Zeolitic imidazolate framework composite membranes and thin films: Synthesis and applications

Journal: Chemical Society Reviews

Manuscript ID: CS-REV-12-2013-060480.R1

Article Type: Review Article

Date Submitted by the Author: 06-Feb-2014

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Zeolitic imidazolate framework composite membranes and thin films: Synthesis and applications

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks, are built of tetrahedral metal ions bridged by imidazolates. They have permanent porosity and relatively high thermal and chemical stability, which make them attractive candidates for many industrial applications. In recent years, significant progress has been made in developing ZIFs into membranes and thin films for gas separation, liquid separation (pervaporation) and functional devices. Various techniques, such as direct synthesis, secondary synthesis, reactive seeding and functional chemicals as linkers, and contra-diffusion synthesis, have been reported for the fabrication of ZIF membranes and films. As ZIFs have good compatibility with polymers, they have been incorporated into polymers with high loadings to form mixed matrix membranes. The resulting symmetric dense or asymmetric composite membranes exhibit good performance in gas separation and liquid separation via pervaporation. The recent developments of ZIF membranes/films, ZIF/polymer mixed matrix membranes and their applications are reviewed in this article.

1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are a class of porous crystals with extended three-dimensional structures constructed from tetrahedral metal ions (e.g., Zn, Co) bridged by imidazolate (Im). The fact that the M-Im-M angle is similar to the Si-O-Si angle (145°) preferred in zeolites has led to the synthesis of a large number of ZIFs with zeolite-type tetrahedral topologies.1,2 Remarkably, ZIFs exhibit permanent porosity and high thermal and chemical stability, which make them attractive candidates for many applications such as adsorption, separation and gas storage. ZIFs are a subclass of metal organic frameworks (MOFs, also known as porous coordination polymers),3 which have been extensively studied over the last 15 years.3,4 In particular, the processing of MOFs into membranes and films is important for many applications, such as separation membranes and chemical sensors.5 The techniques for the fabrication of MOF membranes and films mainly translate from the two closely related fields: (1) Zeolite films, particularly the direct synthesis and secondary growth methods, and (2) coordination polymer films with Langmuir-Blodgett and layer-by-layer thin-film preparation techniques on which the literature is abundant.6,7 In recent years, MOF membranes and films have been intensively studied, and several excellent reviews have been published,5,8-12 where ZIF membranes and films were partially discussed.

In comparison to the other MOFs, ZIFs share many riches of zeolite chemistry, both in structural topologies and in coordination factors, and show exceptional thermal and chemical stability.13,14 Therefore, ZIFs hold much great promise as porous materials for a variety of applications. In this review, we only focus on the synthesis and applications of ZIF membranes and films, and the mixed matrix membranes incorporated with ZIFs for gas separation, pervaporation, and functional devices, although the synthesis methods and applications presented here may be applicable to other MOFs. The first literature for the synthesis of ZIF crystals was published in 200315 and the ZIF membranes have rapidly emerged since 2010. This review is organized as the following sections: 1) Introduction; 2) Synthesis of ZIF separation membranes for gas separation and pervaporation; 3) ZIF/polymer mixed matrix membranes; 4) ZIF films for microelectronics; and 5) Conclusions and perspectives. The synthesis and applications of ZIF composite membranes and films are summarized in Scheme 1.

Scheme 1. Summary of the synthesis and applications of ZIF composite membranes and films.

2. Synthesis of ZIF separation membranes for gas separation and pervaporation

The well-defined porous structures of ZIFs allow them to achieve gas separation with high selectivity due to the molecular sieving...
effect. Table 1 summarizes the porous structures of ZIFs discussed in this review. The pore size of ZIFs is usually less than 5 Å, which is in the range of small molecular gases and liquids. Due to the versatility of imidazolate linkers, the pore size and surface property of ZIFs could be adjusted by using different (functionalized) linkers. Therefore, considerable efforts have been made to develop ZIF membranes for gas separations such as hydrogen purification, CO₂ capture, natural gas purification, light hydrocarbon separation, and for liquid separation via pervaporation.

Like zeolite membranes, ZIF membranes are prepared by growing a thin ZIF layer on porous substrates such as porous ceramic and stainless steel discs and tubes, and porous polymer sheets. The porous substrates provide mechanical support for ZIF layer, and exhibit minimal permeation resistance. The quality and nature of the substrates, such as surface roughness, pore size and chemical composition, has a significant effect on the formation of ZIF layer. The main task for the synthesis of high-quality ZIF membranes is to control ZIF heterogeneous nucleation and crystallization on the substrate surface, and minimize intercrystal voids. The quality of ZIF membranes is evaluated in terms of crystal structure and morphology and separation properties. In particular, the gas separation properties of the membranes are determined by using single gas and mixed gas permeation experiments.⁶⁻¹⁰,¹³⁻¹⁹

The permeance \( P_i \) (mol m⁻² s⁻¹ Pa⁻¹) of single gas \( i \) (or component \( i \) in the mixed gas feed) is defined as

\[
P_i = \frac{N_i}{\Delta p_i A}
\]

where \( N_i \) is the permeating flow rate of single gas (or component \( i \)) (mol s⁻¹), \( \Delta p_i \) is the transmembrane pressure difference of \( i \) (Pa), and \( A \) is the membrane area (m²). Similarly, the permeance \( P_j \) can be written for single gas \( j \) (or component \( j \)). The ideal selectivity (or separation factor), \( S_{ij} \) is defined as the ratio of the two permeances \( P_i \) and \( P_j \).

\[
S_{ij} = \frac{P_i}{P_j}
\]

ZIF composite membranes have been studied for liquid separation via pervaporation. Pervaporation is considered as one of the most promising technologies in the molecular-scale liquid/liquid separations for biorefinery, petrochemical and pharmaceutical industries.⁰⁻¹⁰ When a mixed liquid stream containing two or more components is placed in contact with one side of the membrane, the components will absorb into/onto the membrane. The penetrants will diffuse through the membrane and evaporate as permeate induced by vacuum or gas purge. The separation of different components is achieved when some of the components preferentially diffuse across the membrane. The flux of a component \( i \) through a membrane can be expressed in terms of the partial vapor pressures on either side of the membrane, \( p_{iO} \) and \( p_{iL} \), by

\[
J_i = \frac{P_i^G}{l} (p_{iO} - p_{iL})
\]

where \( J_i \) is the flux, \( l \) is the membrane thickness and \( P_i^G \) is the gas separation permeability coefficient. A similar equation can be written for component \( j \) in the feed. The separation achieved by a pervaporation membrane is proportional to the fluxes \( J_i \) and \( J_j \) through the membrane.²¹

The techniques for the synthesis of ZIF membranes can be roughly classified as direct synthesis, secondary growth, surface functionalization and special seeding, and contra-diffusion (counter-diffusion) for convenience of discussion. The synthesis processes and the properties of ZIF membranes are reviewed below.

Table 1. ZIFs for the preparation of membranes and films.

<table>
<thead>
<tr>
<th>ZIF type</th>
<th>Molecular structure</th>
<th>Topology</th>
<th>Pore size (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-7</td>
<td>Zn(benzimidazole)</td>
<td>SOD</td>
<td>0.30</td>
<td>2⁵, 2⁷</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Zn(2-methylimidazole)</td>
<td>SOD</td>
<td>0.34</td>
<td>2², 2²</td>
</tr>
<tr>
<td>ZIF-9</td>
<td>Co(benzimidazole)</td>
<td>SOD</td>
<td>&lt;0.30</td>
<td>2²</td>
</tr>
<tr>
<td>ZIF-22</td>
<td>Zn(5-azabenzimidazole)</td>
<td>LTA</td>
<td>0.35</td>
<td>1³</td>
</tr>
<tr>
<td>ZIF-69</td>
<td>Zn(cbIM)(nIM)</td>
<td>GME</td>
<td>0.44</td>
<td>2³</td>
</tr>
</tbody>
</table>

2.1. Direct synthesis

In the direct synthesis, a porous membrane substrate without surface modification is immersed in a ZIF synthesis solution, where a ZIF layer directly grows on the substrate. Many different types of ZIF membranes have been successfully synthesized using this method. For instance, as the promising porous materials, ZIF-8 membrane is able to separate H₂ (its kinetic diameter ~2.9 Å) from larger molecules as the pore size of ZIF-8 is ~3.4 Å. Another important feature of ZIF-8 is its hydrophobic nature, whereas ultramicroporous zeolites are usually hydrophilic. This should give ZIF-8 membrane an advantage over zeolites in the separation of H₂ from a mixture with water vapor. Bux et al. prepared ZIF-8 membrane on titania support by microwave-assisted solvothermal synthesis.²⁹ A cleaned and dried support was firstly immersed into the precursor and left standing for 20 min. Afterwards the solution with the support was transferred into a 200 ml Teflon autoclave and heated in a microwave oven to 100 °C for 4 h to complete the membrane preparation. The resulting membrane is about 30 μm in thickness (Fig. 1), and the single gas permeation test showed the permeances clearly depend on the molecular size of the gases (Fig. 1). The single gas separation performance of various ZIFs is summarized in Table 2. The separation factor for a 1:1 H₂/CH₄ mixture at 298 K and 1 bar was determined to be 11.2, which considerably exceeds the Knudsen separation factor for H₂/CH₄ (~2.8). The permeation selectivity of CO₂/CH₄ could be predicted by IR-diffusion studies and molecular modelling, and the results fitted the experimentally measured permeation selectivities.²⁹, ³⁰ ZIF-8 was predicted by Haldoupis et al. to have extraordinarily high membrane...
selectivity for CO₂/CH₄ mixtures in theoretical calculations based on a rigid crystal structure. Furthermore, the ethene/ethane separation by ZIF-8 membrane was also estimated with sufficient accuracy by using the adsorption and diffusion selectivity on a ZIF-8 large single crystal by IR microscopy. ZIF-8 membrane showed ethene/ethane separation factors of 2.8 and 2.4 at room temperature for 1 and 6 bar feed pressure, respectively.

The role of sodium formate was investigated to the synthesis of ZIF-8 membrane. A one step in situ synthesis of ZIF-8 membranes on unmodified porous α-alumina supports was developed in the presence of sodium formate. Sodium formate was found to enhance the heterogeneous nucleation of ZIF-8 crystals on alumina supports as well as to promote intergrowth of ZIF-8 crystals. In this in situ method, sodium formate played a critical role in formation of well-intergrown continuous ZIF-8 membranes, and the ideal selectivity of H₂/N₂ increased to 12.0 with a H₂ permeance of 2.4 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹. A substituted imidazolate-based ZIF (SIM-1) membrane was also crystallized in situ on a tubular asymmetric alumina support. SIM-1 has the same SOD topological structure as ZIF-8 with 4-methyl-5-imidazolecarboxaldehyde as the imidazolate linker. The size and the shape of the functionalized imidazolate linker make the SOD cavity much smaller in SIM-1. The thickness of the resulting SIM-1 membrane was ca. 25 µm. The H₂/N₂ ideal selectivity of 2.5 was obtained, which was smaller than its Knudsen selectivity (3.7); its CO₂/N₂ selectivity (1.1) was slightly greater than the corresponding Knudsen selectivity (0.78), thus indicating an adsorption-diffusion based mechanism. For a ternary mixture CO₂/N₂/H₂O (10/87/3 vol%), a CO₂/N₂ separation factor of 4.5 was measured, which is much higher than the corresponding Knudsen separation factor (0.78).

**Fig. 1.** SEM image and EDXS mapping of the cross section of a simply broken ZIF-8 membrane, and Single (squares) and mixed (triangles) gas permeances for a ZIF-8 membrane vs kinetic diameters. Adapted with permission from ref. 29. Copyright 2009 American Chemical Society.

ZIF-69 is composed of zinc nitrate coordinated with 2-nitromidazole (nIM) and 5-chlorobenzimidazole (cbIM), forming a zeolite GME topology that has 12-membered ring (MR) straight channels along the c-axis and 8 MR channels along the a- and b-axes. Continuous and c-oriented ZIF-69 membranes were successfully synthesized on porous α-alumina substrates with a thickness of ca. 50 µm by an in situ solvothermal method. Single-gas permeation experiments through ZIF-69 membranes were carried out by the vacuum permeation method at room temperature using H₂, CH₄, CO, CO₂ and SF₆ respectively. The permeances were in the order of H₂ > CO₂ > CH₄ > CO > SF₆. The separation of CO₂/CO gas mixture was investigated by gas chromatography and the permselectivity (or separation factor) of CO₂/CO was 3.5 with CO₂ permeance of 3.6 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ at room temperature.

Many ZIF membranes have been synthesized using the direct synthesis method so far. Given that the crystallization depends on many factors, it is often difficult to control ZIF crystallization on unmodified substrate, resulting in defective ZIF membranes with many intercrystal voids. To improve the quality of ZIF membranes, secondary growth and other new techniques are usually required.

### 2.2. Secondary growth

Secondary growth, also called seeded growth, is more commonly used in the membrane preparation. In this synthesis process, ZIF crystals are synthesized first and deposited on substrates using different methods such as dip coating and rubbing of dry ZIF powder. The ZIF crystals deposited on the substrate serve as seeds for promoting ZIF crystallization. Secondary growth allows for more effective control of crystal growth and orientation of ZIF membranes.

Thin ZIF-8 membranes with ~5-9 µm thicknesses were synthesized by secondary seeded growth on tubular α-alumina supports. The separation performance of these membranes for equimolar CO₂/CH₄ gas mixtures was demonstrated. The membranes displayed CO₂ permeances as high as ca. 2.4 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ with CO₂/CH₄ separation selectivities of 4.1-7.0 at 295 K and a feed pressure of 139.5 KPa. Bux et al. prepared highly oriented ZIF-8 composite membranes by seeding and secondary growth. By dip-coating, ZIF-8 nanocrystals were attached onto the surface of a porous α-alumina support using polyethyleneimine (PEI) as a coupling agent. The membrane showed preferred orientation of the {100} plane parallel to the support (Fig. 2). The crystallographic preferred orientation (CPO) indices of the dominant 200 reflection in relation to the 110 (CPO₂00₁₁₀) and the 211 reflections (CPO₂₁₀₂₁₁) were calculated to be 83 and 81, respectively. Both values clearly demonstrated the pronounced {100} orientation with only a low fraction of crystals taking different orientations. In binary gas permeation experiments, the membrane showed good performance in H₂/hydrocarbon separation. A sharp molecular sieve separation was observed for an equimolar H₂/C₃H₈ mixture with a separation factor above 300. The addition of PEI in the seeding solution could improve the adhesion between the seed crystals and the support surface.

**Fig. 2.** (a) SEM top view of the well-intergrown ZIF-8 layer after 2 h of secondary growth. (b) SEM top down view on the corresponding crosssection of the broken membrane. Reprinted with permission from ref. 36. Copyright 2011 American Chemical Society.
Exceptionally high quality ZIF-8 membranes were prepared in aqueous solutions at near room temperature, which is more economical and greener compared to other synthesis procedures requiring organic solvents and high synthesis temperature. The membrane thickness was around 2.5 μm, and exhibited excellent separation performance for C2/C3 hydrocarbon mixtures. The separation factors for mixtures of ethane/propane, ethylene/propylene and ethylene/propane are ~80, ~10 and ~167, respectively.\(^{39}\) For the propylene/propane binary mixture separation, the ZIF-8 membrane showed a permeability of propylene up to ca. 3.0×10\(^{-6}\) mol m\(^{-2}\) Pa\(^{-1}\) s\(^{-1}\) and a propylene to propane separation factor up to 50 at optimal separation conditions, well surpassing the “upper-bound trade-off” lines of existing polymer and carbon membranes.\(^{36}\) The diffusivity value of the high quality ZIF-8 membrane decreased with increasing molecular size in the order He>H\(_2\)>CO\(_2\)>N\(_2\)>CH\(_4\).\(^{41}\) Gas permeance for the above light gases remained constant while C\(_2\)H\(_6\) and C\(_3\)H\(_8\) permeance decreased with increasing pressure due to the specific pressure dependency of the adsorption isotherm for each gas. The determined diffusivity for propylene and propane is 1.25×10\(^{-8}\) and 3.99×10\(^{-9}\) cm\(^2\) s\(^{-1}\) with respective activation diffusion energy of 12.7 and 38.8 kJ/mol. With an equimolar binary feed, the ZIF-8 membranes exhibited a consistent C\(_2\)H\(_6\)/C\(_3\)H\(_8\) selectivity of about 30 and a C\(_3\)H\(_8\) permeance of 1.1×10\(^{-8}\) mol m\(^{-2}\) Pa\(^{-1}\).\(^{41}\) By using the secondary growth method, Yao et al. prepared continuous ZIF-8 membranes in a diluted aqueous solution with a Zn\(^{2+}\):hmm: H\(_2\)O molar ratio of 1:70:4952, and their thicknesses were about 0.8-1.4 µm. ZIF-8 membranes and micro-sized crystals could be prepared simultaneously in such diluted aqueous solution. Gas permeation tests indicated the ZIF-8 membranes were continuous and compact.\(^{42}\)

As hollow fiber membranes can be easily assembled into compact membrane modules for industrial separation processes, the development of ZIF hollow fiber membranes is desirable for practical applications. Xu et al. prepared ZIF-8 membranes on the outer surface of alumina hollow fibers from a concentrated synthesis gel by three times of solvothermal synthesis.\(^{43}\) The crystalline ZIF-8 membranes were compact and continuous, and contained micro-cavities. Single gas permeances of H\(_2\), N\(_2\), CH\(_4\) and CO\(_2\) were determined as a function of permeation time at 25°C. H\(_2\), N\(_2\) and CH\(_4\) permeances almost did not change with the permeation time. However, CO\(_2\) permeance decreased from 9.8×10\(^{-8}\) to 1.7×10\(^{-8}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\) within 12 h, and CO\(_2\) permeation led to an unrecoverable reduction in gas permeation rates in the further permeation experiments. After the first round tests, H\(_2\), N\(_2\), CH\(_4\) and CO\(_2\) permeances in the second round permeation tests dropped by 40%, 24%, 11%, and 6%, and remained constant in the further repeated measurements; the ideal selectivities of H\(_2\)/CO\(_2\), N\(_2\)/CO\(_2\) and CH\(_4\)/CO\(_2\) were 32.2, 12.9, and 11.9, respectively. For a H\(_2\)/CO\(_2\) binary mixture (45% H\(_2\)), the H\(_2\)/CO\(_2\) separation factor was 7.1. The small CO\(_2\) permeance should arise from strong CO\(_2\) adsorption in ZIF-8 membranes with microcavities, and the adsorbed CO\(_2\) partially blocked the gas permeation.\(^{39}\) Such membranes may be further explored for CO\(_2\) related separation applications. By a crystallizing-rubbing seed deposition and secondary growth, a continuous well-intergrown ZIF-8 membrane on hollow ceramic fiber tube was synthesized. The obtained ZIF-8 membrane was compact and continuous, with a thickness of about 5 µm. The membrane displayed high H\(_2\) molecular sieve separation performance. Specifically, the H\(_2\) permeance reached an excellent value of 1.1×10\(^{-6}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\), and the ideal separation factors for H\(_2\)/CO\(_2\), H\(_2\)/N\(_2\) and H\(_2\)/CH\(_4\) were calculated to be 5.2, 7.3 and 6.8 at room temperature, respectively.\(^{44}\) Pan et al. prepared yttria-stabilized zirconia (YSZ) hollow fiber-supported ZIF-8 membranes by using a mild and environmentally friendly seeded growth method in aqueous solution. Single gas permeation studies demonstrated that the membrane had a very high hydrogen permeance (1.5×10\(^{-6}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)) and an ideal selectivity of H\(_2)/C\(_3\)H\(_6\) of more than 1000 at room temperature (Fig. 3).\(^{45}\)

![Fig. 3. The permeation of single gases through ZIF-8 membrane in relation to the kinetic diameters of the gases measured at room temperature. Reprinted with permission from ref. 45. Copyright 2012 Elsevier.](image-url)
The secondary growth has been shown to be more effective for controlling the crystal orientation and thickness of ZIF membrane than the direct synthesis. For instance, a highly c-oriented and well intergrown ZIF-69 membrane on porous α-alumina substrates was prepared by seeded secondary growth method. For the single gas permeation, the permeance of CO$_2$ was higher than those of N$_2$, CO and CH$_4$. The possible reason was that the permeation behavior of CO$_2$ was controlled by surface diffusion, which was attributed to the strong selective adsorption of ZIF-69 for CO$_2$. The permeances of CO$_2$, N$_2$, CO and CH$_4$ were 23.6×10$^{-9}$, 10.6×10$^{-9}$, 8.2×10$^{-9}$ and 8.6×10$^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 298 K under 1 bar, respectively. The mixture-gas separation studies showed that the ZIF-69 membrane had separation factors of 6.3, 5.0, 4.6 for CO$_2$/N$_2$, CO$_2$/CO and CO$_2$/CH$_4$, respectively, and a permeance of ca. 1.0×10$^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for CO$_2$ in almost all mixtures. Both the separation factor and permeance were better than those of the ZIF-69 membranes prepared by the in situ solvothermal method due to improvement in the membrane microstructure (i.e. thickness and the oriented crystal direction) by the seeded growth method.

Shekhar et al. prepared an ultra-thin and defect-free ZIF-8 membrane on alumina substrate by the liquid phase epitaxy approach (step-by-step deposition). The thickness of the membrane was controllable in the range of ~0.5–1.6 µm with growth cycles of 150–300. The ideal selectivity obtained at 308 K was 5, 11, 12, 70 and 3.5 for H$_2$/CO$_2$, H$_2$/N$_2$, H$_2$/CH$_4$, H$_2$/C$_2$H$_6$ and C$_2$H$_6$/C$_2$H$_4$, respectively. However, the resultant membrane fabricated by this method exhibited significantly lower gas permeance. The significant decrease in gas permeance indicated the effective fabrication of a higher quality ZIF-8 continuous membrane with minimal grain boundary micro-defects. In the equimolar gas mixture, the selectivity for C$_2$H$_6$/C$_2$H$_4$ decreased with time, reaching a steady-state value of ~2.2 after 2 days. Such a ZIF-8 membrane showed a selectivity of 4 at 308 K in the separation of 75/25 CH$_4$/N$_2$ gas mixture after being tested at steady state for 30 h and the selectivity was improved to ca. 16 when the temperature was raised to 323 K.

Polymer-supported ZIF-8 membrane was first prepared on the porous Nylon membrane by the contra-diffusion method. Good compatibilities between ZIFs and polymers were expected due to favorable interactions between organic ligands and polymers. Ge et al. synthesized ZIF-8 thin layer on an asymmetrically porous polyethersulfone (PES) substrate via secondary growth. The continuous ZIF-8 layer containing microcavities had good affinity with the PES support. Molecular sieving separation was achieved for selectively separating hydrogen from larger gases. At 333 K, the H$_2$ permeance could reach ~4×10$^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, and the ideal selectivity of H$_2$ from Ar, O$_2$, N$_2$, and CH$_4$ were 9.7, 10.8, 9.9, and 10.7, respectively. The membrane showed stable hydrogen permeance and H$_2$/N$_2$ separation performance in the gas permeation tests. The binary gas selectivity exceeded the corresponding Knudsen selectivity. In order to improve the performance of ZIF membrane supported on polymer substrate, the flexibility of polymer substrate should be reduced to avoid ZIF layer cracking. Dehydrogenation, cyclization and crosslinking reaction of polyacrylonitrile (PAN) hollow fiber in solvothermal treatment could greatly improve the stiffness and compression strength of the support. A continuous and well intergrowth ZIF-8 membrane on PAN was successfully fabricated. Nargaraju et al. prepared ZIF-8 membrane supported on a polysulfone based porous asymmetric ultrafiltration membrane by the Layer-by-Layer deposition of crystals and subsequent crystal growth. The H$_2$/C$_2$H$_4$ and H$_2$/CO$_2$ selectivity was increased by ~45% and 25%, respectively.
ZIF-90 could be prepared through solvothermal reaction of zinc(II) salt and imidazolate-2-carboxaldehyde (ICA), and showed permanent microporosity with a narrow size of the six-membered ring pores (~3.5 Å). ZIF-90 was used as an example to show that it was possible to synthesize continuous ZIF membranes on polymeric hollow fiber surfaces by a facile, low-temperature, technologically scalable method. By dip-coating of ZIF-90 crystals (~400 nm) and secondary growth, continuous ZIF-90 membranes were fabricated on macroporous Torlon® (a polyamide-imide) hollow fibers. Torlon was chosen as a suitable substrate polymer for separation applications because it is chemically resistant, withstands high pressures (up to 2000 psi) without plasticization, and is amenable to the engineering of hollow fibers of controlled macroporosity. Single-gas permeation showed a strong trend of decreasing permeance with increasing kinetic diameter, showing that the permeation properties are mainly influenced by transport through the ZIF-90 pores and not through defects such as pinholes, cracks, or grain boundaries. The CO₂/N₂ and CO₂/CH₄ selectivities of 3.5 and 1.5, respectively are above the Knudsen selectivities (0.8 and 0.6), further confirming that gas transport is mainly through the ZIF-90 crystals. For the single-component pervaporation test, the permeance of n-hexane, benzene, and cyclohexane were 3900, 600, and 5400, respectively above the Knudsen selectivities (414 and 4.14). ZIFs have been used to improve the separation properties of other membranes. For example, vertically-aligned carbon nanotube forests fabricated by chemical vapor deposition (CVD) growth were made into membranes by filling epoxy into the interstices, followed by mechanical polishing to open the CNTs. These membranes had characteristically high permeation fluxes (1-2 orders greater than the Knudsen flow) and low hydrogen selectivities (H₂/Ar=4.14, H₂/O₂=3.82, H₂/N₂=3.48, H₂/CH₄=2.58 and H₂/CO₂=4.89). To improve the gas separation performance, a ZIF-8 layer of about 5-6 μm was synthesized onto the surfaces of the aligned carbon nanotube membranes via secondary seeded growth. The ideal selectivities of H₂ to CO₂, Ar, O₂, N₂, and CH₄ of the ZIF-8 membrane were significantly improved, reaching up to 4.9, 7.0, 13.6, 15.1 and 9.8, respectively with a H₂ permeance of ca. 8.1×10⁻⁸ mol m⁻²s⁻¹Pa⁻¹. Demdre reported the synthesis of the continuous, inter-grown ZIF-8 membrane via the secondary growth method on a carbon nanotube bucky-paper. ZIF-8 crystals were seeded and strongly anchored onto porous carbon nanotube bucky-paper supports and hydrothermally grown into a dense and continuous ZIF-8 network. The high selectivity of N₂ over Xe demonstrated that the membranes were nearly defect-free and that the growth procedure was successful for creating an even interface between the CNTs and the ZIF-8 crystals. The low CO₂ selectivity over N₂ was shown to be related to very strong physisorption between the CO₂ and 2-methylimidazole molecules remaining within the ZIF-8 matrix. Mixed gas permeation tests (equimolar N₂/CO₂) confirmed this trend as nitrogen was found to permeate nearly 7 times faster than CO₂. The commercial anodic aluminum oxide (AAO) membrane was also used as the support to the preparation of ZIF-8-AAO composite membrane by a fast in situ seeding and secondary growth method. ZIF-8 nanocrystals were plugged in the AAO nanochannels to form the separation layer and the ZIF-8-AAO composite membrane exhibited high gas separation performance with H₂/CO₂ and H₂/N₂ ideal selectivities of 6.38 and 4.19, respectively.

From the literature, it is clear that seeded secondary growth has been used as a predominant method for growth of ZIFs on different substrates. This method offers better controllability in the formation of membranes by tailoring the crystal size of ZIF seeds, the seeding density and the interactions between seeds and substrate and optimizing the secondary growth process.

<table>
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<th>Type</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Membrane thickness (μm)</th>
<th>Synthesis method</th>
<th>Temp. Permeance (×10⁻⁷ mol m⁻²s⁻¹Pa⁻¹)</th>
<th>Ideal selectivity</th>
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<td>Direct synthesis</td>
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DMF: N,N-dimethylformamide, 1 GPU = 1 × 10$^4$ cm s$^{-1}$ cm Hg$^{-1}$

2.3. Surface functionalization and special seeding

Due to semi-organic nature of ZIFs, organic functionalization of the substrate surface, creation of seeding layer by chemical reactions on the substrate, and post-functionalization have attracted growing attention, and they provide additional means for facilitating ZIF crystallization on substrates and modifying ZIF membrane surface, thus improving the quality of ZIF membranes.

2.3.1. Surface functionalization by covalent linkers and post-functionalization

In order to provide active sites for nucleation and enhance the adhesion between ZIF membranes and supports, many methods have been developed to modify the surface of the supports. In addition, post-functionalization has been carried out to improve the selectivity of membranes. In this section, the surface functionalization and post-functionalization by attaching different functional groups will be discussed.

ZIF-90 is a good candidate for separating H$_2$ from other large molecules. By using 3-aminopropyltriethoxysilane (APTES) as a covalent linker, a continuous ZIF-90 membrane was prepared by Huang and co-workers. A preparation scheme is shown in Fig. 6. In the first step, the ethoxy groups of the APTES react with surface hydroxyl groups of the Al$_2$O$_3$ support. In the second step, the amino groups react with the aldehyde groups of imidazolate-2-carboxaldehyde via imines condensation, and then the nucleation and crystal growth of the ZIF-90 start at these fixed sites on the surface of the porous ceramic supports. The ideal selectivities of H$_2$ from CO$_2$, N$_2$, CH$_3$, and C$_2$H$_4$ were 7.2, 12.6, 15.9, and 63.3, respectively, suggesting that ZIF-90 membrane displayed molecular sieving performance with a high H$_2$ permeability. For the 1:1 binary mixtures, the mixture separation factors of H$_2$/CO$_2$, H$_2$/N$_2$, H$_2$/CH$_4$, and H$_2$/C$_2$H$_4$ were 7.3, 11.7, 15.3, and 62.8, respectively, which by far exceeded the corresponding Knudsen selectivities (4.7, 3.7, 2.8, and 3.7, respectively).

As reported by Yaghi and co-workers, the free aldehyde groups in the ZIF-90 framework allow the covalent functionalization with amine groups by an imine condensation reaction. Reprinted with permission from ref. 65. Copyright 2010 American Chemical Society.
functionalization, the H₂/O₂ selectivity could be increased from 7.3 initially to 62.5. The modified ZIF-90 membrane showed good stability in 3 vol% steam at 200 °C for 48 h, and was stable at 325 °C in the H₂/O₂ separation for at least 24 h. They used APTES to post-modify ZIF-90 by forming covalent linkages between the free aldehyde groups of the ZIF-90 and the amino group of APTES. The post-functionalization process could be finished in 30 min by refluxing the ZIF-90 membrane in APTES methanol solution. However, the similar process using ethanolamine as reactant was rather long (usually over 10 h), leading to some decomposition of ZIF-90 material. For equimolar binary mixtures at 225 °C and 1 bar, the separation factors of CO₂/CH₄, H₂/CO₂, H₂/CH₄, H₂/CH₃OH, and H₂/C₃H₈ mixtures were found to be 4.7, 20, 71, 250, and 458, and a relatively high H₂ permeance of about 2.9×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ could be obtained to avoid pore blocking.

A ZIF-90 membrane was successfully grown on inner surface of A hybrid ZIF-9-67 membrane on α-Al₂O₃ support was developed by using a mixed-linker synthesis method. The alumina supported was modified with vinyltrimethoxysilane and then oxidized to terminating vinyl group. Compared with the existing ZIF membranes, this ZIF-9-67 hybrid membrane exhibited good ideal selectivities for H₂/CO₂, CH₄/CO₂, CO₂/CO₂, and N₂/CO₂ while having high permeances of H₂, CH₄, CO and N₂. Furthermore, the ZIF-9-67 hybrid membrane was less permeable to CO₂ than all other gases tested. Therefore, this membrane is very promising for efficient CO₂ removal from industrial mixtures that are composed of these gases. As mentioned before, the addition of polyethyleneimine in the dip-coating solution is important to prepare continuous and dense membranes because the polyethyleneimine acted as the linkers between ZIF nanocrystals and the substrates.

By using the organosilane as the binder, ZIF-8 films with controllable thickness were grown on a modified substrate at room temperature. The 3-(2-imidazolin-1-yl)propyltrioctoxysilane (PITPS) was used to form a pseudo-surface of ZIF-8 on a glass substrate, followed by layer-by-layer growth (Fig. 8). The film thickness of ZIF-8 was controlled within the range from 220 to 640 nm per growth cycle by changing the reactivity of the zinc source. The reactivity of zinc acetate was lower than that of zinc nitrate at the same concentration, and dense ZIF-8 films were obtained using a low reactivity growth solution. By the similar technique, (110)-oriented ZIF-8 thin films with controllable thickness were deposited on indium tin oxide (ITO) electrodes at room temperature. APTES was used as the covalent linkers, and the layer-by-layer method was then applied to coat the ZIF-8 thin films. The observed cross-sectional SEM images and fluorescence spectra of the ZIF-8 thin films indicated that the number of layers grown was proportional to the number of immersion cycles. The crystallographic preferential orientation (CPO) index showed that the ZIF-8 thin films were (110)-oriented.

A ZIF-8 membrane was successfully grown on inner surface of
hollow fiber from cycling precursors (Fig. 9). APTES effectively enhanced the heterogeneous nucleation of the ZIF-8 crystals. After the modified in-situ seeding process, a strong adhesive and uniform ZIF-8 seeding layer was formed on the inner surface of the APTES modified ceramic hollow fiber in a single step. The as-prepared inner-side hollow fiber ZIF-8 membrane was of high integrity and thin. The ideal selectivities of H$_2$ over CO$_2$, N$_2$, and CH$_4$ are 3.54, 12.28 and 13.41, respectively. The permeation behaviors of binary gas mixtures (H$_2$/CO$_2$, H$_2$/N$_2$ and H$_2$/CH$_4$ with an equal volume ratio) were also studied. As the separation factors of H$_2$/CO$_2$, H$_2$/N$_2$ and H$_2$/CH$_4$ were 3.28, 11.06 and 12.13, respectively.

2.3.2. Surface special seeding

In addition to the formation of functional linkers on substrate surface, a number of other methods including imidazolate deposition, precursor infiltration and reactive seeding, have been shown to be effective for substrate modification for facilitating ZIF crystallization. Jeong et al. reported the hot support modification by imidazolate linkers (Fig. 10) to create strong covalent bonds between α-Al$_2$O$_3$ supports and imidazolate ligands, which promoted the heterogeneous nucleation and growth of ZIF crystals. ZIF-8 membrane was then prepared by the solvothermal synthesis, and the resulting ZIF-8 membranes was continuous and well-intergrown with a thickness of ca. 12 µm, exhibiting ideal selectivities of 11.6 and 13 for H$_2$/N$_2$ and H$_2$/CH$_4$, respectively. ZIF-7 films were also fabricated to demonstrate the potential for general applicability of this method. Tao et al. used the hot dip-coating seeding method to prepare alumina hollow fiber supported ZIF-8 membrane. A preheated alumina hollow fiber (150 °C, 4 h) was immediately dipped into a 1.5 wt% ZIF-8 seed suspension for 20 seconds. The dispersed ZIF-8 crystals rapidly moved to the support and sank into the support channels under the capillary and vacuum forces during this process. Thus, a uniform and robust seed layer could be formed on the support. Subsequently, the seeded support was dried and subjected to a solvothermal synthesis. The resulting ZIF-8 membrane revealed a molecular sieving behavior, and the ideal selectivities for H$_2$/CO$_2$, H$_2$/O$_2$, H$_2$/N$_2$ and H$_2$/CH$_4$ were calculated to be 5.4, 7.1, 9.2 and 10.8, respectively, which are much higher than corresponding Knudsen factors.

By infiltrating precursors into a porous alumina support as a seed-and-nutrient layer, Li et al. developed a new method to synthesize ZIF-8 membrane. The alumina support was immersed in melting 2-methylimidazole (~145 °C) and then hydrothermally treated at zinc nitrate aqueous solution. A precursor layer with a thickness of about 10 µm was formed inside the porous alumina support, and after solvothermal synthesis, the ZIF-8 membrane grew from both the seeds embedded in the precursor layer and the synthesis solution under solvothermal synthesis conditions. A continuous and stable ZIF-8 membrane with a thickness of ca. 12 µm and an intermediate layer of ca. 10 µm was prepared at 120 °C for 8 h (Fig. 11). Gas permeation tests indicated the membrane was continuous and compact, and had H$_2$/N$_2$ ideal selectivity of 5.7 with a H$_2$ permeance of 1.7×10$^{-7}$ mol m$^{-2}$ Pa$^{-1}$ s$^{-1}$. An electrospinning technique has also been introduced into the synthesis of supported microporous membranes. A continuous and uniform seed coating composed of ZIF-8 and polyvinylpyrrolidone (PVP) was coated on the support surface, and the thickness of the seed layer could be precisely controlled. ZIF-8 membrane was then prepared by the secondary growth method. The resulting ZIF-8 membranes exhibited H$_2$/N$_2$, H$_2$/CO$_2$ and H$_2$/CH$_4$ separation factor of 4.94, 7.31, and 4.84, respectively, with the H$_2$ permeance of about 3.3×10$^{-7}$ mol m$^{-2}$ Pa$^{-1}$ s$^{-1}$. By electrospinning of ZIF-8 and PVP mix solution, it was possible to fabricate the self-supported non-woven ZIF-8/PVP fiber mat. The adsorption measurements showed that the ZIF-8 nanoparticles were fully accessible, and such ZIF textile could be useful for gas adsorption and separation.

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The reactive seeding method was first developed for the preparation of continuous MOF MIL-53 and MIL-96 membranes on alumina porous supports, in which the porous support acted as the inorganic source reacting with the organic precursor to grow a seeding layer. Dong et al. used the reactive seeding method to prepare ZIF-78 membrane on ZnO support. The GME ZIF-78 consists of divalent zinc cations bridging by 2-nitroimidazolate and 5-nitrobenzimidazolate anions, and the cage size in ZIF-78 is 7.1 Å and the window size is 3.8 Å. However, the removal of organic solvents from the ZIF crystals is one of the key steps and a challenge in preparing high-quality ZIF membranes. For instance, given that DMF has a kinetic diameter of 5.5 Å, it is not easy to remove it through the narrower ZIF-78 windows due to the relatively rigid imidazolate frameworks, and hence DMF removal may induce intercrystalline defects or even cracks in the membranes and a loss of performance. The authors used a new solvent activation-exchange method to achieve effective removal of DMF, where a series of methanol-DMF mixtures with different methanol concentrations of 25, 50, 75 and 100 vol% were used.

The membrane activation process is illustrated in Fig. 12. The single gas permeation of H₂, N₂, CH₄, and CO₂ was tested on ZIF-78 membrane, and the permeance of these small gas molecules decreases in the order H₂ > N₂ > CH₄ > CO₂, with increasing the molecular sizes except for CO₂. The ideal selectivities of H₂/CO₂, H₂/N₂ and H₂/CH₄ are 11.0, 6.6 and 6.0, respectively. The relatively low permeance of CO₂ was attributed to the strong interaction between CO₂ and ZIF-78 frameworks because of the dipole-quadrupole interactions between -NO₂ and CO₂. For the binary gas mixture, the separation factors of H₂/CO₂, H₂/N₂ and H₂/CH₄ were 9.5, 5.7 and 6.4, respectively. All these mixture-separation factors exceeded the corresponding Knudsen diffusion selectivity values. ZIF-8 was also grown on alumina hollow fibers by the reactive seeding method. A 0.5 µm thick nanoporous ZnO layer was deposited on the inner surface of the hollow fiber by the slip-casting method. The hollow fiber was then treated with 2-methylimidazole solution to activate the ZnO layer for ZIF-8 deposition, followed by the secondary growth to prepare the low-defect ZIF-8 layer with a thickness of about 8 µm. The ZIF-8 membrane showed a high H₂ permeance of 2.08 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹ with H₂/N₂, H₂/CH₄, H₂/C₇H₈, H₂/n-C₇H₁₅ and H₂/SF₆ ideal selectivities of 10.3, 10.4, 149.6, 195.7 and 281.5, respectively. Table 3 summarizes the mixed gas separation data obtained from various ZIF membranes discussed in this review for easy comparison (more details in S-Table 1, Supplementary Information).

Despite the gas separation has been the main focus for the development of ZIF membranes, liquid separation via pervaporation has also been demonstrated. By the same reactive seeding method, an integrated ZIF-71 membrane was prepared for the first time and used for pervaporation separation of alcohol (methanol and ethanol)-water and dimethyl carbonate (DMC)-methanol mixtures. The ZnO support was used to react with 4,5-dichlorimidazole (dclm) to produce the seed layer. The ZIF-71 membrane showed good pervaporation performance especially in DMC-methanol separation. The total flux and separation factor in the separation of 5 wt% DMC-MeOH at 25 °C were 271 g m⁻² h⁻¹ and 5.34, respectively. Fan et al. developed a novel approach to synthesize ZIF-78 membrane by replacing the crystal seeds with nanosized amorphous ZIF-78 precursors, which could provide better distributed nucleation sites. During the secondary growth process, the crystal size and intergrowth degree of the membrane was adjusted by adding triethylamine to the reaction solution. The high quality membrane synthesized under this method was tested for pervaporation separation of cyclohexanone/cyclohexanol mixture with equal volume ratios at room temperature with permeability of 1.2 and total flux around 8.7 × 10⁻⁷ kg m⁻² h⁻¹. The above work demonstrated that ZIF-71 and ZIF-78 were promising membrane materials for the pervaporation separation of not only organics-water but also organics-organics systems.
Table 3. Mixed binary gas (1:1) separation data obtained from various ZIF membranes discussed in this review.

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2.4. Contra-diffusion (counter-diffusion) synthesis

In the contra-diffusion synthesis, two precursor solutions (e.g., metal ion solution and organic ligand solution) separated by a porous substrate counter-diffuse through the porous channels of the substrate; ZIF nucleation and crystallization start on the substrate when the two solutions meet with each other. Such a methodology is similar to that developed for mesoporous silica and zeolite membrane synthesis. But in the ZIF synthesis, diffusion rates of metal ion solution and imidazolate solution can be different because of their different interactions with the substrates. Therefore, in conjunction with surface modification and seeding of substrate, the contra-diffusion method provides more degrees of freedom in controlling the synthesis of ZIF membranes.

Yao et al. for the first time extended the contra-diffusion method to prepare ZIF-8 on a macroporous Nylon membrane. Zinc nitrate methanol solution and 2-methylimidazole methanol solution are separated by the porous Nylon membrane (Fig. 13a). Similar to the synthesis of single crystals by slow diffusion, the...
two solutions crossover the Nylon membrane and crystallize at the interface (Fig. 13b). After 72 h of contra-diffusion synthesis, a continuous film with a thickness of ca. 16 µm was formed on the zinc side, and exhibited a H$_2$/N$_2$ ideal selectivity of 4.3 with H$_2$ permeance of 1.97×10$^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and N$_2$ permeance of 4.6×10$^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. By using the same contra-diffusion method, ZIF-8 films were prepared on both sides of Nylon membrane in aqueous solutions using a stoichiometric ratio of Zn$^{2+}$ and 2-methylimidazole (hmim) with the addition of ammonium hydroxide.$^{75}$ ZIF-8 films prepared with a Zn$^{2+}$: hmim: NH$_4^+$ molar ratio of 1: 2: 32 at room temperature for 24 h exhibited an intergrown ZIF-8 layer on hmim side with a thickness of ca. 2.5 µm, which was greatly reduced compared to that prepared in methanol solvent. The membrane exhibited H$_2$ and N$_2$ permeance of 1.13×10$^{-6}$ and 2.45×10$^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, respectively, with a H$_2$/N$_2$ ideal selectivity of 4.6.

![Fig. 13.](image)  
(a) Diffusion cell for ZIF-8 film preparation and (b) the schematic formation of ZIF-8 films on both sides of nylon support via contra-diffusion of Zn$^{2+}$ and Hmim through the pores of Nylon support.

Reproduced from Ref.54.

Yang et al. further modified the contra-diffusion method to promote ZIF-8 growth on substrate. They chemically modified the support by depositing 3-aminopropyltriethoxysilane (APTES)-functionalized Al$_2$O$_3$ particles onto a coarse macroporous support (Fig. 14). The two synthesis solutions: zinc nitrate solution and 2-methylimidazole solution were separated by the deposited support, and the crystallization was carried out at 150 °C for 5 h. APTES grafted on the α-Al$_2$O$_3$ particles played an important role in growth of ZIF-8 membrane. A continuous, defect-free and thin ZIF-8 membrane was successfully prepared and exhibited remarkably high H$_2$ permeance of 5.73×10$^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ with H$_2$/N$_2$ and H$_2$/CO$\text{2}$ ideal selectivity of 15.4 and 17.0, respectively.$^{76}$ Very recently, Hara et al. prepared ZIF-8 membranes on the outer surface of porous alumina hollow fibers using the counter diffusion method, resulting in the formation of an 80 µm-thick ZIF-8 layer.$^{77}$ The zinc nitrate methanol solution was kept in the inner section of the hollow fiber, and then immersed the hollow fiber in the 2-methylimidazole methanol solution at 50 °C for a predefined reaction time (e.g. 72 h). The ZIF-8 membrane permeances of hydrogen and propylene reached 9.1×10$^{-8}$ and 2.5×10$^{-8}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, respectively. The ideal selectivities for H$_2$/C$_3$H$_6$ and C$_3$H$_4$/C$_2$H$_8$ at 25 °C were found to be 2000 and 59, respectively.$^{77}$

![Fig. 14.](image)  
Schematic diagram of the “two-in-one” strategy of deposition of chemically modified α-Al$_2$O$_3$ particles onto the support for preparation of ZIF-8 membrane: (a) support; (b) support with deposition of chemically modified α-Al$_2$O$_3$ particles; (c) ZIF-8 membrane constructed on the deposited support prepared using chemically modified α-Al$_2$O$_3$ particles. Reproduced from Ref.76.

Jeong et al. developed in situ counter-diffusion method to form ZIF-8 membranes. The zinc source was pre-deposited in the porous alumina support and then diffused out in the 2- methylimidazole solution to form ZIF-8 membrane at the interface of the porous support (Fig. 15) under solvothermal synthesis for 4 h at 120 °C, and the resulting ZIF-8 membranes exhibited high separation performance toward propylene over propane.$^{88}$ The high-quality ZIF-8 membranes showed an excellent separation performance for a propylene/propane (50/50) mixture (selectivity ~55). Furthermore, the ZIF-8 membranes were found to be mechanically very strong with their separation performance maintained high even after 2 h of intensive sonication. The prototypical ZIF-7 and SIM-1 membranes were also successfully synthesized using this counter-diffusion method. Similarly, by using microwave heating, a densely packed ZIF-8 seed layer could be rapidly formed on porous alumina supports in the aqueous solution by the same research group.$^{89}$ The microwave seeding process involves three steps: (1) saturation of a porous support with a metal precursor solution, (2) exposure of the support soaked with metal ions to a ligand precursor solution, and (3) rapid crystal formation under microwave irradiation. It is critically important to maintain relatively high concentrations of both metal ions and ligand molecules in the vicinity of the support (“reaction zone”) by soaking the support with metal ions prior to microwave irradiation. The high-quality ZIF-8 membranes exhibited an average propylene/propane selectivity of ca. 40. The unique feature of the counter-diffusion synthesis allowed the poorly intergrown membranes to be healed. Furthermore, ZIF-7 and SIM-1 membranes were also synthesized using this method to demonstrate its potentially general applicability.
3. ZIF/polymer mixed matrix membranes

Mixed matrix membranes are another important class of membranes being pursued over the last decades. They are composed of a polymer and a dispersed additive, and have great potential to achieve high separation properties and scale up for industrial applications by taking advantage of both materials. In a dense polymer membrane, the separation process is based on the solution-diffusion mechanism (Fig. 16). The selectivity is determined by two factors: the components solubility and the diffusivity. Many studies have shown that the separation properties of polymer membranes can be significantly improved by incorporation of a dispersed phase including carbon molecular sieves, zeolites, mesoporous materials, activated carbons, carbon nanotubes, and metal-organic frameworks. The composite membranes thus prepared are commonly referred to as mixed matrix membranes (MMMs).

The Maxwell model as shown below has been widely used for the performance prediction of mixed matrix membranes:

$$P_{\text{eff}} = P_c \left[ \frac{P_0 + 2P_c - \Phi_d (P_c - P_d)}{P_0 + 2P_c + \Phi_d (P_c - P_d)} \right]$$

where $P_{\text{eff}}$ is the effective permeability, $P_c$ and $P_d$ represent the permeabilities of the continuous phase and dispersed phase, respectively, and $\Phi_d$ is the volume fraction of the dispersed phase.

Like other mixed matrix membranes, ZIF/polymer membranes are usually prepared by dispersing ZIF particles in a polymer solution and using conventional polymer membrane fabrication techniques such as solution casting and hollow fiber spinning. However, in many cases, there exists a significant problem associated with the compatibility of the polymeric and inorganic phases for optimum dispersion and interfacial contact, which only allows for moderate loadings of dispersed materials.

Compared with other materials, ZIFs (MOFs) with functional ligands intrinsically have better compatibility; importantly, many different types of ZIFs are available, ZIF/polymer mixed matrix membranes with more functionalities can be developed.

Polyimides are very attractive for gas separation due to their high gas selectivity, high chemical, thermal, and mechanical resistance. ZIF-8/Matrimid® MMMs were fabricated with loadings up to 80 wt%, which were much higher than the typical loadings achieved with selected zeolite materials. Only at the highest loading did the ZIF-8/Matrimid® composite membranes show a loss of mechanical strength, leading to a decrease in flexibility. The ZIF-8/Matrimid® MMMs permeation properties were tested for $H_2/CO_2, H_2/O_2, H_2/CH_4, CO_2/CH_4,$ and $H_2/C_2H_6,$ and gas mixtures of $H_2/CO_2$ and $CO_2/CH_4.$ The permeability values increased as the ZIF-8 loading increased to 40% (w/w). However, at higher loadings of 50% and 60% (w/w), the permeability decreased for all gases, and the selectivities increased consistent with the influence of the ZIF-8 additive. The ideal selectivities of gas pairs containing small gases, such as $H_2/O_2, H_2/CO_2, H_2/CH_4, CO_2/CH_4,$ $CO_2/C_2H_6,$ and $H_2/C_2H_6,$ showed improvement with the 50% (w/w) ZIF-8 loading, demonstrating a transition from a polymer-dominated to a ZIF-8-controlled gas transport process. Song et al. directly incorporated as-synthesised ZIF-8 nanoparticles (~60 nm) into a model polymer matrix (Matrimid® 5218) by solution mixing, and produced flexible transparent membranes with excellent dispersion of nanoparticles and good adhesion within the polymer matrix. Pure gas permeation tests showed enhanced permeability of the mixed matrix membrane with negligible losses in selectivity. For the ZIF-8/Matrimid® membrane with a 20% ZIF-8 loading, the permeability of $H_2, CO_2, O_2, N_2$ and $CH_4$ was 63.53, 16.63, 5.63, 0.88 and 0.46 Barrer, respectively, with $H_2/N_2, H_2/CH_4, CO_2/CH_4$ and $O_2/N_2$ ideal selectivity of 72.5, 137.0, 35.8 and 6.4, respectively.

Table 4 summarizes the ZIF/polymer mixed matrix membranes and their performance for gas separation and pervaporation. In addition, for the ZIF-8/Matrimid® composite membranes, the ultrasonication treatment induced significant changes in the shape, size distribution, and structure of ZIF-8 particles suspended in an organic solvent during membrane processing. The membrane with 25 wt% ZIF-8 loading fabricated with high-intensity sonication showed significantly enhanced CO$_2$ permeability (23.2 Barrers) and increased CO$_2$/CH$_4$ ideal selectivity (39). In contrast, the composite membranes prepared with low-intensity sonication were found to be ineffective. Positron annihilation lifetime spectroscopy (PALS) indicated that the increase in the free volume of the polymer with ZIF-8 loading...
together with the free diffusion of gas through the cages of ZIF-8 contributed to an increase in gas permeability of the composite membrane, and the gas transport properties of the composite membranes could be well predicted by Maxwell model.100 Yang et al. demonstrated, for the first time, the incorporation of ZIF-7 nanoparticles into the polybenzimidazole (PBI) polymer matrix without much ZIF agglomeration by using an excessive amount of benzimidazole during the ZIF-7 synthesis. PBI was specifically chosen because it has remarkable resistance to high temperatures (up to 500 °C) with superior compression strength. In addition to exhibiting characteristics of high transparency and mechanical flexibility, the resultant composite membranes showed superior separation performance with enhanced H₂ permeability and ideal H₂/CO₂ permeability selectivity compared to both neat PBI and ZIF-7 membranes.102 For the composite membranes, the gas permeability of H₂ exhibited significant enhancement with increasing ZIF-7 loadings, from 3.7 Barrer for pure PBI to 26.2 Barrer for 50/50 (w/w) ZIF-7/PBI, while the ideal selectivity of H₂/CO₂ improved from 8.7 to 14.9. For the H₂/CO₂ binary mixture, the separation factor of H₂/CO₂ was almost the same (6.8-7.2) with increasing ZIF-7 loading, but the H₂ permeability increased from 2.9 Barrer for pure PBI to 13.3 Barrer for 50/50 (w/w) ZIF-7/PBI.102 In another attempt, ZIF-8 nanoparticles were incorporated into PBI, and the 30/70 ZIF-8/PBI dense membrane had a H₂ permeability of 105.4 Barrer and a H₂/CO₂ ideal selectivity of 12.3 at 180 °C.103 This performance is far superior to ZIF-7/PBI membranes.102 Intercalation may occur when one local particle loading is high enough that some of them bridge one another across the entire membrane thickness. As a result, gas penetrants preferentially transport across the membranes via low-selectivity ZIF-8 particles (Fig. 17). The incorporation of ZIF-8 particles significantly enhanced both solubility and diffusion coefficients but the enhancement in diffusion coefficient was much greater. Mixed H₂/CO₂ separation tests were conducted from 35 to 230 °C, and ZIF/PBI membranes exhibited remarkably high H₂ permeability and H₂/CO₂ selectivity. The 30/70 (w/w) ZIF-8/PBI membrane had an H₂/CO₂ selectivity of 26.3 with an H₂ permeability of 470.5 Barrer, while the 60/40 (w/w) ZIF-8/PBI membrane had an H₂/CO₂ selectivity of 12.3 with an H₂ permeability of 148.4 Barrer at 230 °C. However, at 35 °C, the 60/40 (w/w) ZIF-8/PBI membrane had an H₂/CO₂ selectivity of only 2.8 with an H₂ permeability of 669.9 Barrer. Mixed gas data showed that the presence of CO or water vapor impurity in the feed gas stream did not significantly influence the membrane performance at 230 °C.104

![Fig. 17. Proposed scheme for gas transportation paths through the nano composite membranes at lower and higher particle loadings. Reprinted with permission from ref. 103. Copyright 2012 John Wiley & Sons, Inc.](image-url)

It was observed that the solubility coefficient of CO₂ increased from 6.6×10⁻² cm² (STP) cm⁻³ cmHg⁻¹ for the PPEES (poly(1,4-phenylene ether-ether-sulfone)) membrane to 0.116 cm² (STP) cm⁻³ cmHg⁻¹ for the membrane with 30% (w/w) of ZIF-8 filler.105 Diaz et al. also fabricated ZIF-8/PPEES mixed matrix membrane.106 The incorporation of ZIF-8 increased the permeability coefficient without significantly affecting the ideal selectivity. The higher the ZIF-8 loading the better the membranes permeability, and the diffusive process was mainly responsible for the selectivity of the membranes.105,106 The ideal selectivity of the ZIF-8/PPEES membrane (ZIF-8 30 wt%) for O₂/N₂ and H₂/N₂ at 303 K was close to that marked by the Robeson upper-bound for this pair of gases, whereas that of H₂/CH₄ and CO₂/CH₄ was about 50% of that predicted in the Robeson limit. The ideal selectivity for C₂H₆/C₃H₈ was 3, with a C₂H₆ permeability of 3.15 Barrer.

Using three 6FDA-based polyimides (6FDA-Durene, 6FDA-Durene/DABA (9/1), 6FDA-Durene/DABA (7/3), Fig. 18) and nano-sized ZIF-8, mixed matrix membranes with uniform morphology and as high as 40 wt% ZIF-8 loading were prepared by directly mixing as-synthesized ZIF-8 suspension into the polymer solution.107 Permeability of all gases (CO₂, CH₄, C₂H₆, and C₃H₈) increased rapidly with increasing ZIF-8 loading. However, the addition of ZIF-8 nanoparticles into the polymer matrix increased the CO₂/CH₄ ideal selectivity of only 6.8%, while the C₂H₆/C₃H₈ ideal selectivity improved by 134% from 11.68 to 27.38 for 6FDA-Durene/DABA (9/1) and 40 wt% ZIF-8. MMMs made of 6FDA-Durene did not show considerable improvements on resistance against CO₂-induced plasticization after annealing at 200-400 °C, while MMMs synthesized from cross-linkable co-polymides (6FDA-Durene/DABA (9/1) and 6FDA-Durene/DABA (7/3)) showed significant enhancements in CO₂/CH₄ and C₂H₆/C₃H₈ selectivity as well as plasticization suppression characteristics up to a CO₂ pressure of 30 atm after annealing at 400 °C due to the cross-linking reaction of the carboxyl acid (COOH) in the DABA moiety. The MMM made of 6FDA-Durene/DABA (9/1) and 40 wt% ZIF-8 possessed a notable C₂H₆/C₃H₈ ideal selectivity of 27.38 and a remarkable C₃H₈ permeability of 47.3 Barrers. After being thermally annealed at 400 °C, the MMM made of 6FDA-Durene/DABA (9/1) and 20 wt% ZIF-8 showed a CO₂/CH₄ selectivity of 19.61 and an impressive CO₂ permeability of 728 Barrer in mixed gas tests.107 ZIF-8 nanoparticles were also incorporated into 6FDA-DAM:DABA(4:1) (6FDA: 2,2-bis (3,4-carboxyphenyl) hexafluoroisopropanedioxydride and DAM: dianaminostyrene) to form the ZIF-8/6FDA-DAM:DABA(4:1) (20 wt% ZIF-8) dense films for CO₂ recovery from post-combustion flue gas streams. Good adhesion between the ZIF-8 and the 6FDA-DAM:DABA (4:1) matrix was observed. The dense film composites had a CO₂ permeability of 550 Barrers and a CO₂/N₂ selectivity of 19 at 35 °C.108 ZIF-8/6FDA-DAM mixed matrix dense membranes were formed with 6FDA-DAM and 200 nm ZIF-8 particles. SEM imaging showed generally good adhesion between the ZIF-8 and 6FDA-DAM without the need for surface-treating ZIF-8. Pure gas permeation showed significantly enhanced C₂H₆/C₃H₈ separation performance over the pure 6FDA-DAM membrane performance. A C₂H₆ permeability of 56.2 Barrer and C₃H₈/C₃H₈ ideal selectivity of 31.0 were found in ZIF-8/6FDA-DAM mixed matrix membrane with 48.0 wt% ZIF-8 loading, which were 258% and 150% higher than those for the pure 6FDA-DAM.
Permeation properties of ZIF-8 were back-calculated using the Maxwell model, which led to a C,H₆ permeability of 277 Barrer and C,H₄/C,H₆ ideal selectivity of 122. These results suggested that this polymer/ZIF-8 pair has the potential for application in reducing the energy intensity of C,H₆/C,H₄ separation process.

Bae et al. prepared ZIF-90 crystals with submicrometer and 2 µm sizes by a nonsolvent-induced crystallization technique, and incorporated them in 6FDA-DAM poly(imide) and two commercially available poly(imide)s (Ultem® 1000 (SABIC) and Matrimid® 5218 (Vantico)) to form the mixed matrix membranes. For ZIF-90/6FDA-DAM membrane with 15 wt% ZIF-90, the highest CO₂ permeability was 720 barrer with a CO₂/CH₄ separation factor of 37 in a 1:1 CO₂/CH₄ mixture; this membrane showed much better performance than the pure 6FDA-DAM membrane (CO₂ permeability of 390 and CO₂/CH₄ separation factor of 24). Nanocrystals of ZIF-90 were synthesized at room temperature through a novel procedure and incorporated into PBI for hydrogen purification. The derived ZIF-90/PBI nanocomposite membranes exhibited homogeneous particle dispersion and fine particle–polymer adhesion, as well as excellent hydrogen purification performance at various testing conditions. The 45/55 (w/w) ZIF-90/PBI membrane with the highest ZIF-90 volume loading of up to 50.9 vol% possessed the best ideal H₂/CO₂ separation performance with a moderate H₂ permeability of 24.5 Barrers and a high H₂/CO₂ ideal selectivity of 25.0 at 35 °C. The membrane also showed promoted gas separation performance during mixed gas tests at 180 °C with an H₂ permeability of 226.9 Barrers and an H₂/CO₂ separation factor of 13.3 that surpasses the latest Robeson upper bound for H₂/CO₂ separation. ZIF-7 nanocrystals with sizes of 30-35 nm were incorporated into commercially available poly (amide-b-ethylenoxide) (Pebax® 1657). The performance of the composite membrane was characterized by single gas permeation measurement of CO₂, N₂ and CH₄. Both permeability and gas selectivity (CO₂/N₂ up to 97 and CO₂/CH₄ up to 30) was increased at a low ZIF-7 loading (8 wt%). The CO₂/CH₄ ideal selectivity was further increased to 44 with the filler loading of 34 wt%, but the permeability was reduced compared to the pure Pebax® 1657 membrane. The membrane thickness of the 34 wt% ZIF-7 loading membrane was ~1 µm. Polymer chain rigidification at high filler loading was likely the reason for the reduced permeability. Overall, the ZIF-7/Pebax mixed matrix membranes showed a high performance for CO₂ separation from methane and other gas streams.

To improve gas selectivity, surface cross-linking was performed on mixed matrix membranes containing 33.3 wt% ZIF-8 filler in 6FDA-durene polyimide, by exposure to ethylenediamine (EDA) vapor for 40 min (Fig. 19). Adding 33.3 wt% loading of nanocrystalline ZIF-8 to 6FDA-durene resulted in approximately a 400% increase in hydrogen and oxygen permeabilities. After the MMM was reacted with EDA vapor, a 10 µm thick cross-linked skin on either side of the 70 µm thick membrane was observed. EDA cross-linking rendered ~10-fold increases in gas selectivities with respect to 6FDA-durene. The observed selectivities for the cross-linked MMM for H₂/CO₂, H₂/N₂, H₂/CH₄, and O₂/N₂ separations were 12, 141, 203, and 8.5, respectively, with corresponding hydrogen and oxygen permeabilities of 283.4 and 16.9 Barrers.

Ionic liquid was also used to prepare mixed matrix membranes. ZIF-8 nanoparticles were incorporated in miscible ionic liquid blend systems for natural gas sweetening and post-combustion CO₂ capture. The miscible blend systems consist of a polymerizable room temperature ionic liquid (poly(RTIL)) and a “free” room temperature ionic liquids (RTILs). Experimental results showed that the free ionic liquids were miscible with poly(RTIL), while ZIF-8 were uniformly dispersed in the MMMs. The presence of ZIF-8 nanoparticles in the MMMs considerably improved gas permeability without much sacrificing CO₂/N₂ and CO₂/CH₄ selectivities as compared to their poly(RTIL)/RTIL counterparts. The ZIF-8 [P[vibin][NTf₂]/[emim][B(CN)₃] (poly(RTIL)= P[vibin][NTf₂]/1-vinyl-3-butyl imidazolium-bis (trifluoromethyl-sulfonyl) imidate ; RTILs= [emim][B(CN)₃]; 1-ethyl-3-methylimidazolium tetracyanoborate) system with 25.8 wt% ZIF-8 exhibited impressive performance for post-combustion CO₂/N₂ (50/50 mol%) separation. It had a CO₂ permeability of 906.4 barrer and a CO₂/N₂ selectivity of 21 at 35 °C and 3.5 bar.

3.2. Symmetrical dense composite membrane for pervaporation

ZIF-8 nanoparticles exhibited exceptional adsorption selectivity and capacity toward isobutanol molecules, and showed a reversible gate-opening effect upon variation of the isobutanol pressure or temperature. Freshly synthesized ZIF-8 nanoparticles were incorporated into polyethyleneoxide (PMPS) to fabricate the ZIF-8/PMPS organophilic pervaporation membranes. The ZIF-8-PMPS membrane (WZF=8: WPMP=0.10)
showed a very promising performance for recovering bio-
alcohols from dilute aqueous solution. For pervaporation
recovery of isobutanol from aqueous 1.0-3.0 wt% solutions at
80 °C, the separation factor of isobutanol over H₂O was of 34.9-
40.1. Besides isobutyronitrile, the ZIF-8/PMPS membrane exhibited
higher selectivity and productivity for recovering other bio-
alcohols from water compared with the pure PMPS membrane
(Fig. 20). The pervaporation performance increases with the
carbon number of the alcohols because of the increased
adsorption selectivity and capacity. The decrease in separation
factor and permeability for n-pentanol is characteristic of the
interplay of adsorption and diffusion effects. However, ZIF-
7/PMPS membrane prepared by the same procedure showed a
lower separation factor and a lower isobutanol permeance
compared with the ZIF-8/PMPS membrane due to the
insignificant isobutanol adsorption of the ZIF-7 nanoparticles. ZIF-8
nanocrystals with improved hydrothermal stability were
achieved via a shell-ligand-exchange-reaction using 5,6-
dimethylbenzimidazole (DMBIM) as the stabilizer, and they were
incorporated into PMPS by the same research group for
pervaporation recovery of isobutanol from water. Compared with
the ZIF-8/PMPS membrane, the DMBIM stabilized ZIF-8/PMPS
exhibited improved selectivity towards isobutanol while keeping
the isobutanol flux constant. The ZIF-8/PMPS membrane was
also fabricated on a hierarchically ordered stainless-steel-mesh
(HOSSM) employing a novel “Plugging-Filling” method. The
membrane exhibited the highest pervaporation separation index
(separation factor 53.3 and total flux 0.90 kg m⁻² h⁻¹) and
excellent stability in a test of more than 120 h at 80 °C for
recovery of furfural (1.0 wt%) from water. This very high
performance should be attributed to the exceptional adsorption
selectivity and capacity of ZIF-8 toward furfural molecules (450
mg g⁻¹ for ZIF-8 nanoparticles) and the effects of space restriction
and physical cross-linking of the HOSSM.

ZIF-8/PBI mixed matrix membranes with a uniform dense
structure have been prepared for pervaporation dehydration of
ethanol, isopropanol (IPA) and butanol. As-synthesized ZIF-8
particles, with sizes smaller than 50 nm, were dispersed in the
PBI phase directly with a loading ranging from 12 wt% to 58
wt%. Pervaporation test data showed that the water permeability
of ZIF-8/PBI (1:1) composite membranes was about one order of
magnitude higher than the original PBI membrane (14,000-
22,000 vs. 1200-2300 Barrer) (Fig. 21). The degrees of
membrane swelling after immersing in alcohols and water
followed the order of ethanol > methanol > water > n-butanol.
Addition of ZIF-8 particles into PBI membranes suppressed the
ethanol-, methanol- and water-induced PBI swelling. The water-
induced swelling was subdued most severely because of the
hydrophobic nature and rigid structure of ZIF-8 particles, while
the n-butanol-induced swelling was enhanced owing to a greater
free volume in the ZIF-8/PBI membrane. ZIF-7 crystal
particles were successfully incorporated into chitosan (CS)
membranes to form ZIF-7/CS mixed-matrix membranes.
Glutaraldehyde (GA) cross-linkers were used to increase the
linking of the chitosan chains. In the H₂O/ethanol pervaporation
test, the separation efficiency of the membrane with 5 wt% ZIF-7
was 19 times higher than that of the pristine CS membranes
because of the rigidified polymer chain of the MMMs. The
highest H₂O/ethanol separation factor was 2812 with a total flux
of 322 g m⁻² h⁻¹.

Fig. 21. (a) Water permeability and (b) selectivity for water of PBI/ZIF-8
MMMs for pervaporation dehydration of alcohols (Feed: alcohol/water
85/15 wt% at 60 °C). Reprinted with permission from ref. 117. Copyright
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New mixed matrix membranes were prepared by incorporating
ZIF-71 particles into polyether-block-amide (PEBA) for
biobutanol recovery from acetone-butanol-ethanol (ABE)
fermentation broth by pervaporation. The incorporation of ZIF-71
particles into PEBA significantly improved the n-butanol
separation performance of the membranes. A simultaneous
enhancement in both separation factor and flux was achieved by
optimizing the amount of ZIF-71. The MMMs with 20 wt%
loading showed high total flux of 520.2 g m⁻² h⁻¹ and n-butanol
separation factor of 18.8 at 37 °C in model ABE solution. In
addition, the membrane exhibited stable performance in the real
ABE fermentation broth for 100 h with average total flux of
447.9 g m⁻² h⁻¹ and n-butanol separation factor of 18.4 (Fig. 22).
Hua et al. synthesized ZIF-90 nanoparticles with an average
particle size of 55 nm and embedded them into P84 polymeric
membranes with excellent dispersion for the dehydration of
isopropanol (IPA)/water mixture via pervaporation. The
effects of ZIF-90 loading as well as feed temperature on pervaporation
performance of the mixed matrix membranes were systematically
investigated. The flux of MMMs increased with increasing ZIF-
90 loading due to the enhanced fractional free volume; the
separation factor of water/IPA could be maintained at 5432 when
the ZIF-90 loading was less than 20 wt%, but reduced to 385
when the ZIF-90 loading was 30 wt%. The application of
sulfonated polyethersulfone (SPES) as a primer to ZIF-90 nanoparticles before fabricating 30 wt% ZIF-90 MMM resulted in an increase in the separation factor from 385 to 5686 due to the enhanced affinity between ZIF-90 particles and P84 as well as the preferential sorption of water over IPA. The best MMM showed a flux of 109 g m⁻² h⁻¹ and a separation factor of 5686 at 60 °C.¹²¹

![Image](74x520 to 290x664)

**Fig. 22.** Stability of ZIF-71/PEBA MMMs with 20 wt% loading in acetone-butanol-ethanol fermentation broth: total flux and separation factor of acetone, n-butanol and ethanol. Reprinted with permission from ref. 120. Copyright 2013 Elsevier.

### 3.3. Asymmetric composite membranes

Although many symmetric dense films studies have been reported, there have been few studies on preparation of asymmetric composite hollow fibers with ZIFs. Asymmetric composite membranes composed of a thin dense selective layer and a macroporous supporting layer usually have much higher flux than symmetric membranes, and hence they are highly desirable for practical applications. Dai et al. reported the first successful production of mixed matrix asymmetric hollow fiber membranes containing ZIF-8 fillers.¹²² ZIF-8 nanoparticles with a size of ca. 200 nm were incorporated into a polyetherimide (Ulem® 1000) matrix and produced dual-layer asymmetric hollow fiber membranes via the dry jet-wet quench method. The hollow fibers were post-treated with a 2 wt% high molecular weight polydimethylsiloxane solution in heptane to seal any pinhole defects in the selective skin layer. The outer separating layer of these composite fibers contained 13 wt% (17 vol%) of ZIF-8 filler. The ZIF-8/Ulem® hollow fibers showed increased CO₂ permeance of 18 GPU with an ideal selectivity of 44, which was as high as 20% over pure polymer (permeance: 11; ideal selectivity: 36). A mixed gas (CO₂/N₂, 20/80) selectivity of 32 was achieved in these hollow fiber membranes at 25 °C.¹²² ZIF-8/PBI composite dual-layer hollow fiber membranes were prepared, and they showed promising hydrogen separation properties at high temperatures.¹⁰³ Defect-free ZIF-8/PBI/Matrimid dual-layer hollow fibers were successfully fabricated, without post-annealing and coating, by optimizing ZIF-8 nanoparticle loadings, spinning conditions, and solvent-exchange procedures. Two types of hollow fibers targeted at either high H₂/CO₂ selectivity or high H₂ permeance were developed: the first type of fibers with a medium H₂/CO₂ permeance of 6.77 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ at 180 °C and a high H₂/CO₂ selectivity of 12.3, and the second type of fibers with a high H₂ permeance of 6.77 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ at 180 °C and a medium H₂/CO₂ selectivity of 7.7 for the separation of H₂/CO₂ (50:50) mixed gas.¹⁰³

The non-network polydioxane PIM-1¹²³ performs at the latest upper bound for a number of important gas pairs as the macromolecular PIM-1 traps free volume in the solid state. Self-supported ZIF-8/PIM-1 films with ZIF-8 contents up to 43 vol% were prepared. Permeability coefficients were determined for the following set of gases: He, H₂, O₂, N₂, CO₂, and CH₄. For “as-cast” films, an increase in ZIF-8 loading resulted in increases in the permeability and diffusion coefficients as well as in the ideal selectivity of H₂/N₂, H₂/CH₄, He/N₂, O₂/N₂ and CO₂/CH₄. For all ZIF-8 contents studied, the permeability was enhanced by treatment with ethanol. The permeability of H₂, He, O₂, N₂, CO₂ and CH₄ was 14430, 5990, 5810, 1760, 19350 and 2660 Barrer, respectively for ethanol-treated ZIF-8/PIM-1 membrane (43 vol% ZIF-8).¹²⁴ Data points on several Robeson diagrams are located above the latest upper bound.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Summary of mixed matrix membranes incorporated with ZIF's for gas separation and liquid separation via pervaporation.</th>
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</thead>
<tbody>
<tr>
<td>Polymers</td>
<td>ZIFs</td>
</tr>
<tr>
<td>Matrimid®</td>
<td>ZIF-8</td>
</tr>
<tr>
<td>Matrimid®</td>
<td>ZIF-8</td>
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<tr>
<td>Matrimid®</td>
<td>ZIF-8</td>
</tr>
<tr>
<td>Polybenzimidazole (PBI)</td>
<td>ZIF-7</td>
</tr>
<tr>
<td>PBI</td>
<td>ZIF-8</td>
</tr>
<tr>
<td>PPEES</td>
<td>ZIF-8</td>
</tr>
<tr>
<td>6FDA-Durene/DABA (9/1)</td>
<td>ZIF-8</td>
</tr>
<tr>
<td>6FDA-DAM/DABA (4/1)</td>
<td>ZIF-8</td>
</tr>
<tr>
<td>6FDA-DMA</td>
<td>ZIF-8</td>
</tr>
<tr>
<td>6FDA-DAM</td>
<td>ZIF-90</td>
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<tr>
<td>PBI</td>
<td>ZIF-90</td>
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4. ZIF films for microelectronics

Apart from the selective separation membranes, ZIF films have also been fabricated as sensors and insulators for microelectronics. Many ZIFs show excellent selective adsorption properties and can be used for sensing chemicals whereas the large microporosity and hydrophobicity of ZIFs are attractive features for use as insulators with low dielectric constants. In these applications, growth of high-quality ZIFs films on dense substrates with tunable thickness, and patterning of ZIF films on substrates are often required.

By using the drain and capillary regimes involved in the dip-coating process, Demessene et al. prepared ZIF-8 films on silicon wafer, and the thickness of the films could be tuned from 40 nm to 1 μm. The high optical-quality thin films showed a dual hierarchical porous structure from the micropores of ZIF-8 and the mesoporous interparticular voids. ZIF-8 crystals are strongly hydrophobic due to the presence of methyl groups positioned at the entrance of the pore opening, and organic molecules such as alcohols, tetrahydrofuran and hydrocarbons tend to be more easily adsorbed. These thin films exhibited selective adsorption properties for organic vapors versus water, which could make those high optical thin films good candidates for vapor sensors. 

Lu et al. prepared ZIF-8 thin film-based Fabry-Pérot device as a selective sensor for chemical vapors and gases. The preparation of the ZIF-8 thin film and a series of ZIF-8 thin films of various thicknesses grown on silicon substrates are shown in Fig. 23. The ZIF-8 sensor displayed some chemical selectivity. For example, linear n-hexane was readily sensed, but the cyclohexane was not.

Exposure the ZIF-8 films to the vapor above ethanol/water mixtures of various ethanol contents gave rise to ethanol-concentration-dependent responses, with the sensor response saturating at ca. 40% ethanol.

Patterned ZIF-8 thin films were generated by using standard photolithography or via selective growth with the aid of microcontact printing (Fig. 24). For the latter method, the surface modification of silicon substrates with hydrophobic silane self-assembled monolayer (CH₃-terminated SAMs) was done by soaking the pre-cleaned substrates in a 5% solution (v/v) of octadecyltrimethoxy silane in toluene with 0.5% n-butylamine. The alternate chemical deposition (of ZIF-8) and physical deposition (of metallic materials) allow the insertion of metal layers in the ZIF-8 film that could serve as multifunctional chemical sensors for vapors and gases.
has been achieved through control of the irradiation conditions to ensure that the crystallinity and the adsorption capacities of ZIF-9 have been preserved, allowing this approach to potentially be applied for gas separation, sensing or transport by adapting the method to a variety of framework materials and substrates. ZIF-8 films were deposited on silicon wafers and characterized to assess their potential as future insulators (low-κ dielectrics) in microelectronics. The dielectric constant was measured by impedance analysis at different frequencies and temperatures, indicating that κ was only 2.33 (±0.05) at 100 kHz, a result of low polarizability and density in the films. Intensity voltage curves showed that the leakage current was only 10⁻⁸ A cm⁻² at 1 MV cm⁻¹, and the breakdown voltage was above 2 MV cm⁻¹. ZIF-8 films have the effective κ value necessary for future chips, good mechanical properties, hydrophobicity, and they outperform other low-κ candidates in terms of pore entrance size and hydrophobicity.¹³²

![Fig. 24. a) Schematic diagram of the processes for patterning ZIF-8 thin films via photolithography (left) and microcontact printing (μCP) (right). Typical SEM images of patterns in ZIF-8 thin films obtained by means of b) photolithography and c) microcontact printing. Insets in b) and c) show the high-magnification SEM images of the edges of pattern features. Reprinted with permission from ref. 130. Copyright 2012 John Wiley & Sons, Inc.]

5. Conclusions and perspectives

Recent years have witnessed a great deal of progress made in the development of zeolitic imidazolate framework membranes and films for separation applications and functional microelectronic devices, and fundamental understanding of the membrane formation and gas transport processes.

To date, ZIF membranes/films have been prepared by various methods including direct synthesis, secondary growth with pre-seeding of the substrate, surface functionalization with covalent linkers, imidazolate deposition, precursor infiltration, reactive seeded growth, and conformational diffusion method. However, due to complex ZIF nucleation and growth processes, it is hard to directly correlate the preparation method with the membrane properties. In general, repetitive growth including secondary growth tends to reduce defects of ZIF membranes. A wide range of parameters should be considered in the fabrication of ZIF membranes, including the surface properties of the substrates, and the crystallization behavior of individual ZIFs. Therefore, a combination of different methods such as surface functionalization, secondary seeded growth and post-functionalization may be required to achieve optimal membrane structures and performances in some ZIF systems.

Studies have shown that ZIF crystals are attractive additives for the fabrication of polymer-based composite membranes (known as mixed matrix membranes), including symmetrical dense composite membranes and asymmetrical composite membranes with relatively high loadings of ZIFs due to good compatibility between ZIFs and polymers. The incorporation of ZIF particles into a polymer increases the free volume of polymer, and thus enhances the solubility and diffusivity of the targeted components.

In terms of applications, both ZIF membranes and ZIF/polymer composite membranes have been widely studied for energy and environment related separations such as hydrogen separation, CO₂ capture, light hydrocarbons separation, and liquid mixture separation (dehydration and organophilic pervaporation). However, the flexible property of imidazolate linkers of ZIFs induces the complex pore changes, such as pore size increase, and gate opening under certain conditions, adding more complexity of ZIF membranes in gas separation and liquid separation.

ZIF films have been fabricated as sensors and insulators for microelectronics. The easy synthesis of ZIF films and the structure versatility of ZIFs may offer some interesting properties for components in future generation microelectronics, but more research is needed to explore real potential of ZIFs over their zeolite counterparts in this area.⁶

Among many different types of ZIFs studied, ZIF-8 has been the most extensively studied ZIF due to its good thermal and chemical stability, and easy synthesis. A few other types of ZIFs also deserve more attention. ZIF-11 with RHO topology possesses larger cages connected through small apertures, and also exhibits exceptional thermal and chemical resistance to water and organic solvents.⁷ The molecular simulation revealed that ZIF-11 has the potential to meet industrial requirements for H₂/CO₂ and H₂/N₂ separations, a critical operation for pre-combustion carbon capture.¹³⁴ However, the synthesis of ZIF-11 at low cost and low environmental impact is yet to be realized.¹³⁵ Theoretical modelling suggested that ZIF-77 may be good for natural gas purification (CO₂/CH₄) while ZIF-71 may be an excellent candidate for air separation for oxy-combustion (O₂/N₂).¹³⁴ Furthermore, ZIF-8 was recently used as a CO₂ adsorbent in aqueous solution, effectively enhancing the photocatalytic CO₂ reduction reaction into liquid fuels.¹³⁶ Since many ZIFs are stable in water, it is worthy of research efforts in investigating their potential use as selective adsorbents in photocatalytic membrane reactors¹³⁷,¹³⁸ and as an additive to modify desalination membranes.¹³⁹,¹⁴⁰

Despite ZIF/polymer mixed matrix membranes have been demonstrated for their potential for gas separations such as CO₂ capture from flue gas,¹²² their structures and separation performances still need to be further optimized for large scale practical applications. Significant efforts are required to synthesize different types of ZIF nanoparticles with sizes smaller than 100 nm in order to investigate the effect of particle size on
membrane properties. In addition, since it is possible to synthesize ZIF nanoflakes\cite{14} and nanorods,\cite{15} it would be interesting to investigate how the ZIF particle shape affects membrane structure and separation properties as observed in the zeolite/polymer composite membranes.\cite{16,17}

Due to the structure diversity of ZIFs, a designed and tunable organic adsorption could be obtained and the organophilic pervaporation could be expected by using ZIF membranes or ZIF/polymer composite membranes.\cite{8,10,11} More studies on long-term stability of ZIF composite membranes under different operational environments such as organic solvents in pervaporation, and gas mixtures containing water and organic vapor in high temperature are required. The scale up of ZIF/polymer mixed matrix membranes is quite straightforward since their fabrication processes are primarily based on well-established polymer membrane technologies. But it would be challenging to fabricate ZIF membranes on a large scale, and a major breakthrough is needed to reliably grow defect-free membranes and eliminate grain boundary defects.\cite{18} Given strong interest in ZIFs in the research community, new concepts and techniques for synthesis of high-quality ZIF membranes and films will continue to emerge in the future.

Acknowledgements

J.Y. thanks Monash University for a Monash Fellowship. H.W. acknowledges the support of the Australian Research Council through a Future Fellowship (FT100100192).

Notes and references

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Reference


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ZIF membranes | ZIF/polymer composite membranes

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