution to produce oxygen-enriched air, recovering of hydrogen from hydrocarbon streams and carbon dioxide removal from natural gas/biogas. © 2022 The Authors

10. Li, H., Wang, F., Li, H., Sengupta, B., Behera, D. K., Li, S., & Yu, M. (2023). Ultra-selective Membrane Composed of Charge-stabilized Fixed Carrier and Amino Acid-based Ionic Liquid Mobile Carrier for Highly Efficient Carbon Capture. *Chemical Engineering Journal, 453*

Abstract: Membrane technology has been extensively studied for CO2 capture applications, especially for flue gas sources. In the past decades, facilitated transport membranes (FTMs) have made breakthroughs overcoming the permeance-selectivity trade-off upper bound restricting traditional CO2 separation membranes, but are still facing challenges towards practical

applications, including limited performance, such as insufficient CO2/N2 selectivity to achieve 95 % CO2 dry-base purity by one step separation, and long-term stability. Herein, we designed and fabricated a novel FTM structure containing an ionic liquid (1-ethyl-3-methylimidazolium aminoacetate, [Emim][Gly]) as mobile CO2-carrier and a polymeric amine (polyethyleneimine, PEI) as fixed CO2-carrier. The fixed carrier is confined within a carbon nanotube (CNT) framework of 230 nm thickness via electrostatic forces adjusted by a polyelectrolyte (polystyrene sulfonate, PSS), while the mobile carrier diffuses freely within the CNT framework. After optimization of the membrane recipe and spray-coating fabrication procedure, following our previous work, the resulting CNT-PSS-PEI ~ IL membranes demonstrated an ultra-high CO2/N2 selectivity up to 1,000 with CO2 permeance up to 2,400 GPU (Gas Permeation Unit, 1 GPU = 3.348 × 10−10 mol·s−1·m−2·Pa−1) under vacuum operation condition. Furthermore, one 100-cm2 flat sheet membrane sample was prepared and exhibited one-stage CO2 enrichment from 15 % to 95 % purity (dry-base) for the first time amongst all reported CO2 separation membranes. The membrane retained a stable performance over 50-h operation period under vacuum condition. The extraordinary CO2 separation performance illustrates the great potential of the CNT-PSS-PEI ~ IL membranes for flue gas carbon capture application.

11. Fattah, I. M. R., Farhan, Z. A., Kontoleon, K. J., kianfar, E., & Hadrawi, S. K. (2023). Hollow Fiber Membrane Contactor based Carbon Dioxide Absorption − Stripping: a Review. *Macromolecular Research*

Abstract: Energy need is predicted to increase by 47% in the next 30 years. Global warming resulting from the continuously increasing atmospheric Carbon dioxide concentration is becoming a serious and pressing issue that needs to be controlled. Carbon dioxide capture and storage/use (CCS/CCU) provide a promising route to mitigate the environmental consequences of Carbon dioxide emission from fossil fuel combustion. In recent years, hollow fiber membrane contactors are regarded as an advanced technique with several competitive advantages over conventional technologies such as easy scale-up, independent control of flow rates, more operational flexibility, absence of flooding and foaming as well as high interfacial area per unit volume. However, many factors such as the membrane material selection, proper choice of solvent, and membrane module design are critical to success. In this regard, this paper aims at covering all areas related to hollow

fiber membranes, including membrane material, membrane modification, membrane surface modification, shape, solvent characterization, operating parameters and costs, hybrid process, hydrophilicity and hydrophobicity of the absorption materials in the membranes, Advantages and Disadvantages of Membrane Contact Technology, membrane lifetime, and energy consumption as well as commercially available systems. Current progress, future potential, and development of pilot-scale applications and thermal fluid of this strategy are also assessed carefully. Furthermore, pore wetting as the main technical challenge in membrane contactor industrial implementation for post- and pre-combustion Carbon dioxide capture processes is investigated in detail. Graphical abstract: [Figure not available: see fulltext.]. © 2023, The Author(s), under exclusive licence to The Polymer Society of Korea.

12. Asif, K., Lock, S. S. M., Taqvi, S. A. A., Jusoh, N., Yiin, C. L., & Chin, B. L. F. (2023). A Molecular Simulation Study on Amine-functionalized Silica/polysulfone Mixed Matrix Membrane for Mixed Gas Separation. *Chemosphere, 311*

Abstract: Polysulfone (PSF) based mixed matrix membranes (MMMs) are one of the most broadly studied polymeric materials used for CO2/CH4 separation. The performance of existing PSF membranes encounters a bottleneck for widespread expansion in industrial applications due to the trade-off amongst permeability and selectivity. Membrane performance has been postulated to be enhanced via functionalization of filler at different weight percentages. Nonetheless, the preparation of functionalized MMMs without defects and its empirical study that exhibits improved CO2/CH4 separation performance is challenging at an experimental scale that needs prior knowledge of the compatibility between the filler and polymer. Molecular simulation approaches can be used to explore the effect of functionalization on MMM's gas transport properties at an atomic level without the challenges in the experimental study, however, they have received less scrutiny to date. In addition, most of the research has focused on pure gas studies while mixed gas transport properties that reflect real separation in functionalized silica/PSF MMMs are scarcely available. In this work, a molecular simulation computational framework has been developed to investigate the structural, physical properties and gas transport behavior of amine-functionalized silica/PSF-based MMMs. The effect of varying weight percentages (i.e., 15–30 wt.%) of amine-functionalized silica and gas concentrations (i.e., 30% CH4/CO2, 50%

CH4/CO2, and 70% CH4/CO2) on physical and gas transport characteristics in amine-functionalized silica/PSF MMMs at 308.15 K and 1 atm has been investigated. Functionalization of silica nanoparticles was found to increase the diffusion and solubility coefficients, leading to an increase in the percentage enhancement of permeability and selectivity for amine-functionalized silica/PSF MMM by 566% and 56%, respectively, compared to silica/PSF-based MMMs at optimal weight percentage of 20 wt.%. The model's permeability differed by 7.1% under mixed gas conditions. The findings of this study could help to improve real CO2/CH4 separation in the future design and concept of functionalized MMMs using molecular simulation and empirical modeling strategies. © 2022 Elsevier Ltd

13. Hayek, A., Alsamah, A., Shalabi, Y. A., Saleem, Q., Ben Sultan, M. M., & Alhajry, R. H. (2022). Molecular Design of Poly(imide–oxadiazole) Membranes for High-Pressure Mixed-Gas Separation. *Macromolecules*, *55*(9), 3747-3761. 10.1021/acs.macromol.2c00650

Abstract: The design of new polymeric materials and the search for new classes of polymers for industrial application in membrane-based gas separation have been the focus of several research groups worldwide. Membranes with high productivity and efficiency under harsh operational conditions of pressure and temperature during mixed-gas separation are of great interest. In this paper, we report the preparation of a series of block copolymers of poly(imide–oxadiazole)s built from 6FDA, Durene, and four different 1,3,4-oxadiazole-based monomers. The pure- and mixed-gas separation properties of their corresponding membranes were measured. The mixed-gas separation data were collected at a high feed pressure of up to 900 psi. Such mixed-gas separation testing under harsh conditions is required to subject the membranes to environments similar to industrial use. For example, the mixed-gas CO2 permeability of 6FDA-Durene/6FDA-4BAO(Me) (3:1) was measured at 900 psi to be ∼130 barrer, and the CO2/CH4 selectivity is around ∼24. These results of permeability and selectivity of poly(imide–oxadiazole) membranes at such high gas feed pressure are considered very attractive and are superior to many glassy polymers reported in the literature and that are industrially observed membranes. This work illustrates well a case scenario of structure–property relationship and demonstrates the exclusivity of mixed-gas testing which could not be predicted from the ideal situation of pure-gas testing. In the near future, the mixed-gas separation properties of thin layer composite and hollow fibers will be evaluated.

14. Hou, R., Fong, C., Freeman, B. D., Hill, M. R., & Xie, Z. (2022). Current Status and Advances in Membrane Technology for Carbon Capture. *Separation and Purification Technology, 300*

Abstract: Membrane gas separation is a promising next-generation technology for post-combustion CO2 capture that can significantly reduce energy consumption, instrument, and chemical footprint relative to mature amine scrubbing that is in widespread use. Nevertheless, despite many studies commercially viable membranes are not widely implemented at a large scale. This review presents a systematic overview of the current status and advances of membrane technologies for CO2 capture from post-combustion flue gas. In particular, the potential for recent developments in membranes for scale-up based upon required performance parameters in these settings will be reviewed. The challenges and barriers to the upscale of membrane technologies are discussed with respect to both materials and engineering perspectives. The technology readiness level of various technologies and remaining barriers to their implementation are provided. © 2022

15. Rehman, A., Jahan, Z., Sher, F., Noor, T., Khan Niazi, M. B., Akram, M. A., & Sher, E. K. (2022). Cellulose Acetate based Sustainable Nanostructured Membranes for Environmental Remediation. *Chemosphere, 307*

Abstract: Membrane-based gas separation has a great potential for reducing environmentally hazardous carbon dioxide (CO2) gas. The polymeric membranes developed for CO2 capturing have some limitations in their selectivity and permeability. There is a need to overcome these issues and developed such membranes having high-performance CO2 capture with cost-effectiveness. The present study aimed to synthesize mixed matrix membranes (MMMs) having improved properties CO2 adsorption performance and stability than that of pure polymer. Further, the effect on CO2 adsorption by increasing the filler concentration in MMMs was investigated. The MMMs were synthesized by incorporating (1–5 wt%) Cu-MOF-GO composites as filler into cellulose-acetate (CA) polymer matrix by adopting the solution casting method. The performance of MMMs was studied by changing the Cu-MOF-GO composite concentration (1–5 wt%) in the

polymer matrix at 45 °C up to 15 bar. Morphological analysis by using SEM confirms that by increasing the concentration of Cu-MOF-GO more than 3% will result in their agglomeration in MMM. The successful incorporation of MOF within the polymer matrix of MMMs was confirmed through the presence of functional groups using FTIR and Raman spectroscopy. XRD analysis revealed that pure CA changes its semi-crystalline behaviour into crystalline by the addition of Cu-MOF-GO. The maximum tensile stress and strain rate of MMMs was 45.1 N/mm2 and 12.8%. In addition, with an increase in (4–5 wt%) Cu-MOF-GO concentration the hydrophilicity of MMMs decreases. The maximum uptake rate of CO2 was 1.79 mmol/g and 7.98 wt% at 15 bar. The adsorption results conclude that Cu-MOF-GO composite and CA-based MMM can be effective for CO2 capture. © 2022 The Authors

16. Ramezani, R., Di Felice, L., & Gallucci, F. (2022). A Review on Hollow Fiber Membrane Contactors for Carbon Capture: Recent Advances and Future Challenges. *Processes, 10* (10)

Abstract: Energy need is predicted to increase by 48% in the next 30 years. Global warming resulting from the continuously increasing atmospheric CO2 concentration is becoming a serious and pressing issue that needs to be controlled. CO2 capture and storage/use (CCS/CCU) provide a promising route to mitigate the environmental consequences of CO2 emission from fossil fuel combustion. In recent years, hollow fiber membrane contactors are regarded as an advanced technique with several competitive advantages over conventional technologies such as easy scale-up, independent control of flow rates, more operational flexibility, absence of flooding and foaming as well as high interfacial area per unit volume. However, many factors such as the membrane material selection, proper choice of solvent, and membrane module design are critical to success. In this regard, this paper aims at covering all areas related to hollow fiber membranes, including membrane material, membrane modification, membrane surface modification, shape, solvent characterization, operating parameters and costs, hybrid process, membrane lifetime, and energy consumption as well as commercially available systems. Current progress, future potential, and development of pilot-scale applications of this strategy are also assessed carefully. Furthermore, pore wetting as the main technical challenge in membrane contactor industrial

implementation for post- and pre-combustion CO2 capture processes is investigated in detail. © 2022 by the authors.

17. Liu, Y., Sim, J., Hailemariam, R. H., Lee, J., Rho, H., Park, K. -., Kim, D. W., & Woo, Y. C. (2022). Status and Future Trends of Hollow Fiber Biogas Separation Membrane Fabrication and Modification Techniques. *Chemosphere, 303*

Abstract: With the increasing global demand for energy, renewable and sustainable biogas has attracted considerable attention. However, the presence of various gases such as methane, carbon dioxide (CO2), nitrogen, and hydrogen sulfide in biogas, and the potential emission of acid gases, which may adversely influence the environment, limits the efficient application of biogas in many fields. Consequently, researchers have focused on the upgrade and purification of biogas to eliminate impurities and obtain high-quality and high-purity biomethane with an increased combustion efficiency. In this context, the removal of CO2 gas, which is the most abundant contaminant in biogas, is of significance. Compared to conventional biogas purification processes such as water scrubbing, chemical absorption, pressure swing adsorption, and cryogenic separation, advanced membrane separation technologies are simpler to implement, easier to scale, and incur lower costs. Notably, hollow fiber membranes enhance the gas separation efficiency and decrease costs because their large specific surface area provides a greater range of gas transport. Several reviews have described biogas upgrading technologies and gas separation membranes composed of different materials. In this review, five commonly used commercial biogas upgrading technologies, as well as biological microalgae-based techniques are compared, the advantages and limitations of polymeric and mixed matrix hollow fiber membranes are highlighted, and methods to fabricate and modify hollow fiber membranes are described. This will provide more ideas and methods for future low-cost, large-scale industrial biogas upgrading using membrane technology. © 2022 The Authors

18. Mohammadi Saadat, M., Norouzbahari, S., & Esmaeili, M. (2022). CO2/N2 Separation by Glycerol Aqueous Solution in a Hollow Fiber Membrane Contactor Module: CFD Simulation and Experimental Validation. *Fuel, 323*

Abstract: In this paper, CO2 separation from CO2/N2 mixed gas was experimentally and theoretically investigated inside a gas–liquid hollow fiber membrane contactor (HFMC) module along with developing and validation of a comprehensive computational fluid dynamic (CFD) model. An aqueous solution of glycerol (10 wt%) (C3H8O3), a green and cost-effective physical solvent, was employed as the liquid absorbent, flowing in the shell side of the hollow fibers. To attain a better insight into the membrane wetting effects on separation performance, all non-wetting, partially-wetting, and completely-wetting conditions were investigated. Moreover, a correlation for CO2 Henry's law constant was developed to estimate the CO2 solubility in aqueous solutions of glycerol via adopting the literature data. The CFD simulation results revealed that the gas to absorbent flow rate ratio (Fg/Fa) is a dominant parameter in controlling the CO2 removal efficiency. CO2 separation performance was augmented via decreasing the gas flow rate, absorption temperature and increasing the membrane porosity to tortuosity ratio as well as glycerol concentration. In contrast, by increment of the membrane wettability from non-wetting to completely-wetting condition, the CO2 removal percentage was dramatically reduced from 72.5 to 18.5%. A fair agreement between the CFD simulation results and experimental data with an absolute average relative error percentage (AARE%) of 2.7% was achieved, confirming the validity of the developed model. © 2022 Elsevier Ltd

19. Zhu, S., Bi, X., Shi, Y., Shi, Y., Zhang, Y., Jin, J., & Wang, Z. (2022). Thin Films Based on Polyimide/Metal-Organic Framework Nanoparticle Composite Membranes with Substantially Improved Stability for CO2/CH4Separation. *ACS Applied Nano Materials, 5*(7), 8997-9007

Abstract: As one of the gas separation membranes, the thin-film nanocomposite (TFN) membrane can effectively reduce gas transport resistance and improve gas permeance. However, due to the high mobility of the chain in the thin film, it is still a great challenge to realize the TFN membrane with stable separation performance. In this work, we report a less destructive and efficient cross-linking strategy based on metal-ion coordination to improve the stability of the TFN membrane for CO2/CH4 separation. The selective layer is made of carboxylated polyimide as a matrix and UiO-66 nanoparticles (diameters of ∼50 nm) as fillers. By simply immersing TFN membranes in Cu(NO3)2 solution, coordination bonds are successfully constructed between Cu2+ and carboxyl

groups (-COOH). The cross-linked TFN membranes exhibit high CO2/CH4 selectivity of up to 29-35 with CO2 permeance of 110-350 GPU, outperforming most previously reported membranes. Moreover, the plasticization pressure of the cross-linked membranes improves from 0.3-0.9 to 0.9-1.5 MPa, higher than most reported asymmetric and hollow fiber membranes. In the CO2/CH4 (50:50 v/v) mixed-gas permeation tests, the cross-linked membranes retain constant CO2/CH4 selectivity at 23.9-25.2 with increasing mixed-gas feed pressure. The cross-linked membranes also demonstrate stable CO2/CH4 selectivity in the range of 27.2-31.2 within 100 h of testing time under a 1.0 MPa CO2 partial pressure. © 2022 American Chemical Society.

20. Yang, J., Tao, L., He, J., McCutcheon, J. R., & Li, Y. (2022). Machine Learning Enables Interpretable discovery of Innovative Polymers for Gas Separation Membranes. *Science Advances, 8*(29)

Abstract: Polymer membranes perform innumerable separations with far-reaching environmental implications. Despite decades of research, design of new membrane materials remains a largely Edisonian process. To address this shortcoming, we demonstrate a generalizable, accurate machine learning (ML) implementation for the discovery of innovative polymers with ideal performance. Specifically, multitask ML models are trained on experimental data to link polymer chemistry to gas permeabilities of He, H2, O2, N2, CO2, and CH4. We interpret the ML models and extract valuable insights into the contributions of different chemical moieties to permeability and selectivity. We then screen over 9 million hypothetical polymers and identify thousands that lie well above current performance upper bounds, including hundreds of never-before-seen ultrapermeable polymer membranes with O2 and CO2 permeability greater than 104 and 105 Barrers, respectively. High-fidelity molecular dynamics simulations confirm the ML-predicted gas permeabilities of the promising candidates, which suggests that many can be translated to reality.

21. Huang, Z., Yin, C., Corrado, T., Li, S., Zhang, Q., & Guo, R. (2022). Microporous Pentiptycene-Based Polymers with Heterocyclic Rings for High-Performance Gas Separation Membranes. *Chemistry of Materials, 34*(6), 2730-2742.

Abstract: Microporous polymers, such as polymers of intrinsic microporosity (PIMs) and thermally rearranged (TR) polymers, have shown promise in advancing the performance of polymer gas separation membranes to overcome the permeability-selectivity trade-off. In this work, a series of thermally rearranged pentiptycene-based polybenzoxazole (PPBO) polymers were prepared from a new pentiptycene-based poly(o-hydroxyl imide) (PPHI) precursor using carefully designed thermal protocols. Fundamental structure-property relationships within the series were established by comprehensively examining the effects of intermediate treatment temperature and the heating rate on the membrane microporosity, properties, and gas separation performance. The incorporation of bulky pentiptycene units into TR PPBO structures, along with optimized TR thermal protocols in this study, provided a route to finely tune and eventually maximize the separation performance of PPBOs, with several films far exceeding the 2015 upper bound for H2/CH4and O2/N2. In CO2/CH4mixed-gas permeation tests, PPBO membranes showed excellent resistance to plasticization under CO2partial pressure as high as 6.6 atm, far surpassing the 2008 mixed-gas upper bound for CO2/CH4. Moreover, a 5 month aged PPBO film maintained its superior separation performance above the 2008 O2/N2upper bound and 2015 H2/CH4upper bound, indicating the excellent aging resistance of PPBOs.

22. León, N. E., Liu, Z., Irani, M., & Koros, W. J. (2022). How to Get the Best Gas Separation Membranes from State-of-the-Art Glassy Polymers. *Macromolecules*, *55*(5), 1457-1473.

Abstract: Herein we focus on fundamental polymer science factors in membrane-based gas separation to open another chapter on this important topic. Realistically thinking about nanometer and angstrom scale matrix attributes that are translatable into higher performance thin glassy polymer asymmetric membrane layers in practical large-scale devices is crucial. Such thinking should be guided by expertise in both polymer and membrane communities to advance the state-of-the-art. Polymer structures, membrane morphologies, and effects of operating conditions are discussed here by using specific examples to illustrate key issues. Rubbery polymers are not the focus of this discussion since they lack diffusive discrimination for size-similar penetrants, which glassy polymers provide and make them the focus here. Four scalable subtopics guide necessary thinking: (i) plasticization, (ii) antiplasticization, (iii) dual-mode transport involving saturation of

unrelaxed free volume, and (iv) nonuniform free volume and stress profiles in thin skin glassy polymer asymmetric or composite membranes. Using these subtopics in the context of macromolecular science, we discuss issues needed to expand the state-of-the-art in gas separation membranes.

23. Theodorakopoulos, G. V., Karousos, D. S., Mansouris, K. G., Sapalidis, A. A., Kouvelos, E. P., & Favvas, E. P. (2022). Graphene Nanoplatelets Based Polyimide/Pebax dual-layer Mixed Matrix Hollow Fiber Membranes for CO2/CH4 and He/N2 Separations. *International Journal of Greenhouse Gas Control, 114*

Abstract: Mixed matrix membranes are key in the preparation of stable, stretchy, durable and efficient membranes for gas separation applications. To this aim, the perfect filler nanomaterials' dispersion is needed. At the same time the replacement of toxic solvents with green ones is also a priority in science, including the membrane technology. Herein, we present the development steps, their structural characteristics and the gas selectivity properties of graphene nanoplatelets (GNPs) based mixed matrix hollow fiber (HF) membranes. In specific, dual-layer composite polymeric hollow fiber membranes, for CO2/CH4 and He/N2 gas separations, were prepared by directly dip-coating a single selective layer on prepared porous HF supports without the use of any gutter layer. Asymmetric BTDA-TDI/MDI (P84) co-polyimide-based HFs that acted as porous supports, were fabricated via the dry-wet phase inversion process and the commercial poly(ether-block-amide) Pebax-1657 was chosen as a high CO2-selective separation layer material, dip-coated on the HF supports. The positive influence of the incorporation of GNPs as promising nanofiller in both, the polymeric matrix (support) and the selective layer, in parallel with the partial replacement of toxic NMP by GBL -a "green" solvent- in the support's spinning process, were all evaluated and confirmed. CO2/CH4 and He/N2 selectivities up to 82 and 20, respectively with CO2 and He permeances of 3 and 2.7 GPU, respectively were measured under real binary gas mixture conditions at 1.3 bar(a) transmembrane pressure at 298 K for dual-layer composite, with GNPs filler, HF (DL-HF) membranes. © 2022 Elsevier Ltd

24. He, S., Zhu, B., Li, S., Zhang, Y., Jiang, X., Hon Lau, C., & Shao, L. (2022). Recent Progress in PIM-1 based Membranes for Sustainable CO2 Separations: Polymer Structure Manipulation and Mixed Matrix Membrane Design. *Separation and Purification Technology, 284*

Abstract: Greenhouse gas separation, storage, and utilization are extremely urgent due to the growing climate problems and resource shortages. Polymer-based membrane separation as one of the most promising technologies for large-scale and high-efficient gas separation has been studied extensively for decades in virtue of its low-cost and energy saving process. The emergence of ultra-permeable polymers of intrinsic microporosity (PIMs), particularly the PIM-1 with excellent solubility in common solvents, has attracted a lot of research interest towards next generation high-performance membrane fabrication for CO2 separations. However, despite the high gas permeability and excellent workability, PIM-1 exhibits relative low gas selectivity and suffers from significant physical aging, therefore the research focused on improving the permselectivity and long-term stability of PIM-1 based membranes has been developed rapidly in recent years. Given that, the latest progress of modification strategies for PIM-1 based membranes are summarized in two perspectives: design and modification of PIM-1 intrinsic structure and fabrication of PIM-1/nanofiller mixed matrix membranes, especially for CO2 separations. Furthermore, the advantages and limitations of existing researches are discussed, and the feasible future research directions are boldly prospected, hoping to be instructive for developing PIM-1 based high-performance membranes for crucial gas separations like CO2 capture, H2 purification and natural gas purification. © 2021 Elsevier B.V.

25. Hammerstein, R., Schubert, T., Braun, G., Wolf, T., Barbe, S., Quade, A., Foest, R., Karousos, D. S., & Favvas, E. P. (2022). The Optimization of Dispersion and Application Techniques for Nanocarbon-Doped Mixed Matrix Gas Separation Membranes. *Membranes, 12*(1)

Abstract: In this work, supported cellulose acetate (CA) mixed matrix membranes (MMMs) were prepared and studied concerning their gas separation behaviors. The dispersion of carbon nanotube fillers were studied as a factor of polymer and filler concentrations using the mixing methods of the rotor–stator system (RS) and the three-roll-mill system (TRM). Compared to the dispersion

quality achieved by RS, samples prepared using the TRM seem to have slightly bigger, but fewer and more homogenously distributed, agglomerates. The green γ-butyrolactone (GBL) was chosen as a polyimide (PI) polymer-solvent, whereas diacetone alcohol (DAA) was used for preparing the CA solutions. The coating of the thin CA separation layer was applied using a spin coater. For coating on the PP carriers, a short parameter study was conducted regarding the plasma treatment to affect the wettability, the coating speed, and the volume of dispersion that was applied to the carrier. As predicted by the parameter study, the amount of dispersion that remained on the carriers decreased with an increasing rotational speed during the spin coating process. The dry separation layer thickness was varied between about 1.4 and 4.7 µm. Electrically conductive additives in a non-conductive matrix showed a steeply increasing electrical conductivity after passing the so-called percolation threshold. This was used to evaluate the agglomeration behavior in suspension and in the applied layer. Gas permeation tests were performed using a constant volume apparatus at feed pressures of 5, 10, and 15 bar. The highest calculated CO2/N2 selectivity (ideal), 21, was achieved for the CA membrane and corresponded to a CO2 permeability of 49.6 Barrer.

26. De Pascale, M., Benedetti, F. M., Lasseuguette, E., Ferrari, M. -., Papchenko, K., Esposti, M. D., Fabbri, P., & De Angelis, M. G. (2021). Mixed Matrix Membranes Based on Torlon® and ZIF-8 for High-temperature, Size-selective Gas Separations. *Membranes*, *11*(12)

Abstract: Torlon® is a thermally and plasticization-resistant polyamide imide characterized by low gas permeability at room temperature. In this work, we aimed at improving the polymer performance in the thermally-enhanced He/CO2 and H2/CO2 separations, by compounding Torlon® with a highly permeable filler, ZIF-8, to fabricate Mixed Matrix Membranes (MMMs). The effect of filler loading, gas size, and temperature on the MMMs permeability, diffusivity, and selectivity was investigated. The He permeability increased by a factor of 3, while the He/CO2 selectivity decreased by a factor of 2, when adding 25 wt % of ZIF-8 at 65◦C to Torlon®; similar trends were observed for the case of H2. The MMMs permeability and size-selectivity were both enhanced by temperature. The behavior of MMMs is intermediate between the pure polymer and pure filler ones, and can be described with models for composites, indicating that such materials

have a good polymer/filler adhesion and their performance could be tailored by acting on the formulation. The behavior observed is in line with previous investigations on MMMs based on glassy polymers and ZIF-8, in similar conditions, and indicates that ZIF-8 can be used as a polymer additive when the permeability is a controlling aspect, with a proper choice of loading and operative temperature.

27. Pulyalina, A., Rostovtseva, V., Faykov, I., Tataurov, M., Dubovenko, R., & Shugurov, S. (2021). Development of Novel Polyamide-IMIDE/DES Composites and their Application for Pervaporation and Gas Separation. *Molecules, 26*(4)

Abstract: Novel polymer composites based on polyamide-imide Torlon and deep eutectic solvent (DES) were fabricated and adapted for separation processes. DES composed of zinc chloride and acetamide in a ratio of 1:3 M was first chosen as a Torlon-modifier due to the possibility of creating composites with a uniform filling of the DES through the formation of hydrogen bonds. The structure of the membranes was investigated by scanning electron microscopy and X-ray diffraction analysis; thermal stability was determined by thermogravimetric analysis and mass spectrometry. The surface of the composites was studied by determining the contact angles and calculating the surface tension. The transport properties were investigated by such membrane methods as pervaporation and gas separation. It was found that the inclusion of DES in the polymer matrix leads to a significant change in the structure and surface character of composites. It was also shown that DES plays the role of a plasticizer and increases the separation performance in the separation of liquids and gases. Torlon/DES composites with a small amount of modifier were effective in alcohol dehydration, and were permeable predominantly to water impurities in isopropanol. Torlon/DES-5 demonstrates high selectivity in the gas separation of O2/N2 mixture.

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