**Integrated Water Gas Shift Membrane Reactors Utilizing Novel, Non
Precious Metal Mixed Matrix Membrane**

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ABSTRACT

Nanoparticles of zeolitic imidazolate frameworks and other related hybrid materials were prepared by modifying published synthesis procedures by introducing bases, changing stoichiometric ratios, or adjusting reaction conditions. These materials were stable at temperatures $>300\text{ }^{\circ}\text{C}$ and were compatible with the polymer matrices used to prepare mixed-matrix membranes (MMMs). MMMs tested at $300\text{ }^{\circ}\text{C}$ exhibited a >30 fold increase in permeability, compared to those measured at $35\text{ }^{\circ}\text{C}$, while maintaining H_2/CO_2 selectivity. Measurements at high pressure (up to 30 atm) and high temperature (up to $300\text{ }^{\circ}\text{C}$) resulted in an increase in gas flux across the membrane with retention of selectivity. No variations in permeability were observed at high pressures at either 35 or $300\text{ }^{\circ}\text{C}$. CO_2 -induced plasticization was not observed for Matrimid[®], VTEC, and PBI polymers or their MMMs at 30 atm and $300\text{ }^{\circ}\text{C}$. Membrane surface modification by cross-linking with ethanol diamine resulted in an increase in H_2/CO_2 selectivity at $35\text{ }^{\circ}\text{C}$. Spectrometric analysis showed that the cross-linking was effective to temperatures $<150\text{ }^{\circ}\text{C}$. At higher temperatures, the cross-linked membranes exhibit a H_2/CO_2 selectivity similar to the uncross-linked polymer. Performance of the polybenzimidazole (PBI) hollow fibers prepared at Santa Fe Science and Technology (SFST, Inc.) showed increased flux and selectivity at $300\text{ }^{\circ}\text{C}$, which is comparable to a flat PBI membrane. A water-gas shift reactor has been built and currently being optimized for testing under DOE conditions.

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INTRODUCTION

The use of membrane technology to replace energy intensive separations is anticipated to result in both energy savings and economic savings. Robust membranes with selective additives provide the advantages of the polymer matrix including flexibility and module design as well as the superior separation performance of the additives.

The overall objectives of the proposed research included the preparation of novel mixed-matrix membranes (MMMs) based on composites of polymers and nanoparticles of zeolitic imidazolate frameworks (ZIF) and related hybrid frameworks. Membranes containing these new materials were used to evaluate hydrogen and carbon dioxide separations (important to coal gasification). The goal was to achieve novel non-precious metal-based separation using ZIF-based MMMs in an integrated water-gas shift (WGS) reactor. Using these ZIFs for separation will allow for the exploitation of their high surface areas, adsorption capacities, and selectivities to achieve the required flux for the H₂ and CO₂ separations [1].

The organization of this final report follows the proposed project management plan, where the major tasks are listed. The *experimental* section describes the synthesis of the proposed ZIFs and related hybrid materials, the synthesis of non-commercially available polymers, and membrane preparation. Due to the extensive number of ZIF/polymer systems, the *results and discussion* section is organized by the polymer matrix. This section also includes the results of membranes tested at high temperatures and high pressures. The results for the hollow fiber testing and characterization as well as the design and optimization of the water-gas shift (WGS) reactor follow this section. Finally, a section listing the scientific and educational *outcomes/impacts* of the project is included.

EXECUTIVE SUMMARY

Our strategy to improve the permeability and selectivity of polymer membranes was to incorporate ZIFs and related hybrid frameworks into polymer matrices. These porous materials are chemically and thermally stable at DOE 2015 target conditions. Additionally, they possess pore apertures small enough to perform molecular sieving of H₂ from CO₂. In addition to these properties, ZIFs, which contain organic ligands, are more compatible with polymer matrices than are zeolites. Among the large variety of ZIFs, metal-organic frameworks (MOFs), and other hybrid materials that have been reported in the open literature, we identified ZIF-7, ZIF-8, ZIF-20, ZIF-90, ZIF-95, MIL-53, NH₂-MIL-53, and MOP-18 as materials suitable for gas separations. We purchased (ZIF-8 and MIL-53) or synthesized nanocrystals of these ZIFs and MOFs in our labs.

We chose polymers with T_gs above 300 °C to prepare mixed-matrix membranes (MMMs) for operation at DOE 2015 target conditions. Polymers such as Matrimid®, PBI, and VTEC are commercially available, but other polymers such as perfluorocyclobutyl ether (PFCB), PIM-1 and the 6FDA derivatives were synthesized in our labs.

Other strategies to improve gas separation were also investigated. The cross-linking of polymer membranes with ethylenediamine (EDA) was applied to 6FDA and Matrimid® polymer membranes and their MMMs. The EDA cross-linking proved to be effective to improve the H₂/CO₂ selectivity of the membranes. Separation factors of 144 were obtained for H₂/CO₂ with EDA cross-linked 6FDA-durene membranes with a H₂ permeability of 52 Barrers at 35 °C and 3 atm. The stability of this chemical modification was examined to determine its applicability in high temperature, high pressure gas separations. The results showed that EDA cross-linking reverses at temperatures above 150 °C with a loss of selectivity. Therefore, these membranes were not tested at high temperature. Another strategy to improve the gas transport properties of the prepared membranes was to coat the MMM surface with a thin (<3 µm), highly selective polymer layer that controls gas flux across the membrane. Since very thin and mechanically stable polymer membranes are difficult to prepare, this strategy solves this problem by combining the MMM and the highly selective polymer layer.

We tested flat membranes at DOE 2015 target conditions of up to 300 °C and 30 atm in a high pressure, high temperature permeameter (HPHT) that we built as part of this project. Permeabilities of H₂, CO₂, and N₂ were obtained for selected membranes. Permeability results at 300 °C and 30 atm demonstrate that the polymers and MMMs are mechanically and thermally stable even after prolonged exposure (>300 h) to gases. VTEC, Matrimid®, and PBI membranes retained their selectivity properties when the temperature was increased from 35 to 300 °C. Permeability, however, increased with increasing temperature and 35-fold increments in H₂ permeability were observed for VTEC membranes when the temperature was increased from 35 to 300 °C. Pressure increments from 3 to 30 atm at 35 °C and at 300 °C resulted in an increased flux across the membrane without changes in permeability. These results indicate that the membranes were free from defects as well as mechanically stable at these extreme conditions. ZIF-8/PBI MMMs also showed significant changes in permeability with increasing temperature. The MMMs showed an increase in H₂ permeability from 5.4 Barrers (35 °C) to 397 Barrers (300 °C), while retaining a H₂/CO₂ selectivity of 14. Thin PBI layers on 35% (w/w) ZIF-8/PBI MMMs resulted in increased H₂ permeability (or flux) and selectivity. The thickness of the spin-coated PBI layer prominently dictates the H₂/CO₂ selectivity, while the flux depended on the porosity of the MMM. It was also discovered that CO₂-induced plasticization of the membrane could be mitigated by increasing the temperature. As was observed for Matrimid® and MOP-18/Matrimid® MMMs, when the temperature was increased from 35 to 70 °C, the H₂/CO₂ selectivity was recovered. The reduction of the plasticization is attributed to the increase of the plasticization pressure when the temperature is increased. In the case of Matrimid®, the plasticization pressure was increased from 30 atm at 35 °C to >30 atm at 70 °C. It is also worth noting that plasticization was not observed for VTEC and PBI membranes in the range of pressures and temperatures at which these materials were tested.

EXPERIMENTAL METHODS

ZIF and related hybrid framework materials

ZIF synthesis

Thermally and chemically stable ZIFs with high affinity and selectivity for H_2 and CO_2 were synthesized and incorporated into polymer to prepare MMMs. Commercially available ZIF-8 (Basolite® Z1200, Sigma Aldrich) was activated by heating in a vacuum oven at 100 °C for 1 d. ZIF-7 [2, 3], ZIF-8 [4], ZIF-20 [3], ZIF-90 [5], and ZIF-95 [6] crystals were synthesized by modifying published procedures.

Amino-MIL-53 and MIL-53 synthesis

Following the synthesis times and molar ratios used by Pera-Titus and coworkers, $Al(NO_3)_3 \cdot 9H_2O$ [7, 8], terephthalic acid or 2-aminoterephthalic acid and water in a 100-mL round bottom flask fitted with a condenser were heated under reflux. Upon cooling, the resulting solid was collected by centrifugation and placed in DMF. The DMF solution was again heated under reflux. To remove the DMF, the yellow (NH_2 -MIL-53) or white (MIL-53) powder was subjected to Soxhlet extraction using CH_2Cl_2 and dried under vacuum at 100 °C. Commercially available MIL-53 purchased from Sigma Aldrich (Basolite® A100) was used as received.

Polymers

Matrimid®-5218 soluble polyimide (Huntsman Corporation), 26 wt% polybenzimidazole in dimethylacetamide with 1.5% w/w LiCl (PBI Performance Products, Inc.), and VTEC PI-1388 (structure similar to Kapton; RBI, Inc) were used as received.

Figure 1. Chemical structures of Matrimid® and Polybenzimidazole (PBI) polymers.

Perfluorocyclobutyl (PFCB) ether polymers

Perfluorocyclobutyl (PFCB) polymers were synthesized by modifying published procedures [9] following the scheme shown in Figure 2.

Figure 2. General scheme for synthesis of PFCB polymers

Polymer of Intrinsic Microporosity-1 (PIM-1)

Following reported procedures [10, 11], the Polymer of Intrinsic Microporosity-1 (PIM-1) was synthesized from dried and purified monomers (Figure 3).

Figure 3. Synthetic scheme for the PIM-1 polymer.

6FDA-ODA/NDA random copolymers

Following reported procedures, [12, 13, 14] five polyimides from 4,4'-hexafluoroisopropylidene bisphthalic dianhydride (6FDA) and 2 diamines (4,4'-oxydianiline, ODA, and 1,5-diaminonaphthalene, NDA) were synthesized. The anhydride was dried under vacuum to remove adsorbed water, while the diamines were purified by sublimation at 150 mtorr prior to use. 6FDA-NDA, 6FDA-ODA, and their copolymers (3:1, 1:1, 1:3 molar ratios) were prepared via the initial formation of a polyamic acid followed by chemical imidization using triethylamine/acetic anhydride (Figure 4). All polymers were precipitated and washed (at least 3x) in methanol, and dried at 150 °C under vacuum for 1 d prior to use.

6FDA-durene

In a similar method, 6FDA-durene was synthesized following a modified literature procedure [14]. 6FDA was added to durene-diamine (1:1 molar ratio in DMAc) at a 20 wt.% monomer concentration. The mixture was stirred at 50 °C for 2 h, and the resulting polyamic acid was converted into the polyimide by adding a 1:1 molar mixture of triethylamine and acetic anhydride. The mixture was further heated following a temperature program (50 °C for 1 h, 75 °C for 1 h and 100 °C for 30 min) under a nitrogen purge. The polymer was precipitated in methanol, washed several times with methanol, and dried at 150 °C under vacuum for 1 d.

Figure 4. Scheme for the synthesis of 6FDA-based polyimides.

6FDA-DAM-DABA polymers

PDMC (Propanediol esterified 6FDA-DAM-DABA, Figure 5) was synthesized using published literature procedures [15, 16].

(A)

(B)

Figure 5. Chemical structures of (A) propanediol cross-linked 6FDA-DAM-DABA (PDMC) and (B) cross-linked propanediol esterified 6FDA-DAM-DABA (CPDM).

Membrane preparation

Matrimid®-based MMMs

MMMs containing 20-75 wt% ZIF (or related hybrid frameworks, i.e., MIL-53 and MOP-18) in Matrimid® were fabricated by preparing a dispersion of ZIF or other hybrid framework in CHCl_3 or THF and mixing it with the polymer solution in the same solvent. The additive dispersion was alternately bath sonicated and stirred (6 cycles, 15 min each time) to obtain a homogenous dispersion. Sonication breaks up particle aggregates and enhances homogeneity. Afterwards, 20% of the polymer solution was added to the additive dispersion as a pre-coating step. To further enhance mixing, the dispersion was subjected to a LabRAM Mixer (Resodyn™ Acoustic Mixers, Inc., purchased with matching funds for this project) set at 20% intensity for 20 min. The additive/Matrimid® dispersion was concentrated by evaporating the solvent until the polymer concentration was 10% by weight. The dispersion was cast onto a glass substrate using an automatic film applicator (Sheen Instruments, Ltd., 1133N) equipped with an adjustable blade (Sheen Instruments, Ltd., 1117). The resulting membranes were peeled off the substrate and annealed at 100 °C (MOP-18 and MIL-53/Matrimid® MMMs), 100 °C (ZIF-7/Matrimid® MMMs), or 240 °C (ZIF-8/Matrimid® MMMs) for 1 d prior to further characterization and testing.

PIM-1-based MMMs

Metal-organic framework nanocrystals (MIL-53, ZIF-8, and ZIF-90) were incorporated into PIM-1 at loadings up to 15 wt%. The preparation of these membranes followed the same steps described in the preparation of Matrimid®-based MMMs using CHCl_3 as the solvent. The resulting membranes were annealed at 60 °C for 1 d.

6FDA-ODA/NDA-based MMMs

Several MMMs comprising the synthesized thermally stable polymers and ZIFs or MOFs were prepared. A 20 wt% ZIF-8/6FDA-NDA MMM was fabricated using ZIF-8 particles having different particle sizes, including commercially available ZIF-8 (Basolite® Z1200, 120-nm particles) and synthesized ZIF-8 (60-nm and 111-nm particle sizes). The additives and polymers were dispersed in DMF, and stirring and sonication protocols for Matrimid®-based MMMs were followed. The solutions were cast on a glass substrate, dried, and annealed following a temperature program prior to further characterization and testing.

6FDA-DAM-DABA-based MMMs

ZIF-8 (33 wt%) PDMC MMMs were fabricated and cross-linked by annealing at 280 °C for 1d.

MMM-EDA surface modification

EDA (20 mL) was equilibrated in a tightly capped 1000 mL glass jar for 6 h. Annealed ZIF-8/6FDA-durene and MIL-53/Matrimid® MMMs were suspended in the EDA vapor for 40 min at 35 °C and then immediately washed with deionized water to remove any unreacted EDA. Finally, these MMMs were dried at 70 °C for 1 d under vacuum.

ZIF-8/PBI MMMs

Following Matrimid®-based membrane preparation protocols, PBI-based MMMs containing different weight loadings of Basolite® Z1200 (ZIF-8) were fabricated as flexible membranes. The MMMs were promptly placed in a heated chamber at 50 °C under a N₂ purge for at least 5 h to remove the solvent (DMAc) used. Afterwards, the MMMs were removed from the glass substrate and dried under vacuum following a temperature program (80 °C, 150 °C, and 220 °C for 1 d each).

Polymer membranes for high temperature and pressure testing

VTEC PI-1388 membranes

A 12 wt% VTEC PI-1388 polyamic acid solution was prepared by stirring for 15 h in *N,N*-dimethylacetamide. The solution was cast onto a Mylar® sheet at room temperature using an automatic film applicator (Sheen 1133N) with a calibrated doctor blade. The membrane, still on the Mylar® sheet, was transferred to a nitrogen purged chamber where it dried for 5 h at 80 °C. High temperatures and long periods of time are required to induce imidization of the polyamic acid. Therefore, the membrane was removed from the Mylar® sheet and heated in a vacuum oven first at 80 °C for 2 d, then at 150 °C for 1 d, and finally at 250 °C for 2 d, followed by cooling to room temperature.

Polymer hollow fibers and coated porous stainless steel tubes

Polysulfone hollow fiber coating and characterization

Polysulfone (PSU) hollow fibers (SFST, Inc.) were dip-coated in a 2% (w/w) Matrimid® solution in 1,2-dichloroethane. The bacteriostat (sodium azide) in the PSU hollow fibers was removed by soaking in DI water and methanol. The coated fibers were dried at room temperature for 2 h, annealed at 100 °C under vacuum for 1 d, and stored in a dessicator.

PBI spin-coated MMMs

A volume of 0.1 μ L of 7 wt% PBI/DMAc solution was deposited onto ZIF-8/PBI MMMs during spinning at 500 or 1000 rpm for 60 s. After drying in air for 12 h, the membrane was heated in a vacuum oven at 50 °C for 5 h, then at 80 °C for 5 h, 120 °C for 5 h, 170 °C for 5 h, and finally at 220 °C for 1 d.

Membrane coating on porous stainless steel tubes

A thin (< 1 μ m) PBI membrane was applied on a rotating porous stainless tube (porosity = 0.5 μ m, porous area = 18.75 cm², Applied Porous Technology) by airbrushing a diluted PBI solution. Different parameters including tube rotation speed, PBI solution viscosity, spray distance, spray length, and spray pressure, were varied to obtain a thin, homogeneous PBI coating.

Water-gas shift membrane reactor and catalyst

Water-gas shift (WGS) membrane reactor

A high temperature and pressure water-gas shift (WGS) reactor is equipped with an LT-10 syngas generator to produce syngas at a controlled flow rate and composition, and a custom-made furnace and thermal system to control experiment temperature. The reactor cell housing the WGS catalyst and the membrane is placed inside the furnace (Figure 6). The composition of the retentate and permeate gases are analyzed by a GC analyzer (8610C GC, SRI instruments). The reactor is fully automated and controlled via LabView 7.1 software (National Instruments).

Figure 6. Optical image of the WGS membrane reactor with a syngas generator and GC analyzer.

The stainless-steel (SS) membrane module for a tubular water-gas shift (WGS) reactor was designed to work at high pressures (up to 30 atm) and temperatures (up to 300 °C). All connections were replaced with stainless steel ferrules. The porous SS tube was used as a support for the PBI membrane. The digital images of the membrane module and the porous SS support are shown below (Figure 7).

Figure 7. (A) Digital image and (B) schematic diagram of the stainless steel housing.

Catalyst Synthesis for Water-Gas Shift reactor

The catalyst was prepared by combining Solution A (8.65 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 5 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 7.35 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 100 mL of water) and Solution B (12.5 g of sodium carbonate in 50 mL of H_2O) [17, 18]. The product precipitated after 1.5 h, was collected by filtration, and allowed to air dry for 12 h. The blue solid was then calcined at 500 °C for 3 h (Figure 8).

Figure 8. Photographs of pre-calcined catalyst (left), and calcined product (right)

An alternative for the catalyst is the commercially available copper based HiFUEL™ W220 manufactured by Alfa Aesar. The compositions of this catalyst include 50% CuO, >25% ZnO and < 25% Al₂O₃.

Characterization of ZIFs and MMMs

The ZIFs, MOFs, MOP-18, polymer films, and MMMs were characterized using a variety of analytical techniques. To determine the crystallinity of the material, X-ray diffraction (XRD) patterns were acquired from 3 to 45° 2θ at a rate of 0.04°/s with a Rigaku Ultima IV diffractometer using Cu Kα X-ray radiation. A Nicolet 360 Fourier transform infrared (FTIR) spectrometer was used to record IR spectra at room temperature in the range of 400-4000 cm⁻¹ of powders (as a KBr pellet), and polymer and MMM films (using an attenuated total reflectance (ATR) accessory equipped with a diamond crystal). Nuclear magnetic resonance (NMR) data for the synthesized polymers are reported in parts per million and were acquired in CDCl₃, CD₃CN or DMSO (d₆) with TMS (¹H) as internal standard. ¹H and ¹³C NMR spectra were acquired on an Eclipse 270 spectrometer (270 MHz). ¹⁹F NMR spectra were acquired on a Bruker Ultra Shield (400 MHz). Thermogravimetric analyses (TGA) of the powders and films were conducted under N₂ using a Perkin Elmer Pyris-1 instrument with a temperature program from 90 to 1000 °C at a heating rate of 10 °C/min. A Zeiss Supra 40 field emission scanning electron microscope (FE-SEM) operated at 10 keV was used to acquire secondary electron images of the materials. Before imaging, samples were mounted on carbon tape adhered to aluminum stubs and coated with 10 nm of Au/Pd using a Technics Hummer VI Sputtering System. To prepare cross-sections of the polymer films and MMMs, the membranes were freeze-fractured after immersing them in liquid N₂ for 2 min. Differential scanning calorimetry (DSC) results for the polymer films and MMMs were obtained using a Mettler Toledo DSC1 Star^e System. The thermograms were recorded under N₂ from 200 to 450 °C at 10 °C/min. The T_g of the MMMs were obtained from the 4th run of the DSC analysis. The T_g is determined by fitting straight lines to the temperature versus heat flow curve before, during, and after taking the points of intersection at the onset and endpoint of transition. The T_g is taken as one-half the change in heat capacity between the onset and the endpoint.

Membrane testing

Low pressure, low temperature (2.5 atm and 35 °C) gas permeation measurements of the prepared membranes were performed using custom made permeameters at constant volume. High pressure, high temperature gas permeation measurements (up to 30 atm and up to 300 °C) were performed with the HPHT permeameter. The HPHT permeameter was built according the diagram shown in Figure 9 using matching funds for this project [19]. Figure 9 shows the main components (pressure transducers, thermocouples, metering valves, and reservoirs). A LabView front panel that controls the instrument was also developed [19].

Figure 9. Schematic diagram of the HPHT permeameter. DS = high pressure downstream valve, US = high pressure upstream valve, MV = metering valve, CV = check valve, TC = thermocouple, PT = pressure transducer.

RESULTS AND DISCUSSION

ZIFs and related hybrid frameworks

ZIF-7

The ZIF-7 particles are 60 to 70 nm in diameter with no defined morphology (Figure 10), and show the expected peaks for XRD analysis (Figure 11).

Figure 10. SEM image of ZIF-7 nanoparticles.

Figure 11. XRD pattern of synthesized ZIF-7 particles.

ZIF-8

Nano-sized ZIF-8 particles were obtained upon the addition of TEA to the synthesis mixture. SEM images of this material show particles that are 60 ± 4 nm in diameter (Figure 12). XRD analysis of the synthesized particles showed the expected peaks for ZIF-8 (Figure 13).

Figure 12. SEM images of ZIF-8 nanoparticles: (A) commercially available ZIF-8 (Basolite®, 120 ± 18 nm), ZIF-8 (B) synthesized without TEA (Batch 1, 111 ± 21 nm), and (C) synthesized with TEA (Batch 2, 60 ± 4 nm).

Figure 13. XRD patterns of synthesized ZIF-8 particles.

ZIF-20

ZIF-20 particles have an average diameter of 180 nm (Figure 14). The XRD pattern for this material is shown in Figure 15. At 160 °C, ZIF-20 underwent a color change (from white to orange). This was unexpected because a published TGA shows that the crystal does not decompose below 300 °C [20]. FTIR of ZIF-20 (not shown) before and after thermal treatment shows that the zinc-nitrogen bond (502 cm^{-1}) is intact. However, the carbonyl peak for DMF (1660 cm^{-1}) was present in the heated material, indicating that the solvent is trapped inside the ZIF cage, even after solvent exchange with methanol.

Figure 14. SEM image of ZIF-20 particles (average diameter = 180 nm)

Figure 15. XRD patterns for ZIF-20: theoretical (bottom) and as-synthesized (top).

ZIF-90

The SEM image of synthesized ZIF-90 shows particles ~50 nm in diameter (Figure 16). XRD analysis shows that the material has the same reflections as the theoretical diffraction pattern (Figure 17). The thermal stability of ZIF-90 was observed to be greater than 300 °C (Figure 18), making it suitable for high temperature gas separations.

Figure 16. SEM image of synthesized ZIF-90 nanoparticles.

Figure 17. XRD pattern of synthesized ZIF-90 nanoparticles (ZIF-90s).

Figure 18. Thermogram of synthesized ZIF-90 nanoparticles.

ZIF 95

Sub-micron-sized particles of ZIF-95 (not shown) were synthesized by shortening the reaction time reported in the literature [21]. XRD revealed the correct XRD pattern (Figure 19).

Figure 19. XRD patterns of ZIF-95: (A) theoretical..., ZIF-95 reported by Huang et al. (B), activated ZIF-95 (C), and activated ZIF-95-Huang (D).

MIL-53 and NH₂-MIL-53

The optical and SEM images of NH₂-MIL-53 and MIL-53 powders, with Basolite® A100 as a comparison, are presented in Figure 20. All synthesized powders display nanometer-sized particles, comparable to the commercially available MIL-53.

Figure 20. Optical (left) and SEM (right) images of NH₂-MIL-53 (A, B), MIL-53 (C, D), and Basolite® A100 (E, F).

X-ray diffraction patterns of MIL-53 acquired at temperatures up to 350 °C show that the material is thermally stable in the crystalline form (Figure 21). Also, the patterns show that, depending on temperature, the material exists in either an open pore form (MIL-53-ht), or a mixed open pore/closed pore (MIL-53-lt) form.

Figure 21. Temperature-dependent XRD patterns of MIL-53.

N₂ adsorption-desorption type I isotherms of MIL-53-ht and MIL-53-lt indicate that both materials are microporous (Figure 22). BET surface areas of 1118 m²/g and 900 m²/g were determined from the isotherms of MIL-53-ht and MIL-53-lt, respectively. The Langmuir surface areas reported for MIL-53(Cr) are estimated to be over 1500 and 1150 m²/g, respectively [17], which are close to those obtained for MIL-53(Al).

Figure 22. N₂ adsorption-desorption isotherms of a) MIL-53-ht and b) MIL-53-lt.

MOP-18

XRD patterns of MOP-18 simulated from experimental single-crystal X-ray data (Figure 23a) [20] and of synthesized MOP-18 particles (Figure 23b,c) are shown below. The position of the main reflection for the material recrystallized from methanol is shifted 0.5° to a higher angle indicating a contraction of the unit cell. When recrystallized from a hexane/heptanol mixture, the XRD pattern (Figure 23c) matches the theoretical pattern confirming that the material is MOP-18 [20].

Figure 23. XRD patterns of MOP-18: a) theoretical, b) experimental, recrystallized from methanol, c) experimental, recrystallized from hexanes/heptanol, and d) 80% (w/w) MOP-18/Matrimid® membrane.

Gas permeability testing of PFCB polymers

Thermally stable and highly processable perfluorocyclobutyl ether (PFCB) polymers were prepared and investigated as matrices for gas separation applications. Preliminary gas permeability results (Table 1) from one of the PFCBs prepared, biphenyl (BP) PFCB (Figure 24, Table 1), showed higher permeabilities than Matrimid®.

Figure 24. Structure of biphenyl (BP)-PFCB polymer

However, these results were highly variable. A similar situation occurred for the CF_3 -PFCB polymer. To minimize polymer chain movement and obtain consistent permeability results, a trifluorovinyl oxybenzene (TFVOB) cross-linker (Tri-CH_3 , Figure 25) was incorporated into the polymers.

Figure 25. Trifunctional TFVOB and PFCB polymers

Reproducible and linear plots of downstream pressure vs. time were obtained upon incorporation of the Tri-CH₃ into BP-PFCB. Permeabilities were observed to increase (Table 2), which may be attributed to the presence of larger free volume than in the pure polymer. However, upon loading 50 % (w/w) of the Tri-CH₃ into the polymer, the permeabilities greatly increased and selectivities approached Knudsen diffusion (Table 3). Future efforts will be directed towards optimizing polymer cross-linking and incorporating ZIF materials into this polymer system.

Table 1. Preliminary testing of pure BP-PFCB polymer

Gas	Permeability, Barrers	
	BP-PFCB	Matrimid®
N ₂	2.19 ± 0.04	0.24 ± 0.03
O ₂	5.55 ± 0.06	1.5 ± 0.2
H ₂	33.27 ± 0.35	17.1 ± 1.5
CO ₂	19.29 ± 1.05	7.3 ± 0.7
CH ₄	3.87 ± 0.54	0.22 ± 0.02

Table 2. Permeability testing of 10 and 50% (w/w) loading of Tri-CH₃ in BP-PFCB

Gas	50XBP	10XBP	Pure Matrimid®
N ₂	603.18	1.35	0.24
H ₂	1911.69	24.04	17.10
O ₂	574.14	4.86	1.50
CH ₄	871.29	1.15	0.22
CO ₂	608.67	22.06	7.30

Table 3. Selectivity values of 10 and 50% (w/w) loading of Tri-CH₃ in BP-PFCB

	Knudsen	50XBP	10XBP	Pure Matrimid®
O ₂ /N ₂	0.93	0.94	3.60	6.14
CH ₄ /N ₂	1.32	1.42	0.85	0.92
H ₂ /O ₂	4.00	3.33	4.89	11.47
H ₂ /CO ₂	4.70	3.14	1.09	2.33
CO ₂ /CH ₄	0.60	0.69	19.18	32.86
H ₂ /CH ₄	2.82	2.19	21.00	76.64
H ₂ /N ₂	3.74	3.12	17.80	70.46

Mixed-matrix membranes

ZIF-7/Matrimid[®] MMMs

Figure 26 shows a SEM image of a cross-section of a 20% (w/w) ZIF-7/Matrimid[®] MMM. The ZIF-7 nanocrystals appear to be well dispersed within the polymer matrix, suggesting a good interface between the ZIF-7 nanocrystals and Matrimid[®]. More importantly, there was no indication that non-selective voids were present in the matrix.

Figure 26. SEM images of surface (left) and cross-section (right) of 20% (w/w) ZIF-7/Matrimid[®] MMM.

Gas permeation measurements revealed that the MMM was less permeable for all gases tested than pure Matrimid[®] (Table 4). The permeability data at this loading suggests that ZIF-7 acts as a filler. While the gas selectivity values were generally lower for the MMM than for pure Matrimid[®] (Table 5), the values were well above Knudsen selectivity, suggesting that the membrane remained structurally sound during the permeability experiments. Compared to the 20% (w/w) loading, hydrogen and carbon dioxide permeability were higher for a 30% (w/w) ZIF-7/Matrimid[®] MMM and the membrane remained selective. However, high permeability values for nitrogen and methane suggest that nonselective voids may have been present in the membrane (Tables 4, 5).

Table 4. Permeability data for 20% and 30% (w/w) ZIF-7/Matrimid[®] MMMs annealed at 100 °C

Gas	20% (w/w) MMM	30% (w/w) MMM	Matrimid [®]
N ₂	0.18 ± 0.05	2285 ± 66.5	0.24
O ₂	1.2 ± 0.34	1639 ± 272.4	1.49
CH ₄	0.13 ± 0.03	3524 ± 39.9	0.22
CO ₂	5.6 ± 0.76	889.7 ± 61.2	7.33
H ₂	16.5 ± 8.10	2368 ± 200.6	17.08

Table 5. Selectivity data for 20% and 30% (w/w) ZIF-7/Matrimid[®] MMMs annealed at 100 °C

Gas	20% (w/w) MMM	30% (w/w) MMM	Matrimid [®]	Knudsen Diffusion
H ₂ /O ₂	13.7 ± 2.99	1.44	11.46	4.00
H ₂ /CO ₂	2.95 ± 1.05	2.66	2.33	4.70
H ₂ /N ₂	91.6 ± 40.1	1.04	70.32	3.74
H ₂ /CH ₄	126 ± 47.9	0.67	76.62	2.82

ZIF-7/6FDA-based polyimides (PI) MMMs

MMMs with loadings of 20 and 50 wt% ZIF-7 in polyimides were fabricated, characterized, and measured for permeability at 35 °C and 3 atm. These MMMs were prepared directly from colloidal ZIF-7 nanoparticles (60-80 nm, Figure 27). The crystallinity of the synthesized particles was confirmed by XRD (Figure 28).

Figure 27. SEM images of dried ZIF-7 nanoparticles (control).

Figure 28. XRD patterns of theoretical and synthesized ZIF-7 nanoparticles (control).

The optical images of the pure PI and its MMMs with colloidal ZIF-7 nanoparticles are presented in Figure 29. Traditionally, MMMs have been prepared from fully dried ZIF particles, i.e. free of synthesis solvent^{17b} (Figure 29, second column). In order to obtain a good dispersion, particles of ≤ 100 nm are used for the MMM fabrication. As the ZIF-8 particle size decreases (120 to 60 nm), 20 wt% ZIF-8/PI MMMs become translucent. However, the MMMs prepared using colloidal ZIF-7 nanoparticles of similar particle size (60-80 nm) at 20 wt% loadings are totally transparent. This observation indicates that the dispersion of the additive particles is not only dependent on its particle size but also on the additive handling (i.e. removal of solvent by drying).

Figure 29. Optical images of MMMs prepared from conventional method (non-colloidal) and colloidal ZIF dispersions.

Figures 30-32 show SEM images of the cross-sections and surfaces as well as the optical images of 20 and 50 wt% ZIF-7/6FDA-NDA MMMs, and 20 wt% ZIF-7/6FDA-NDA-ODA (3:1) MMM. SEM images of the membrane cross-sections display polymer veins, indicating favorable interaction between the ZIF-7 and the polyimide backbones. As mentioned previously, all MMMs are transparent films. The transparency of the films further confirmed the good dispersion of the ZIF-7 in the polyimides. In the SEM images of the MMM cross-sections, it is difficult to distinguish ZIF-7 particles from polymer nodules. The SEM images also show that the MMMs are free of defects and ready for permeability testing.

Figure 30. SEM image of the (A) cross-section and (B) Optical image of a 20 wt% ZIF-7/6FDA-NDA MMM.

Figure 1. SEM images of the (A) cross-section and (B) surface, and (C) Optical image of a 50 wt% ZIF-7/6FDA-NDA MMM.

Figure 32. SEM images of the (A) cross-section and (B) surface, and (C) Optical image of a 20 wt% ZIF-7/6FDA-NDA-ODA (3:1) MMM.

Figure 33 shows the XRD patterns for the MMMs. The XRD patterns of the 20 and 50 wt% ZIF-7/6FDA-NDA MMMs show the expected peaks based on the theoretical ZIF-7, indicating that some (but not necessary all) ZIF-7 nanocrystals remain intact in 6FDA-NDA polyimide polymer matrix.

Figure 33. XRD patterns of synthesized ZIF-7 and ZIF-7/6FDA-NDA MMMs.

ATR-FTIR spectroscopic analyses (Figure 34-35) were also performed to confirm the presence of the ZIF-7 nanoparticles in the MMMs. The IR spectra of the MMMs display all the expected peaks from the polyimides and the ZIF-7 nanoparticles. No shifts were observed in the peaks for either ZIF-7 or the polyimides.

Figure 34. ATR-FTIR spectra comparison of ZIF-7, 6FDA-NDA and their MMM.

Figure 35. ATR-FTIR spectra comparison of ZIF-7, 6FDA-NDA-ODA (3:1) and their MMM.

Table 6 shows the gas separation performance of the synthesized polyimides and colloidal ZIF-7 MMMs at 35 °C and 3 atm. Upon incorporation of ZIF-7 into the polyimides, permeabilities increased for all gases tested. In the case of ZIF-7 in 6FDA-NDA polyimide, H₂ permeability increased by 77%, without any change in H₂/CO₂ selectivity ($\alpha = 1.8$). Encouraged by the increase in H₂ permeability, the ZIF-7 loading was increased to 50 wt%. At this loading, both permeability (>300%), and selectivity increased (100%). At this loading, the ZIF-7 crystals are

dictating the gas separation properties of the MMM. This result lies close to Robeson's upper bound line for H₂/CO₂ separations (Figure 86).

Table 6. Gas separation performances for synthesized polyimides and colloidal ZIF-7 MMMs (35 °C, 2.5 atm).

ZIF-7 loading (wt%)	Polymer	Permeabilities (P, Barrers)			Selectivities (α)	
		H ₂	CO ₂	CH ₄	H ₂ /CO ₂	CO ₂ /CH ₄
0	6FDA-NDA	48±0.72	26±0.25	0.58±0.03	1.8	46
20	6FDA-NDA	85±4	47±5	-	1.8	-
50	6FDA-NDA	200±2	55±2	-	3.6	-
0	6FDA-NDA-ODA (3:1)	33±2	16±0.14	0.45±0.01	2.06	36
20	6FDA-NDA-ODA (3:1)	93±3	60±1	0.92±0.03	1.55	65

ZIF-8/Matrimid® MMMs [22]

The SEM image of a 50% (w/w) ZIF-8/Matrimid® MMM cross-section shows uniform dispersion of the ZIF-8 material in the polymer matrix (Figure 36). The presence of the concentric cavities in the MMM indicates that there is a strong interfacial contact between Matrimid® and the ZIF-8 nanoparticles.

Figure 36. SEM images of air-surface (left) and cross-section (right) of a 50% (w/w) ZIF-8/Matrimid® MMM.

The permeability values (Figure 37) obtained for all gases tested increased as the ZIF-8 loading increased up to 40% (w/w). However, at higher loadings of 50% and 60% (w/w), the permeability decreased for all gases. This result suggests a transition from a polymer-driven to a ZIF-8-controlled gas transport process, where at higher loadings the sieving effect of the ZIF-8 nanocrystals is more evident. Increases in ideal selectivities (Figure 38) were obtained at the higher ZIF-8 loadings for gas pairs containing small gas molecules, such as H₂/O₂ and CO₂/C₃H₈, suggesting that the ZIF-8 may act as a molecular sieve for smaller gas molecules [18].

Figure 37. Plot of permeability versus loading for O₂, CO₂, and H₂ at 0%, 20%, 30%, 40%, 50%, and 60% (w/w) ZIF-8 loadings [23].

Figure 38. Ideal selectivity plots of ZIF-8/Matrimid[®] MMMs for O₂/N₂, CH₄/N₂, H₂/O₂, H₂/CO₂, and CO₂/C₃H₈ at 0%, 20%, 30%, 40%, 50%, and 60% (w/w) ZIF-8 loadings [23].

EDA cross-linked ZIF-8/Matrimid[®] and EDA cross-linked, spin-coated Matrimid[®] ZIF-8/Matrimid[®] MMMs

Figure 39 shows SEM images of EDA cross-linked ZIF-8/Matrimid[®] MMMs. When compared to Matrimid[®], a decrease in gas permeabilities for EDA cross-linked Matrimid[®] was observed for all gases tested (Figure 40). Permeabilities decreased by 52% for H₂, 95% for CO₂, 89% for O₂, 75% for N₂, and 73% for CH₄. The decrease in permeabilities can be attributed to the presence of densified polymer chains. However, the permeabilities increased for both the EDA cross-linked

40% and 50% (w/w) ZIF-8/Matrimid[®] MMMs compared to the 40% and 50% (w/w) ZIF-8/Matrimid[®] MMMs. The cross-linked 40% (w/w) ZIF-8/Matrimid[®] MMM exhibited an increase in permeabilities of 152% for H₂, 122% for CO₂, 170% for O₂, 495% for N₂, and 15% for CH₄, while the cross-linked 50% (w/w) ZIF-8/Matrimid[®] MMM increased 340% for H₂, 274% for CO₂, 186% for O₂, 959% for N₂, and 84% for CH₄. The increase in permeabilities could be due to the delamination of ZIF-8 as a consequence of the dissolution of Matrimid[®] upon long exposure to EDA vapor. This would weaken the polymer-MOF interface creating voids or defects on the surface of the MMM resulting in increased permeabilities of the penetrant gases.

The selectivity plots in Figure 41 show an increase in selectivity for hydrogen-containing gas pairs including H₂/CO₂, H₂/O₂, H₂/CH₄ and H₂/N₂ for the EDA cross-linked Matrimid[®] compared to Matrimid[®]. The increase in the selectivities of the EDA cross-linked Matrimid[®] membranes can be attributed to the cross-linking of the diffusive pathways for gases such as CO₂. This increase in selectivity suggests that there was a reduction in the diffusive pathways for the larger gas molecules compared to the smaller H₂ molecule. For the cross-linked ZIF-8/Matrimid[®] MMMs, the selectivities of some gas pairs are close to Knudsen selectivity values, which could be due to defects in the MMMs brought about by cross-linking. However, compared to the uncross-linked MMMs, the H₂/CO₂ selectivity stayed the same for both loadings of the cross-linked ZIF-8/Matrimid[®] MMMs, and thus the separation of H₂ and CO₂ remains challenging due to the trade-off between H₂/CO₂ solubility selectivity and diffusivity selectivity.

Figure 39. SEM images of cross-sections (top) and surfaces (bottom) of a Matrimid[®] membrane (a,c) and a ZIF-8/Matrimid[®] MMM (b,d) both cross-linked with EDA vapor. The cross-linked layers are noted by the red bars in (a) & (c).

Figure 40. Permeability plots for ZIF-8/Matrimid® MMMs cross-linked with EDA vapor.

Figure 41. Selectivity plots for ZIF-8/Matrimid® MMMs cross-linked with EDA vapor.

Figure 42 shows an SEM image of 40% and 50% (w/w) ZIF-8/Matrimid® MMMs with an EDA cross-linked Matrimid® layer of 1.8 μm . The permeabilities (Figure 43) for all gases decreased for the cross-linked, spin-coated Matrimid® 40% and 50% (w/w) ZIF-8/Matrimid® MMMs compared to their corresponding uncross-linked MMMs. The cross-linking provided a densified polymer component rendering the slower diffusion of gas molecules and, consequently, resulting in a decrease in the gas permeabilities of the membranes. Another factor that may contribute to the observed decrease in permeabilities is the blockage of ZIF-8 pores at the interface of the cross-linked, spin-coated Matrimid® layer. Compared to the 40% and 50% (w/w) ZIF-8/Matrimid® MMMs, increases in selectivities were measured for both the cross-linked, spin-coated Matrimid® 40% and 50% (w/w) ZIF-8/Matrimid® MMMs for H₂/CO₂, H₂/O₂, H₂/CH₄, and H₂/N₂ gas pairs (Figure 43). The increase in the ideal selectivities for these gas pairs is most probably the result of an increase in diffusivity selectivity because smaller molecules, like H₂, could more easily

penetrate the less accessible cross-linked structure (lower fractional free volume) than larger molecules like N₂, O₂, and CH₄. In these gas pairs, the H₂ gas molecules have a small kinetic diameter (H₂: 2.89 Å; CO₂: 3.3 Å; O₂: 3.46 Å; N₂: 3.64 Å; CH₄: 3.8 Å) and can diffuse faster as compared to nitrogen, oxygen, and methane gases that are bigger and quite soluble (critical temperature: H₂: 32.97; CO₂: 87.98; O₂: 154.6; N₂: 190.56; CH₄: 304.13) in the polymer.

Figure 42. SEM images of cross-sections and surfaces of a) 40% (w/w) and b) 50% (w/w) ZIF-8/Matrimid[®] MMMs that were spin-coated on one surface with Matrimid[®] and cross-linked with EDA.

Figure 43. Permeability plot for EDA cross-linked, spin-coated Matrimid® ZIF-8/Matrimid® MMMs.

Figure 44. Selectivity plot for EDA cross-linked, spin-coated Matrimid® ZIF-8/Matrimid® MMMs.

Despite these promising results, this approach is not suitable for high temperature (e.g., 300 °C) measurements, as we have determined that EDA crosslinking of the polymers is reversible at 150 °C.

MIL-53/Matrimid® MMMs

SEM images (Figure 45) of a 50% (w/w) MIL-53-It/Matrimid® MMM cross-section showed that there was good dispersion of the MIL-53-It additive in the MMM and that no major defects were present at this magnification. The MIL-53-ht/Matrimid® and MIL-53-as/Matrimid® MMMs exhibited higher values of permeability compared to Matrimid® (Figure 46) as well as increases in CO₂/CH₄ selectivity (Figure 47) suggesting that the open-pore MIL-53 framework was maintained in the polymer matrix.

Figure 45. SEM images of 50% (w/w) MIL-53-It/Matrimid® MMM cross-sections.

Figure 46. Permeability plots of 50 and 60% (w/w) MIL-53-ht/Matrimid® MMMs.

Figure 47. Selectivity plots of 50 and 60% (w/w) wt MIL-53-ht/Matrimid® MMMs.

PIM-1-based MMMs

The molecular weight of the synthesized PIM-1 as measured by GPC was 126 kDa with a PDI of 2.7. The thin and flexible PIM-1 film that was prepared by casting in chloroform is shown in Figure 48.

Figure 48. Images of a PIM-1 membrane: (A) SEM image of cross-section, and (B) optical image of film.

Metal-organic framework nanoparticles (ZIF-8, ZIF-90, MIL-53) were incorporated into PIM-1 at weight loadings up to 18% (w/w) (Figure 49). The 10% (w/w) ZIF-90/PIM-1 MMM is transparent at this loading due to the good dispersion of the nanosized ZIF-90 particles (Figure 49C). The ZIF-8 and MIL-53 MMMs retained the crystallinity of the MOFs even after annealing at 300 °C for 2 d (Figures 50A and B). Preliminary permeability results of the ZIF-8/PIM-1 and MIL-53/PIM-1 MMMs (annealed at 300 °C) show increased permeabilities for all gases tested (H_2 permeabilities increased at least 20x when compared to a pure PIM-1 film), but without any significant improvement in selectivities. These results also show that the thermal treatment applied to PIM-1 films greatly affects their permeability properties.

Figure 49. Photographs of PIM-1-based MMMs: (A) 10% (w/w) MIL-53/PIM-1 MMM, (B) 18% (w/w) ZIF-8/PIM-1 MMM, and (C) 10% (w/w) ZIF-90/PIM-1.

Figure 50. XRD patterns of PIM-1 based MMMs after methanol treatment and annealing at 300 °C for 2 d: (A) 18% (w/w) ZIF-8/PIM-1 MMM, and (B) 10% (w/w) MIL-53/PIM-1 MMM.

6FDA-ODA/NDA-based MMMs

Five polyimide (PI) polymers (6FDA-NDA, 6FDA-ODA, and their copolymers (3:1, 1:1, 1:3 molar ratios)) were synthesized with high molecular weights (Table 7) following published procedures.

Table 7. Molecular weights of synthesized polyimides as measured by GPC

<i>Polymer</i>	<i>M_w, Da</i>	<i>M_n</i>	<i>PDI</i>
6FDA-NDA	71,000	31,840	2.23
6FDA-ODA	60,000	25,860	2.32
6FDA-NDA-ODA (3:1)	70,000	29,166	2.40
6FDA-NDA-ODA (1:1)	89,000	31,700	2.80
6FDA-NDA-ODA (1:3)	80,000	25,000	3.20

The thermal stabilities of these polymers were demonstrated by only a 10 wt% loss occurring at temperatures up to 480 °C (Figure 51). Their *T_g*'s as measured by DSC were at least 300 °C (Table 8).

Figure 51. Thermograms of synthesized PIs.

Table 8. Thermal properties of synthesized PIs

<i>Polymer</i>	<i>T_d at 10%, °C</i>	<i>T_g, °C</i>
6FDA-NDA	480	394
6FDA-ODA	480	304
6FDA-NDA-ODA (3:1)	480	350
6FDA-NDA-ODA (1:1)	480	337
6FDA-NDA-ODA (1:3)	480	325

The PI polymers were prepared as films by dissolving in DMF or chloroform and casting onto glass substrates. Thin and flexible films were characterized by SEM (Figure 52). The textured morphology observed for the 6FDA-NDA polymer at the 200 nm scale is characteristic of polyimide membranes (Figure 52). Several MMMs with these PIs as polymer matrix were prepared and the results will be discussed in the following sections.

Figure 52. SEM images of 6FDA-NDA polymer cross-section. Insert shows the optical image of a 6FDA-NDA film.

MMMs were prepared comprising the PI polymers and ZIFs or MOFs. MMMs of 20 wt% ZIF-8/6FDA-NDA were fabricated using ZIF-8 of different particle sizes including commercially available ZIF-8 (Basolite® Z1200, 120 nm particles) and synthesized ZIF-8 (111 nm and 60 nm particle sizes) (Figure 53). It was expected that the smallest particles would disperse best in the polymers. Improved polymer wetting of ZIF-8 was observed for the smallest 60 nm particles, but severe aggregation was also present. To overcome this aggregation, colloidal ZIF-8 particles were prepared and used for MMM fabrication. The use of a colloidal ZIF synthesis solution directly for MMM fabrication (without drying the particles) led to transparent MMMs and better dispersion (as shown by the SEM images) at the same ZIF-8 loading (Figure 54). Due to the small size of the ZIF-8 particles, it was challenging to identify what was ZIF or polymer nodules in the SEM images.

Figure 53. Optical and SEM images of 25% (w/w) ZIF-8/6FDA-NDA MMMs prepared using ZIF-8 with different particle sizes.

Figure 54. (A, B) SEM images and (C) optical image of a 25% (w/w) colloidal ZIF-8/6FDA-NDA MMM.

The use of colloidal ZIF solutions for MMM fabrication was extended to ZIF-7/PI MMMs. A 25% (w/w) ZIF-7/6FDA-NDA MMM was fabricated to form a transparent and flexible film (Figure 55). The loading of the ZIF-7 in 6FDA-NDA was increased to 100% (w/w) (Figure 56), and the resulting film was still transparent. XRD patterns of the MMMs show that ZIF-7 particles (not necessarily all) are intact in the polymer (Figure 57). However, at ZIF-7 loadings higher than 25% (w/w) the MMMs become brittle. To provide better interaction between polymer and ZIF without lowering the thermal stability of the polymer, a 3:1 mol ratio 6FDA-NDA-ODA copolymer ($T_g = 350$ °C, Table 9) was used as the polymer matrix for ZIF-7 (Figure 58). Similar to the other MMMs with ZIF-7, the 25% (w/w) ZIF-7/6FDA-NDA-ODA (3:1) MMM was also transparent.

Figure 55. (A) SEM image of MMM cross-section and (B) optical image of a 25% (w/w) ZIF-7/6FDA-NDA MMM.

Figure 56. SEM images of the MMM (A) cross-section and (B) surface, and (C) optical image of a 100% (w/w) ZIF-7/6FDA-NDA MMM.

Figure 57. XRD patterns for ZIF-7/6FDA-NDA MMMs.

Figure 58. SEM images of the MMM (A) cross-section, (B) surface, and (C) optical image of a 25% (w/w) ZIF-7/6FDA-NDA-ODA (3:1) MMM.

Gas permeability testing of these MMMs showed increased permeabilities for all gases tested upon incorporation of ZIF-7 (Table 9). Increasing the ZIF-7 loading in 6FDA-NDA to 100% (w/w) increased both the hydrogen permeability and H_2/CO_2 selectivity placing this result on Robeson's upper bound (Figure 86). The 25% (w/w) ZIF-7/6FDA-NDA-ODA (3:1) MMM showed significantly improved performance for CO_2/CH_4 separations (Tables 9 and 10, Figure 86).

Table 9. Permeabilities (in Barrers) of ZIF-7/PI MMMs

Permeabilities in Barrers	H ₂	CO ₂	CH ₄	N ₂	O ₂
6FDA-NDA	48 ± 0.72	26 ± 0.25	0.58 ± 0.03	2.38 ± 0.15	6.67 ± 0.04
6FDA-NDA-ODA (1:3)	33 ± 2.0	16 ± 0.14	0.45 ± 0.01	0.68 ± 0.02	4.15 ± 0.09
25% (w/w) ZIF-7/6FDA-NDA	85 ± 4	47 ± 5	-	-	-
100% (w/w) ZIF-7/6FDA-NDA	200 ± 2	55 ± 2	-	-	-
25% (w/w) ZIF-7/6FDA-NDA-ODA (1:3)	93 ± 3	60 ± 1	0.92 ± 0.03	2.13 ± 0.01	6.2 ± 0.10

Table 10. Ideal selectivities of ZIF-7/PI MMMs

Selectivities	H ₂ /CO ₂	H ₂ /N ₂	H ₂ /CH ₄	H ₂ /O ₂	CO ₂ /CH ₄	CO ₂ /N ₂
6FDA-NDA	1.8	20	84	7.2	46	11
6FDA-NDA-ODA (1:3)	2.06	49	73	8	36	24
25% (w/w) ZIF-7/6FDA-NDA	1.81	-	-	-	-	-
100% (w/w) ZIF-7/6FDA-NDA	3.6	-	-	-	-	-
25% (w/w) ZIF-7/6FDA-NDA-ODA (1:3)	1.55	44	101	15	65	28

ZIF-8/6FDA-durene and ZIF-8/6FDA-durene-EDA surface modification

XRD patterns of the ZIF-8 particles reacted with EDA vapor for 40 min (Figure 59) suggest that the crystal structure of ZIF-8 is intact after EDA exposure. The stability of the ZIF-8 functional groups to EDA vapor was verified by ATR-FTIR.

Figure 59. XRD patterns of (a) ZIF-8 and of (b) ZIF-8 exposed to EDA for 40 min and then dried at 70 °C for 12 h under vacuum.

An SEM image of the cross-section of a 50% (w/w) ZIF-8/6FDA-durene MMM reveals efficient wetting of the ZIF-8 particles by the polymer as evidenced by polymer veins (Figure 60a). An SEM image of the air-surface of the MMM demonstrates that the ZIF-8 nanoparticles have agglomerated into sub-micron sized particles in the 6FDA-durene polymer matrix (Figure 60b).

Figure 60. SEM images of (a) cross-section and (b) surface of a 50% (w/w) ZIF-8/6FDA-durene MMM.

After reacting the MMM with EDA vapor for 40 min, SEM revealed a dense skin with a thickness of $\sim 10 \pm 0.8 \mu\text{m}$ on both sides of the MMM (Figure 61), which can be attributed to cross-linking.

Figure 61. SEM image of a cross-section of a 50% (w/w) ZIF-8/6FDA-durene MMM after cross-linking with EDA for 40 min.

TGA plots of 6FDA-durene and the MMMs prior to reaction with EDA vapor showed thermal stability up to $>400^\circ\text{C}$ (Figure 62). A weight loss of $\sim 5\%$ from $150\text{--}300^\circ\text{C}$ was observed for the EDA cross-linked MMM due to the elimination of diamine.

Figure 62. TGA of (a) 6FDA-durene, (b) 50% (w/w) ZIF-8/6FDA-durene MMM, and (c) 50% (w/w) ZIF-8/6FDA-durene MMM after reacting with EDA for 40 min.

The chemical modification that occurred to the MMM from exposure to EDA vapor was examined using ATR-FTIR spectroscopy. Distinctive bands were observed for the ZIF-8/6FDA-durene MMM (Figure 63A) at 1721 cm^{-1} (imide C=O symmetric stretch), 1781 cm^{-1} (imide C=O asymmetric stretch), and 1353 cm^{-1} (imide C-N stretch) due to the imide ring in 6FDA-durene. When exposed to EDA vapor for 40 min (Figure 63d), these bands disappeared, and peaks characteristic of the amide group appeared at 1671 cm^{-1} (amide C=O stretch) and 1524 cm^{-1} (amide C-N stretch). The band at 1253 cm^{-1} (C-F stretch) remained unchanged. Shifts in these IR bands are similar to those observed for EDA cross-linked 6FDA-durene, and demonstrate that the chemical reaction taking place during EDA vapor reaction is the ring-opening of the imide group in 6FDA-durene to an amide group followed by cross-linking.

Figure 63. ATR-FTIR spectra of (a) 50% (w/w) ZIF-8/6FDA-durene MMM, (b) 50% (w/w) ZIF-8/6FDA-durene MMM treated with EDA for 40 min and annealed at $250\text{ }^{\circ}\text{C}$, (c) EDA treated MMM after annealing at $150\text{ }^{\circ}\text{C}$ and (d) EDA treated MMM after annealing at $70\text{ }^{\circ}\text{C}$. (All membranes were annealed for 1 d).

A 50% (w/w) ZIF-8/6FDA-durene MMM showed small increases in H₂/CO₂ (from 1 to 1.4), H₂/N₂ (from 14.9 to 16), and O₂/N₂ (from 3.1 to 3.3) selectivities as compared to the unfilled polymer. An increase in gas permeability along with small enhancements in selectivity suggest good compatibility between ZIF-8 nanoparticles and 6FDA-durene with no major defects.

After cross-linking the MMM with EDA vapor, H₂ and O₂ permeabilities of the cross-linked MMM are 283.4 and 16.9 Barrers, respectively, which is 55% of the H₂ permeability and 16% of the O₂ permeability of 6FDA-durene. The observed CO₂, CH₄ and N₂ permeabilities were 5.5%, 4.7%, and 5.1% of those observed for 6FDA-durene (Table 11). Cross-linking led to one order of magnitude increases in selectivities for H₂/CO₂ (10.9 fold), H₂/N₂ (9.5 fold), and H₂/CH₄ (11.4 fold) separations, whereas O₂/N₂ selectivity increased by a factor of 2.7 in the cross-linked MMM as compared to 6FDA-durene (Table 12) [24].

Table 11. Permeability (Barrers) values for 6FDA-durene, 6FDA-durene cross-linked by reacting with EDA for 12 min, 50% (w/w) ZIF-8/6FDA-durene MMM, 50% (w/w) ZIF-8/6FDA-durene MMM cross-linked by reacting with EDA for 40 min, and the cross-linked skin of the MMM all measured at 35 °C and 3.5 atm [24]

Membrane	Permeability (Barrers)				
	H ₂	CO ₂	N ₂	CH ₄	O ₂
6FDA-durene	518.5	468.5	34.9	30.0	107.7
Cross-linked 6FDA-durene	52.1	0.4	*	*	2.0
MMM	2136.6 ± 189.9	1552.9 ± 138.4	137.3 ± 17.6	140.3 ± 38.4	449.7 ± 100.2
Cross-linked MMM	283.5 ± 33.0	23.7 ± 2.8	2.0 ± 0.17	1.40 ± 0.13	16.9 ± 2.7
Cross-linked skin of MMM	89.4	6.8	0.58	0.40	5.0

* Permeability was too low to be detected

Table 12. Ideal gas selectivities for 6FDA-durene, 6FDA-durene cross-linked by reacting with EDA for 12 min, 50% (w/w) ZIF-8/6FDA-durene MMM, 50% (w/w) ZIF-8/6FDA-durene MMM cross-linked by reacting with EDA for 40 min, and the cross-linked skin of the MMM all measured at 35 °C and 3.5 atm [24]

Membrane	Ideal gas selectivity			
	H ₂ /CO ₂	H ₂ /N ₂	O ₂ /N ₂	H ₂ /CH ₄
6FDA-durene	1.1	14.9	3.1	17.9
Cross-linked 6FDA-durene	144	-	-	-
MMM	1.4 ± 0.0	16.0 ± 3.1	3.3 ± 0.14	15.3 ± 0.56
Cross-linked MMM	12.0 ± 0.07	141.4 ± 4.7	8.5 ± 2.1	203.3 ± 3.7
Cross-linked skin of MMM	13.1	155.0	8.6	222.1
Knudsen factor	4.7	3.7	0.9	2.8

After reacting the 50% (w/w) ZIF-8/6FDA-durene MMM with EDA vapor, SEM revealed a dense skin of $\sim 10 \pm 0.8 \mu\text{m}$ thickness on both sides of the MMM (Figure 64), which can be attributed to cross-linking. When 6FDA-durene was spin coated onto annealed 50% (w/w) ZIF-8/6FDA-durene MMMs, a $2.7 \pm 0.3 \mu\text{m}$ thick 6FDA-durene layer was observed by SEM (not shown). As shown in Figure 64, adding ZIF-8 to 6FDA-durene increased H_2 permeability to 2137 ± 190 Barrers, and EDA cross-linking of the MMM increased the H_2/CO_2 selectivity to 12 ± 0.07 while maintaining a moderate H_2 permeability. Asymmetric membranes having a thin cross-linked 6FDA-durene layer on a ZIF-8/6FDA-durene MMM showed a high H_2/CO_2 selectivity of 30.0 ± 3 with a high H_2 permeability close to the original permeability of 6FDA-durene.

Figure 64. SEM image of a cross-section and the surface of a 50% (w/w) ZIF-8/6FDA-durene MMM after cross-linking with EDA.

Similar to the cross-linked ZIF-8/Matrimid MMMs, although the results are promising, this system is not suitable for high temperature (e.g., 300°C) measurements.

6FDA-DAM-DABA-based MMMs

The SEM image of a 50% (w/w) ZIF-8 /PDMC MMM (Figure 65a) shows good polymer-particle interaction as evident from the polymer vein morphology. Cross-linking the MMM changes this morphology to a flake-like structure where polymer veins are less evident (Figure 65b). The XRD patterns in Figure 66 verify the presence of ZIF-8 in the fabricated MMMs. Adding ZIF-8 to PDMC increased gas permeability for all the gases with no loss in CO_2/CH_4 , H_2/CH_4 , and H_2/N_2 gas selectivity (Table 13) placing the 50% (w/w) ZIF-8/CPDM MMM above the 2008 Robeson upper bound for the separation of H_2/CH_4 and H_2/N_2 and on or close to the upper bound for CO_2/CH_4 separations [23].

Cross-linking 50% (w/w) ZIF-8/PDMC to obtain 50% (w/w) ZIF-8/CPDM further enhanced the permeabilities of the gases, but was accompanied by decreases in CO_2/CH_4 , H_2/CH_4 , and H_2/N_2 gas selectivity (Table 13). The performance of the cross-linked MMM is above the 2008 Robeson upper bound for the separation of H_2/CH_4 and H_2/N_2 and on or close to the upper bound for CO_2/CH_4 separation [23]. As shown by TGA, the uncross-linked MMMs are stable up to 450°C . The 10% weight loss starting from 200°C is due to the removal of propanediol. The cross-linked MMMs are also stable up to 450°C as shown in Figure 67.

Figure 65. SEM images of cross-sections of (a) 50% (w/w) ZIF-8/PDMC and (b) 50% (w/w) ZIF-8/CPDM.

Figure. 66. XRD patterns for ZIF-8 and MMMs containing 50% (w/w) ZIF-8 loadings.

Table 13. Permeability data (Barrers) and selectivity for PDMC, CPDM and MMMs containing 50% (w/w) ZIF-8 loadings.

Membrane	Gas permeability (Barrer)				Gas pair selectivity		
	N ₂	CH ₄	CO ₂	H ₂	CO ₂ /CH ₄	H ₂ /CH ₄	H ₂ /N ₂
PDMC	0.5	0.7	10.4	20.6	15.1	30.1	41.2
PDMC[25]	-	-	17.1	-	34.0	-	-
CPDM	-	2.4	91.7	159.0	37.9	65.7	-
CPDM[25]	-	-	77.3	-	39.9	-	-
Z8/PDMC	17.7	13.8	415.5	805.8	30.1	58.5	45.5
Z8/CPDM (210 °C)	29.6	24.7	484.9	995.5	19.6	40.2	33.6
Z8/CPDM (280 °C)	82.8	65.0	1230.3	1903.5	18.9	29.3	23.0

Figure 67. TGA plots of ZIF-8, CPDM and 50% (w/w) ZIF-8/CPDM MMMs.

VTEC PI-1388 membranes

Figure 68 shows an optical image of a VTEC PI-1388 membrane. Table 14 shows the permeability, flux, and selectivity results for N₂, H₂, and CO₂ measured at pressures up to 30 atm and at temperatures of 35 °C and 300 °C. At these pressures and temperatures, the H₂/CO₂ selectivity remains constant. The effect of temperature on permeability is notable at high temperatures as seen in the Robeson plot (Figure 86). Although pressure does not affect permeability, it does influence the gas flux across the membrane [19].

When the effects of both pressure and temperature are combined, the H₂ flux increases 300 times from $0.02 \text{ ft}_{\text{STP}}^3 \text{ h}^{-1} \text{ ft}^{-2}$ at 35 °C and 3 atm to $6.10 \text{ ft}_{\text{STP}}^3 \text{ h}^{-1} \text{ ft}^{-2}$ at 300 °C and 30 atm. Experiments revealed that temperature had a greater contribution; a 10-fold increase in temperature induced a 32-fold increase in flux, whereas a 10-fold increase in pressure resulted in only a 9-fold increase in flux. These results suggest that VTEC PI-1388 is stable at high temperatures and high pressures and that the increase in permeability may arise from the relaxation of the packing of the polymer chains at high temperature. In addition, the significant increase in flux at high temperature and high pressure suggests that VTEC PI-1388 could be a good candidate for high pressure, high temperature H₂/CO₂ separations.

MOP-18/Matrimid® MMMs

Temperature- and pressure-dependent permeation experiments (Table 15) revealed that for Matrimid® and MOP-18/Matrimid® membranes H₂ permeation increased by 100% when the temperature was increased from 35 to 70 °C. This trend can be attributed to a combination of increased kinetic energy for H₂ and the loosening of the polymer chain packing that reduces the energy required for H₂ to diffuse through the membrane. In the case of CO₂, the changes in permeability with changes in temperature are coupled to pressure changes. At 35 °C for both Matrimid® and the MOP-18/Matrimid® MMM, the CO₂ permeability increased 100% with a 10-fold increase in pressure resulting in membrane plasticization and loss of H₂/CO₂ selectivity. When the temperature was then increased to 70 °C, CO₂ permeability remained constant with pressure increments and the H₂/CO₂ selectivity was recovered, suggesting that plasticization of the membranes was reversed. The high pressure gas permeation experiments showed that MOP-18/Matrimid® MMMs were resilient and sufficiently mechanically robust to perform gas separations at high transmembrane pressures and that the incorporation of the MOP-18 molecules did not introduce defects in the membranes. From the temperature-pressure permeability experiments, it can be concluded that temperature has more of an effect than pressure on the gas separation properties of Matrimid® and MOP-18/Matrimid® MMMs. The H₂/CO₂ separation result of this MMM is shown in the Robeson plot (Figure 86).

Table 15. Permeability* (Barrers) of H₂ and CO₂ and H₂/CO₂ selectivity in Matrimid® and 30% (w/w) MOP-18/Matrimid® MMMs at 35 and 70 °C and at 3 and 30 atm.

	Matrimid®				30% (w/w) MOP-18/Matrimid®			
Temperature	35 °C		70 °C		35 °C		70 °C	
Pressure (atm)	3	30	3	30	3	30	3	30
H ₂	22.1 ± 5.9	22.2 ± 1.4	40.4 ± 5.3	37.5 ± 3.6	22.7 ± 4.9	21.2 ± 3.5	55.5 ± 1.1	51.1 ± 3.2
CO ₂	9.7 ± 2.6	18.7 ± 4.5	12.8 ± 3.2	15.48 ± 0.8	14.1 ± 3.2	25.0 ± 1.9	24.0 ± 0.8	25.1 ± 1.4
H ₂ /CO ₂	2.27 ± 0.01	1.22 ± 0.25	3.22 ± 0.40	2.42 ± 0.11	1.61 ± 0.01	0.84 ± 0.07	2.3 ± 0.03	2.04 ± 0.01

*average of 2 membranes

ZIF-8/PBI MMMs

PBI-based MMMs containing different loadings of ZIF-8 (Sigma Aldrich, Basolite® Z1200) nanoparticles were fabricated as flexible membranes and characterized (Figure 69). XRD patterns of the MMMs show that the crystallinity of ZIF-8 is intact in the PBI polymer matrix (Figure 70). Figure 71 shows that these membranes are flexible even at high ZIF-8 loadings.

Figure 69. (A) Chemical structure of PBI and SEM image of a PBI film cross-section and (B) SEM image of Basolite® Z1200 particles and ZIF-8 pore.

Figure 70. XRD patterns of ZIF-8/PBI MMMs at different ZIF loadings: (A) 43 wt%, (B) 35 wt%, and (C) 26 wt%. (D) XRD pattern of ZIF-8 nanoparticles.

Figure 71. Optical images of ZIF-8/PBI MMMs at different ZIF loadings: (A)(A1) 75% (w/w), (B)(B1) 55% (w/w), and (C)(C1) 35% (w/w) all before annealing at 250 °C.

SEM images of cross-sections and surfaces of MMMs with several ZIF-8 loadings show that the ZIF-8 is uniformly dispersed after several cycles of stirring and sonication, followed by mixing in an acoustic mixer (Figure 72). Due to the nodular morphology of PBI, it is difficult to identify ZIF-8 in the PBI matrix. The annealing temperature of the MMMs significantly affected the gas permeability results. The 35% (w/w) ZIF-8/PBI MMM annealed at 250 °C showed a lower H_2 permeability than the MMM annealed at 180 °C, but displayed a H_2/CO_2 selectivity of 16. The permeabilities of the annealed MMMs. The XRD pattern did not change following annealing at 250 °C, and there were no peaks in the IR spectra that would indicate oxidation (not shown).

Figure 72. SEM images of MMM cross-sections (A, A1, B, B1, C, C1) and surfaces (A2, B2, C2) for different loadings of ZIF-8, A: 26 wt%, B: 35 wt%, C: 55 wt% in PBI after annealing at 250 °C.

A pure PBI membrane displayed a H_2/CO_2 selectivity of 18 and a H_2 permeability of 2.7 Barrers (Table 16). Increasing the ZIF-8 loading to 55% (w/w) in PBI increases the H_2 permeability, but decreases selectivity. Further increasing the loading to 55 wt% ZIF-8 decreased both the permeability and selectivity (data now shown), which could be attributed to the increased tortuosity of gas transport and/or blocked pores of ZIF-8. The permeability results lie close to Robeson's upper bound for H_2/CO_2 separations (Figure 86). Density measurements of these MMMs were performed to investigate the free volume changes that occur with increased ZIF loading (Table 17).

Table 16. Permeability and selectivity of ZIF-8/PBI MMMs with different loadings at 35 °C and 3 atm.

ZIF-loading, % (w/w)	H_2 , Barrers	CO_2 , Barrers	$\alpha \text{H}_2/\text{CO}_2$
0	2.6 ± 0.12	0.15 ± 0.06	16
35	5.4 ± 0.70	0.33 ± 0.05	16
55	11.8 ± 0.12	1.6 ± 0.02	7
75	6.6 ± 0.10	1.3 ± 0.06	5

Table 17. Density measurements of MMMs by pycnometry using isooctanol as solvent.

ZIF loading, wt%	Density, g/mL
0	1.30 ± 0.11
35	1.28 ± 0.03
55	1.26 ± 0.00
75	1.26 ± 0.01
ZIF-8	1.00 ± 0.02

The permeabilities of these MMMs were also measured at high temperatures (100 and 300 °C) and high pressures (up to 15 atm). An increase in permeability for the 35% (w/w) ZIF-8 loading was observed at 300 °C and 15 atm (Table 18), making this result above Robeson's upper bound line for the H₂/CO₂ separation (Figure 86).

Table 18. Permeability (Barrers) and selectivity of a 35% (w/w) ZIF-8/PBI MMM.

Temp, °C	35	300	
P, atm	3	10	15
H ₂	5.40 ± 0.70	397 ± 9	397 ± 2
CO ₂	0.33 ± 0.05	36.00 ± 0.15	29 ± 1
α H ₂ /CO ₂	16	11	14

To confirm the materials' stability under realistic conditions, a PBI flat membrane and a 35% (w/w) ZIF-8/PBI MMM were exposed to steam at 250 °C for 24 h. Both membranes are stable as shown by their unchanged infrared spectra (Figure 73). The crystallinity of ZIF-8 is also intact after steam exposure (Figure 74).

Figure 73. FTIR spectra of PBI membrane and 35% (w/w) ZIF-8/PBI MMM before and after exposure to steam.

Figure 74. X-ray diffraction pattern of a 35% (w/w) ZIF-8/PBI MMM before and after exposure to steam.

Spin-coating of PBI layer

Figures 75 and 76 show SEM images of cross-sections of 35% (w/w) ZIF-8/PBI MMMs spin-coated with PBI layers of different thicknesses. The spin-coated PBI layer was thin, uniform, and dense, and its surface was typically defect free (Figure 75). A high magnification image (Figure 76) showed different morphologies for the PBI layer (left) and the 35% (w/w) ZIF-8/PBI MMM layer (right). The two layers appeared to interact well, and no voids were observed between the two layers. The thicknesses of the PBI layers were 950 nm (Figure 75) and 2.5 μm (Figure 76).

Figure 75. SEM images of a cross-section of a 35% w/w ZIF-8/PBI MMM with a 950 nm PBI skin. Inset shows image of surface (top) and a high magnification view (bottom) of the PBI layer.

Figure 76. SEM image of a cross-section of a 35% w/w ZIF-8/PBI MMM spin-coated with a 2.5 μm PBI layer. Inset shows image of surface of PBI layer.

The 35% (w/w) ZIF-8/PBI MMM has lower H_2/CO_2 selectivity and higher H_2 and CO_2 permeability compared to the pure PBI membrane (Table 19). The gas separation properties of ZIF-8/PBI MMMs can be improved by coating with a very thin, dense, and uniform layer of PBI. In this structure, the thin PBI coating is the selective layer and the ZIF-8/PBI MMM contributes to the permeability. A 2.5 μm PBI layer increased H_2/CO_2 selectivity from 16 to 26.

Table 19. Gas permeation properties of 35% (w/w) ZIF-8/PBI MMM spin-coated with a 950 nm PBI layer.

	H ₂ , Barrers	CO ₂ , Barrers	H ₂ /CO ₂
UTD-PBI (35 °C)	2.59	0.11	23
35% w/w ZIF-8/PBI MMM (35 °C)	5.36	0.33	16
35% w/w ZIF-8/PBI MMM with 950 nm PBI skin (35 °C)	4.13	0.31	13
35% w/w ZIF-8/PBI MMM with 2.5 µm PBI skin (35 °C)	4.16	0.16	26

For these MMMs with a PBI layer, the flux controls the properties of gas permeability and selectivity, as shown in Table 20. When the PBI skin was 950 nm, the flux of the PBI skin was higher than that of the MMM layer. As a result, the MMM with the 950 nm PBI layer exhibited gas permeability and selectivity similar to the uncoated MMM. However, when the PBI skin thickness was increased to 2.5 µm, the flux of the PBI skin was lower than the flux of the MMM layer, which led to a gas selectivity close to that of the pure PBI membrane.

Table 20. Flux (J) of 35% w/w ZIF-8/PBI MMM with PBI layer.

		950 nm PBI layer	2.5 µm PBI layer
PBI layer	H ₂	50.0	17.9
	CO ₂	2.34	0.836
MMM layer	H ₂	35.1	29.2
	CO ₂	2.16	1.80

ZIF-95/PBI and ZIF-95/6FDA-ODA-NDA MMMs

ZIF-95 is a chlorine-containing ZIF, which makes it incompatible with some high-performance polymers. The compatibility of ZIF-95 with PBI and 6FDA-ODA-NDA was tested. An optical image (not shown) of a 20 wt% ZIF-95/PBI MMM revealed separation between the ZIF-95 particles and the polymer matrix indicating poor compatibility and an optical image (not shown) of a 20 wt% ZIF-95/6FDA-ODA-NDA MMM showed a non-homogenous dispersion of ZIF-95. An SEM image of the 20 wt% ZIF-95/6FDA-ODA-NDA MMM (Figure 77) showed that the polymer did not wet the ZIF-95 additive.

Figure 77. SEM image of 20 wt% ZIF-95/6FDA-ODA-NDA MMM.

Permeability testing of PBI hollow fibers

PBI hollow fibers in stainless steel modules (with and without plasticizer) obtained from Santa Fe Science and Technology, Inc. were characterized and measured for hydrogen and carbon dioxide permeability. The SEM images of the hollow fiber cross-sections with and without plasticizer are presented in Figure 78. With the incorporation of the plasticizer (Figure 78a), the nodular morphology usually observed in PBI flat films (Figure 78d) disappeared in the hollow fiber cross-section (Figure 78b).

Figure 78. (a) Cross-section of a PBI hollow fiber with plasticizer (b) Cross-section of a PBI hollow fiber without plasticizer (c) Cross-section of a PBI hollow fiber without plasticizer (d) Cross-section of a PBI flat membrane.

The permeances of these fibers at 35 °C and 3 atm in Table 21 are higher for the hollow fibers without the plasticizer (Module 1). The selectivity for H₂/CO₂ is comparable to the reported data (ICL-HFM).

Table 21. Permeance (in GPU) of PBI hollow fibers obtained from Santa Fe Science and Technology, Inc.

Module	Hollow fiber	T (°C)	P (atm)	H ₂ Permeance	CO ₂ Permeance	α H ₂ /CO ₂
B1	With plasticizer	35	3	0.0161	0.0105	1.53
1	Without plasticizer	35	3	0.128	0.0144	8.86
4	Without plasticizer	35	3	0.566	0.117	4.82
70, 43-2	Without plasticizer	35	3	0.310	0.0640	4.84
UTD-PBI	(Flat film)	35	3	2.59	0.11	23
ICL-HFM ⁵	Without plasticizer	100	5-8	0.33	0.046	7.89

A H₂/CO₂ selectivity of 22 was measured at 300 °C and 15 atm for PBI hollow fiber membranes (Figure 79) in stainless steel modules fabricated at Santa Fe Science and Technology, Inc. (Table 22). This value of selectivity is close to that obtained for a PBI flat membrane. Thermal treatment of the PBI hollow fibers is required to stabilize the selectivity.

Figure 79. PBI hollow fibers soaked in nonsolvent (left) and stainless steel modules housing PBI hollow fibers (right).

Table 22. Permeance (in GPU) and H_2/CO_2 selectivity of PBI hollow fiber membranes.

Temperature		35 °C		100 °C	200 °C	300 °C	35 °C	300 °C	35 °C
Pressure [atm]		3	15	15	15	15	15	15	15
	H_2	0.316	0.313	0.681	1.090	1.644	0.111	1.431	0.113
	CO_2	0.039	0.040	0.082	0.080	0.075	0.007	0.064	0.007
	H_2/CO_2	8.10	7.83	8.30	13.63	22.07	14.98	22.43	15.52

1 GPU = 10^{-6} ($cm^3_{STP}/s \cdot cm^2 \cdot cm\ Hg$)

Optimization of the WGS membrane reactor

The custom-built membrane reactor equipped with a syngas generator, furnace and GC unit is presented (Figure 80). To test the membranes under consideration for WGS testing, thin layers of membrane material are coated onto robust porous substrates. A thin PBI layer ($<1\ \mu m$) was applied by airbrushing a diluted solution of PBI on a rotating stainless steel tube. The optical image (Figure 81) shows a PBI layer on the tube.

Figure 80. Optical image of a reactor cell inside the furnace.

Figure 81. Optical image of PBI coating on stainless steel tube.

Spin-coated PBI layer on ZIF-8/PBI MMM

Figures 82 and 83 present SEM images of a thin, defect-free PBI layer on a 26% wt ZIF-8/PBI MMM. The improvement in permeability and selectivity of the PBI on a ZIF-8/PBI MMM (Tables 23 and 24) can be attributed to the porous substrate (ZIF-8/PBI MMM) and the thin PBI film, respectively.

Figure 82. SEM images of the cross-section of 950-nm thick PBI spun coated on a 26% wt ZIF-8/PBI MMM (Inset showed surface image (upper) and high magnification image of the PBI layer).

Figure 83. SEM images of the cross-section of a 2.5-micron thick PBI film on a spun coated 35% w/w ZIF-8/PBI MMMs (Inset showed the image of the surface of PBI layer).

Table 23. Gas permeation properties of PBI spun-coated 35% (w/w) ZIF-8/PBI MMMs with PBI layer of 950 nm thick.

	H ₂ , Barrers	CO ₂ , Barrers	H ₂ /CO ₂
UTD-PBI (35 °C)	2.59	0.11	23
35 % w/w ZIF-8/PBI MMMs (35 °C)	5.36	0.33	16
35 % w/w ZIF-8/PBI MMMs with 950 nm PBI skin (35 °C)	4.13	0.31	13
35 % w/w ZIF-8/PBI MMMs with 2.5 µm PBI skin (35 °C)*	3.66	0.13	28

Table 24. Flux performance of PBI skins on ZIF-8/PBI MMM.

		35% (w/w) ZIF-8/PBI MMMs with 950 nm PBI skin	35% (w/w) ZIF-8/PBI MMMs with 2.5 µm PBI skin
The PBI skin	$\left(\frac{J}{A}\right)_{P_{H_2}}$	50.0	17.9
	$\left(\frac{J}{A}\right)_{P_{CO_2}}$	2.34	0.836
The MMM layer	$\left(\frac{J}{A}\right)_{M_{H_2}}$	35.1	29.2
	$\left(\frac{J}{A}\right)_{M_{CO_2}}$	2.16	1.80
Comparison of flux of a PBI layer and a MMM layer		$\left(\frac{J}{A}\right)_{P_{H_2}} > \left(\frac{J}{A}\right)_{M_{H_2}}$ $\left(\frac{J}{A}\right)_{P_{CO_2}} > \left(\frac{J}{A}\right)_{M_{CO_2}}$	$\left(\frac{J}{A}\right)_{P_{H_2}} < \left(\frac{J}{A}\right)_{M_{H_2}}$ $\left(\frac{J}{A}\right)_{P_{CO_2}} < \left(\frac{J}{A}\right)_{M_{CO_2}}$

Unit of flux = $\times 10^{-5} \left(\frac{cm^3_{STP}}{cm^2 \cdot s} \right)$

High temperature and high pressure stability studies

The stability of several pure polymer and mixed-matrix membranes was tested by continuously exposing them to H₂, CO₂, N₂, and CH₄ at temperatures up to 300 °C and pressures up to 30 atm. Over 4,000 hours of testing was conducted with the longest individual test performed for over 300 hours.

Gas permeation measurements of H₂, CO₂, CH₄, and N₂ in VTEC membranes were performed at 35 and 300 °C and up to 30 atm. The results showed a 35-fold increase in permeability for these gases with increasing temperature (Table 25, Figure 84), with no decrease in their ideal selectivities. The VTEC membrane was also tested for long term stability of up to 60 days at 300 °C. The permeability tests (at 300 °C and 30 atm) showed the membrane retained its permeability and selectivity for the gases tested.

Table 25. VTEC permeability at 35 °C and 300 °C and up to 30 bars (in Barrers)

Temperature		35 °C				300 °C			
Pressure [atm]		3	10	20	30	3	10	20	30
Permeability [Barrers]	N ₂	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	8.76 ± 0.09	7.9 ± 0.26	7.72 ± 0.44	8 ± 0.05
	H ₂	3.79 ± 0.06	3.65 ± 0.05	3.57 ± 0.05	3.57 ± 0.04	133.33 ± 3.23	133.2 ± 1.62	118.64 ± 1.14	124.58 ± 0.85
	CH ₄					11.27 ± 0.5	10.05 ± 0.56	9.67 ± 0.35	9.74 ± 0.28
	CO ₂	0.74 ± 0.02	0.6 ± 0.01	0.52 ± 0.02	0.5 ± 0.02	25.39 ± 1.03	24.47 ± 0.56	23.58 ± 0.38	24.43 ± 1.35
Ideal Selectivity	H ₂ /CO ₂	5.10	6.08	6.92	7.09	5.25	5.44	5.03	5.10
	CO ₂ /N ₂	17.15	13.85	12.30	10.86	2.90	3.10	3.06	3.05
	N ₂ /CH ₄					0.78	0.79	0.80	0.82
	CO ₂ /CH ₄					2.25	2.43	2.44	2.51

Figure 84. Permeability of H₂, CO₂, CH₄, and N₂ up to 300 °C and 30 atm in VTEC PI-1388 membrane.

A pure PBI membrane (6.4 μm , Figure 85) that was annealed at 250 $^{\circ}\text{C}$ for 1d was tested for gas permeation at 35 $^{\circ}\text{C}$ and 3 bars. The membrane showed a low H_2 permeation of 2.2 Barrers and a H_2/CO_2 selectivity of 18 which is close to the values reported by Freeman at 300 $^{\circ}\text{C}$. Other gas pair selectivities, including O_2/N_2 , H_2/CH_4 , and N_2/CH_4 (Tables 26 and 27), also improved.

Figure 85. SEM of the cross-section of a PBI membrane annealed at 250 $^{\circ}\text{C}$ for 1 d

Table 26. PBI (annealed at 250 $^{\circ}\text{C}$) permeability at 3 bars

	Permeability [Barrers]				
	H_2	CO_2	N_2	CH_4	O_2
UTD's PBI (35 $^{\circ}\text{C}$)	2.2	0.12	0.0031	0.0019	0.035
Freeman's PBI (23 $^{\circ}\text{C}$)	1.4	0.20	-	-	-
INL's PBI (250 $^{\circ}\text{C}$)	48	4.9	-	1.3	-

Table 27. Ideal selectivity of PBI at 3 bars (PBI annealed at 250 $^{\circ}\text{C}$, 1d)

	Selectivity						
	O_2/N_2	CO_2/CH_4	CH_4/N_2	H_2/CH_4	H_2/N_2	H_2/O_2	H_2/CO_2
UTD's PBI, 35 $^{\circ}\text{C}$	11.4	63.1	0.6	1138.3	701.1	61.7	18.1
Freeman's PBI, 23 $^{\circ}\text{C}$	-	-	-	-	-	-	7
Freeman's PBI, 300 $^{\circ}\text{C}$	-	2	1	40	40	-	20
INL PBI, 250 $^{\circ}\text{C}$	-	3.8	-	37.5	-	-	9.9

Robeson plot of H₂/CO₂ separations

Table 28 provides a list of the membranes prepared in this project and Figure 86 presents the gas H₂/CO₂ separation results in the form of a Robeson plot. The plot combines of the results for membranes tested at 35, 70, and 300 °C.

Figure 86. Robeson plot for H₂/CO₂ separations at 35, 70, and 300 °C [24]. Data points listed in Table 28.

Table 28. Gas transport properties of membranes

Membrane	#	P_{H_2}	H_2/CO_2
VTEC PI-1388 [35 °C]	1	3.89	5.29
VTEC PI-1388 [300 °C]	2	139	5.25
6FDA-durene	3	518.5	1.1
33.3 wt% ZIF-8/6FDA-durene MMM	4	2136.6	1.4
33.3 wt% ZIF-8/6FDA-durene MMM EDA cross-linked	5	283.5	12
EDA cross-linked 6FDA-durene layer on 33.3 wt% ZIF-8/6FDA-durene MMM	6	89.4	13.1
EDA cross-linked 6FDA-durene	7	52.1	144
Matrimid® [35 °C]	8	28.88	3.03
40% w/w ZIF-8/Matrimid®	9	70	2.96
PDMC	10	20.6	1.98
CPDM	11	159	1.73
50% w/w ZIF-8/CPDM	12	805.8	1.94
PBI [35 °C]	13	2.6	24
PBI [300 °C]	14	71	24
26 wt% ZIF-8/PBI [35 °C]	15	5.4	16
26 wt% ZIF-8/PBI [300 °C]	16	397	14
6FDA-NDA	17	48	1.8
6FDA-NDA-ODA (1:3)	18	33	2.06
20 wt% ZIF-7/6FDA-NDA	19	85	1.81
50 wt% ZIF-7/6FDA-NDA	20	200	3.6
20 wt% ZIF-7/6FDA-NDA-ODA (1:3)	21	93	1.55
26 wt% ZIF-8/PBI with PBI layer [35 °C]	22	4.16	26
Matrimid® [70 °C]	23	40.4	3.22
30% w/w MOP-18/Matrimid® [35 °C]	24	22.7	1.61
30% w/w MOP-18/Matrimid® [70 °C]	25	55.5	2.3
30% w/w ZIF-7/Matrimid®	26	2368	2.66